CHAPTER 4

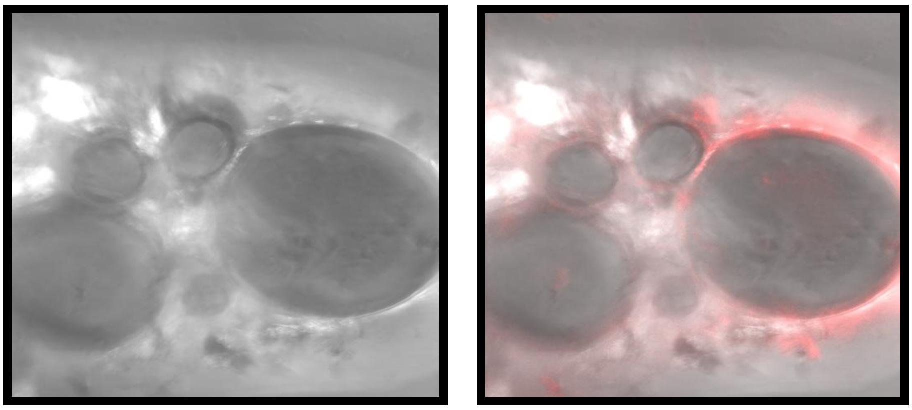
Foam formation in aqueous sodium dodecyl sulfate solutions and its characterization

Foams are highly transient entities and since they do not retain their shape for even a short while they tend to defy rigorous analysis. However, in spite of their transience considerable effort has been put in by investigators to understand foam physics i.e. behavior related to their geometric pattern, morphology, flow behavior etc. The foaming behavior of surface active solutions, like surfactants in aqueous solutions, is usually characterized by foamability and foam stability. Foamability also known as foaming capacity refers to the ability of a given solution to produce foam and can be evaluated either as the foam volume formed in a certain period of time or as the time required to obtain a certain volume of foam. Carey and Stubenrauch (2010) have reported that the foamability of a surfactant solution depends on the rate at which surfactants adsorb and on the total amount of surfactant adsorbed at the air –water interface.

4.1 Structure of foam

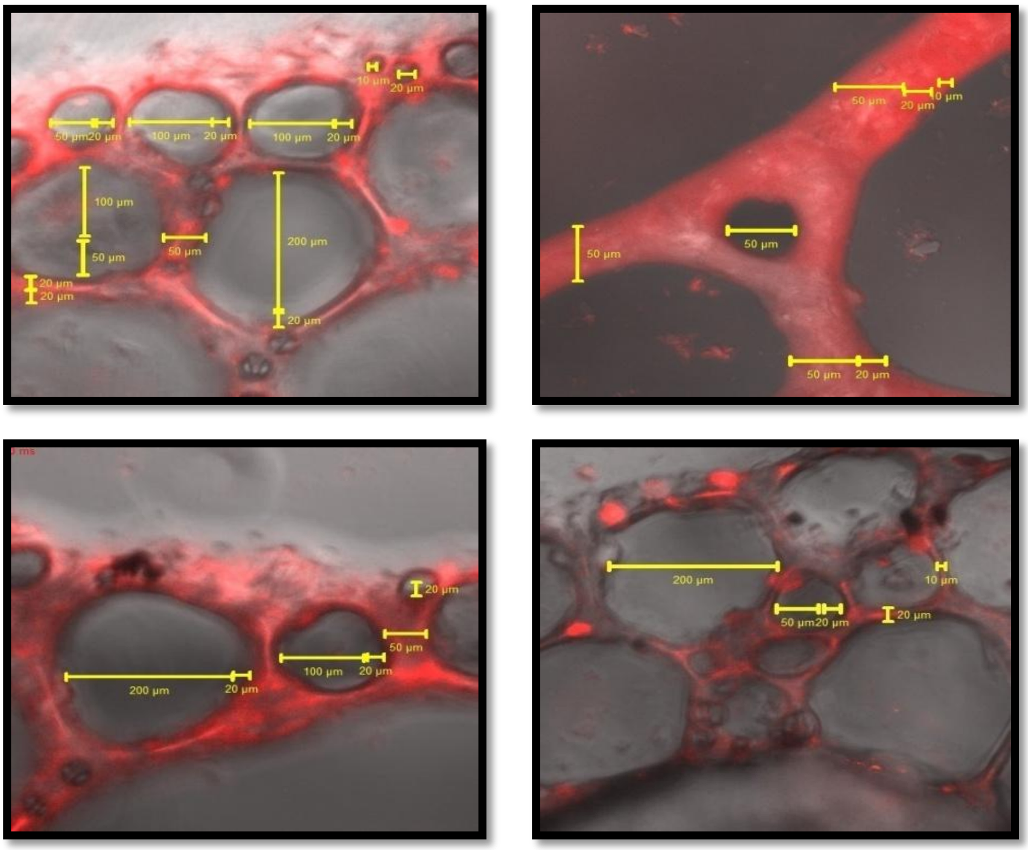
Foam is a two-phase system- a gas in liquid dispersion, in which gas bubbles are entrapped within liquid boundaries. The liquid in foam primarily resides in (a) the thin films surrounding the bubbles (b) plateau borders, at which three films meet and (c) at the vertex, the junction of four borders. When the foam is allowed to drain freely, the liquid in it drains through the random network of plateau borders and/or vertices because of gravity. In a foam bed after a period of time most of the liquid accumulates at the bottom, leaving the foam at the top dry. When the liquid films becomes too thin adjacent bubbles coalesce leading to formation of a coarse foam– a dispersion of large bubbles enclosed by thin liquid films. The macroscopic appearance of foam also changes due to the gas diffusion from smaller bubbles to larger bubbles following the well-known Laplace Young law leading to coarsening of the foam.

The morphology of foams formed by dispersing air into Sodium dodecyl sulfate solution (0.1 gm/l) was imaged using confocal microscopy. Fig. 4.1 shows monochrom and fluroscence image obtained. Rhodamine B dye was added for fluroscence generation (1mg/10 ml) 0.1 wt% . Fig. 4.2 shows foam structure of SDS foams.



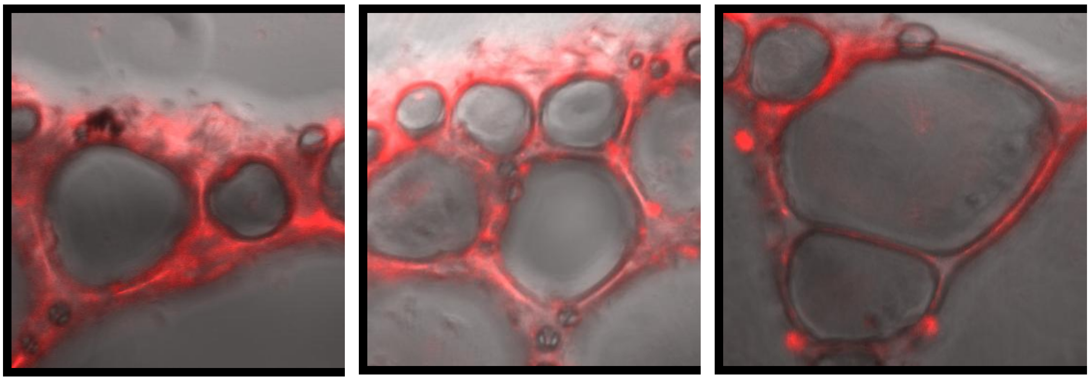
(a) **(b)**

Fig. 4.1: Foam morphology t =0 min (a) monochrome image (b) fluorescence image

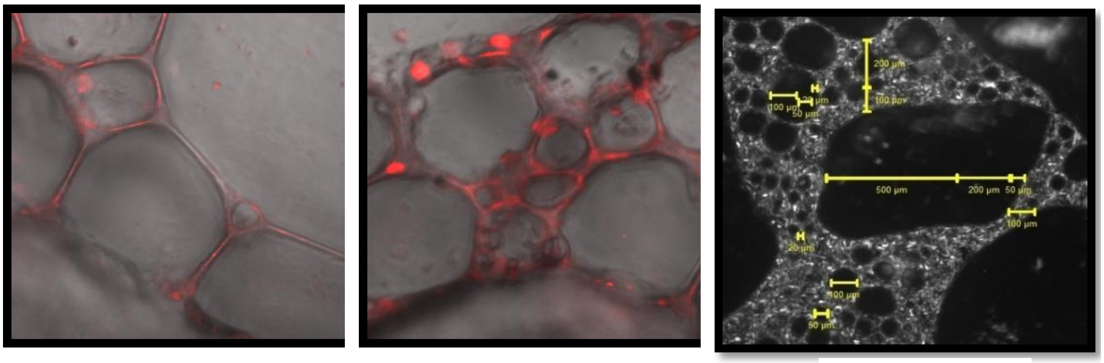


(a) **(b)**

Fig. 4.2: (a) Plateau border (b) Vertex in SDS foams



time 0 min time 10 min time 15min



time 15 min time 15 min time 30 min

Fig. 4.3: Various stages observed during foam formation to drainage for SDS foams

Both effects, drainage and coarsening, in wet foam can occur at the same time-scale and can thus be coupled. If free drainage was a consequence of gravity, capillary and viscous forces alone, the drainage would have saturated when gravity balanced the capillary and viscous forces.

Experimental observations show that drainage proceeds well past this point and continues till most of the liquid is drained from the foam. The same can be observed in SDS foams. Fig. 4.3 shows various stages observed from foam generation to drainage for SDS foams using LSM-710 Confocal Microscope, Carl Zeiss Germany.

Foam stability is monitored by the change in foam volume as a function of time. Three types of self destructive processes govern foam stability, namely foam drainage, Ostwald ripening and bubble coalescence. These processes take place simultaneously and thus are quite difficult to examine separately. Foam drainage is the flow of liquid through the continuous phase channels which separate the bubbles and is driven by gravity and capillarity. Ostwald ripening is due to the diffusion of the dispersed phase from smaller to larger bubbles and can be altered by adjusting the polydispersity of the gas bubbles or by varying the gas permeability through the surfactant layer. Finally, coalescence is due to the rupture of thin liquid films that separate adjacent cells.

Foaming behavior with single surfactant systems, foams stabilized by protein–surfactant mixtures, polymer–surfactant mixtures, alcohol–surfactant mixtures (Karakashev et. al. 2007, Alahverdjieva et. al. 2008, Ropers et. al. 2008) etc. has been extensively investigated. Effect of solid particles (Horozov et al 2008) and liquid crystals (Shrestha et al 2008) on foaming has also been investigated. However, there is lack of experimental data and therefore a lack of knowledge on the foaming properties of surfactant-heavy metal mixtures.

4.2 Sodium dodecyl sulfate in solution

Sodium dodecyl sulfate (SDS) used in this study, is a well investigated surfactant there is considerable information available in the literature regarding its behavior in aqueous solutions. However, it is known that even presence of small amount of impurities such as NaCl can lead to drastic change in aggregation behavior of the surfactant in solution. In view of this the critical micelle concentration of SDS was experimentally determined and its surface excess was evaluated from the data of surface tension as a function of concentration.

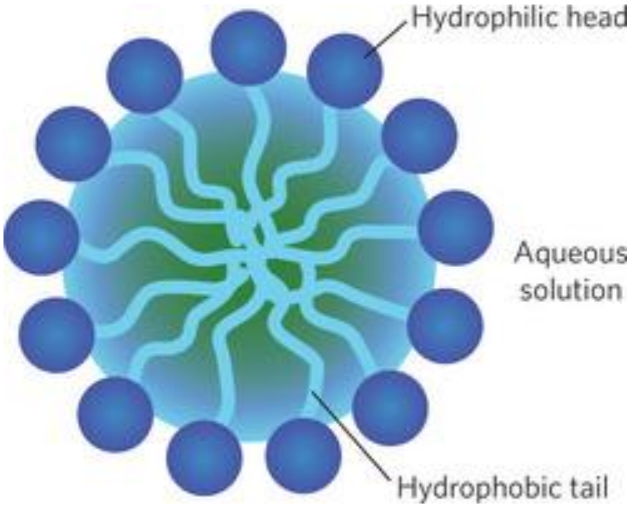


Fig. 4.4: Surfactant micelle

It is well known, that presence of surfactants in solution reduce the surface tension of the solution, however after reaching a threshold concentration of the surfactant called the *critical micelle concentration* there is no further reduction in the surface tension of the solution with increase in the surfactant concentration. At cmc the surfactants self organize to form aggregates that shield their hydrophobic tails from the water molecules by pushing them inside, and retaining the hydrophilic head groups to be in contact with water as shown in Fig 4.4.

The cmc of SDS was evaluated based on surface tension measurements and compared with the data reported in the literature, further SDS being ionic in nature its cmc values would be influenced by the presence of metal ions in solution. In general cmc values are considerably reduced for ionic surfactants in presence of counter-ions. This effect is simply explained in terms of the screening action of the counter-ions, i.e. the associated counter-ions reduces the magnitude of the forces of repulsion between the charged head groups in the micelle and consequently decrease the electrical work of micellization.

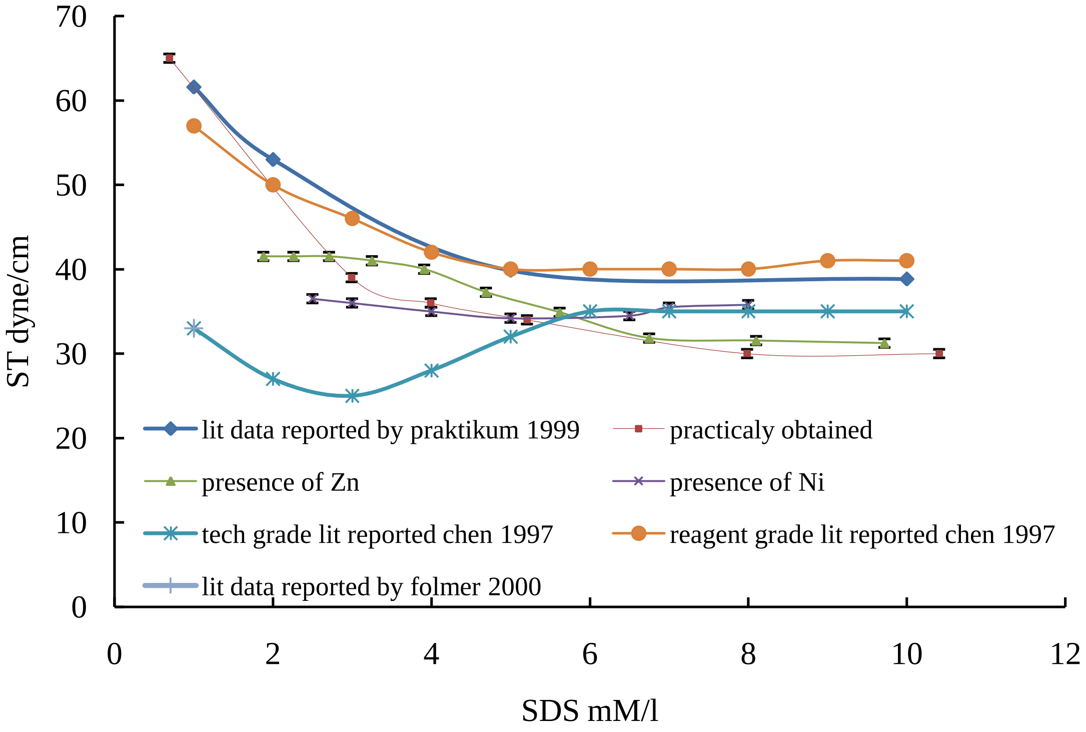


Fig. 4.5: CMC of SDS solutions, effect of metal ions on CMC

Fig 4.5 depicts the concentration versus surface tension plots of SDS as reported by different investigators, also shown is the influence of Zn and Ni on the surface tension - concentration plots.

4.3 Liquid holdup in foams

Ross-Miles pour test method (ASTM D1173-63) was used to evaluate liquid hold up and the stability of foams generated in aqueous SDS solutions. The influence of metal ions such as zinc, cadmium, nickel on the liquid holdup in foams formed in SDS solutions as well as the effect of binary metal ions such as zinc-cadmium and nickel-cadmium on the liquid holdup of SDS foams were studied. Effect of the polymer PVP on foam stability and liquid holdup were examined.

4.3.1 Effect of SDS concentration on liquid holdup

The Ross Miles test detailed Ch. 3.2.1 involves pouring 200 ml of the surfactant solution in the receiver column containing 50 ml of the same solution from a height of 90 cm. Liquid holdup was determined by making a series of measurements and calculations such as measuring the foam height in the receiver column after the last drop of solution fell from the foam pipette, the clear liquid height in the receiver, evaluating the foam bed volume, evaluating the clear liquid volume, the amount of liquid volume in foam was calculated by material balance deducting clear liquid volume in the column from the total volume of SDS solution in the system (250 ml. = volume of liquid in column + volume of liquid in pipette). The ratio of volume of liquid in foam to the foam volume gave the fraction of liquid in foam.

Foam bed volume and holdup profiles at different SDS concentrations of 7.97mM, 5.98 mM and 3.98mM corresponding to 1 cmc, 0.75 cmc and 0.5 cmc respectively are shown in Fig 4.6

Surfactant concentrations of 7.97 mM/L, 5.98 mM/L, and 3.98 mM/L resulted in initial liquid hold up of 13.76 %, 13.42% and 10.26% respectively. Foams with higher SDS concentrations were more stable but they drained faster in the initial phase.

Foamability increases with increasing SDS content in solution. Within the range of experiments the foamability of the surfactant solution was found to be the highest at SDS solution concentration of 7.97 mM/L. This is likely due to the higher adsorption of the surfactant at the water-air interface during the foaming process

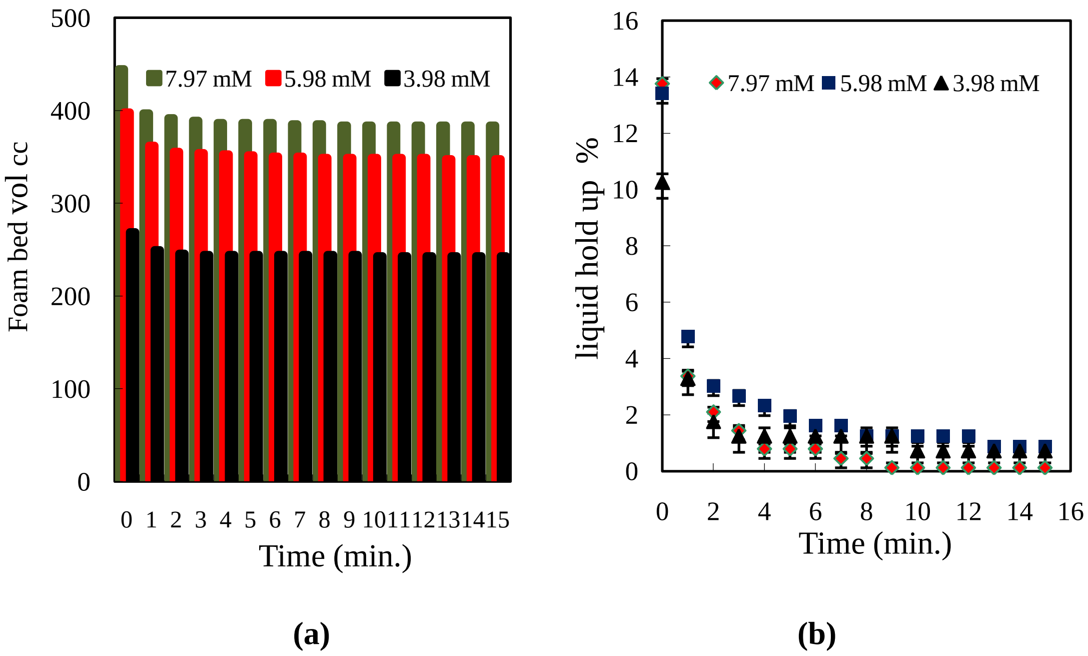


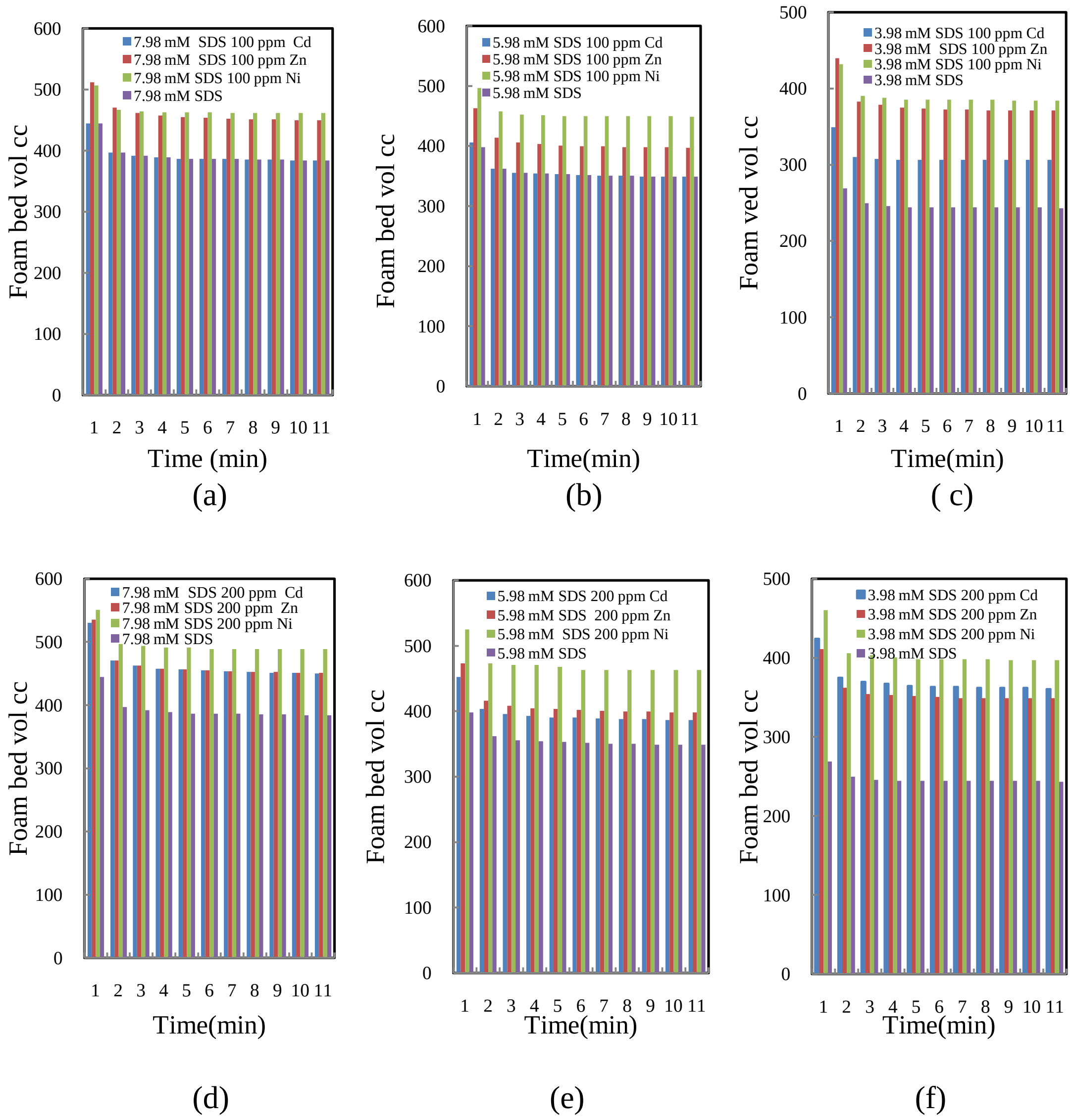
Fig 4.6: Effect of surfactant concentration on (a) foam bed volumes (b) on liquid hold up profiles

Enhanced adsorption on gas liquid interface consequently results in higher foamalility. In the case of surfactants with lower surfactant concentration the transport of the surfactant to the gas liquid interface is not likely to be fast enough resulting in lower foamability.

4.3.2 Effect of metal ions on foam bed volume

The decay of the foam bed volume in the presence of 200 ppm and 100 ppm metal ions in solution is shown in Fig. 4. 7 for SDS solution concentration of 7.97, 5.98 and 3.98 mM/L respectively.

Foam bed volumes were in the order SDS= 100 ppm Cd <100 ppm Zn<100 ppm Ni for surfactant concentrations 7.98 mM/L and 5.98 mM/L. while for 3.98 mM/L SDS foam bed volume is in the order of SDS< 200 ppm Cd <200 ppm Zn <200 ppm Ni .



(a) (b) (c)

(d) (e) (f)

Fig. 4.7: Effect of presence of metal on foam bed volume for varying SDS concentrations of 7.98 , 5.98 and 3.98 mM for (a) (b) , (c) 100 ppm Cd, Zn , Ni (d), (e) ,(f) 200 ppm Cd, Zn, Ni

The foamability of SDS solution increased with increasing SDS solution concentration. For all the cases foam bed volume is more in presence of Ni

4.3.3 Effect of zinc ions on liquid holdup

The effect of zinc concentration on liquid hold up profile is shown in Fig.4.8. Foam formed from aqueous solutions containing 100 ppm zinc ions had initial liquid hold up of 12.46 %, 14.34% and 15.69% for surfactant concentration of 7.97, 5.98 and 3.98 mM/L respectively. While foams formed from solutions containing 200 ppm zinc has initial liquid hold up of 16.26%, 16.21% and 16.14% respectively at the three surfactant concentrations mentioned above.

For 100 ppm Zn concentration there is fair degree of variation in the initial liquid holdup with changing surfactant concentration but at Zn levels of 200 ppm in feed the initial liquid holdup is nearly the same at the three surfactant concentrations, this is attributed to the formation of water bridge between the metal cation and the dodecyl sulfate anions.

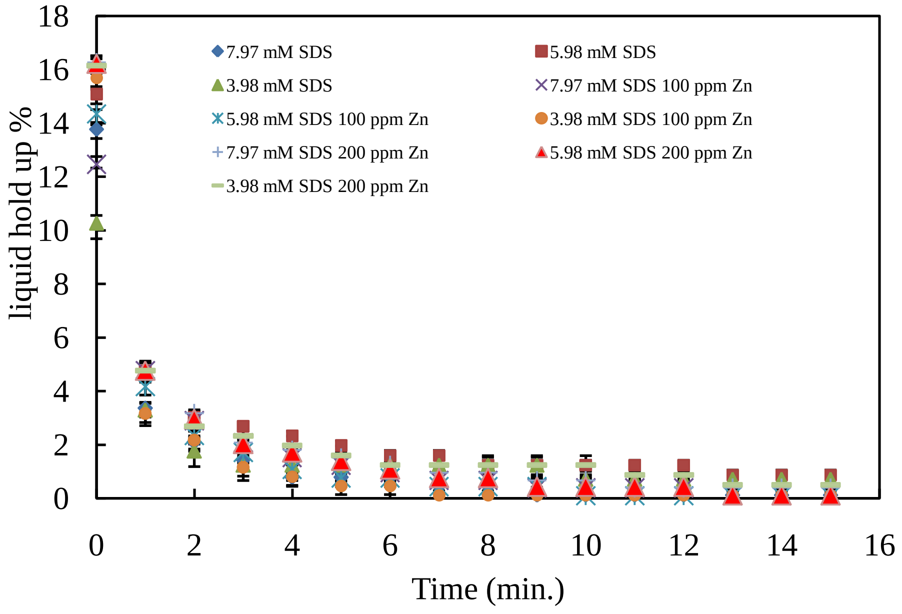


Fig. 4.8.: Effect of 100 and 200 ppm zinc metal ions on liquid holdup in foam for varying SDS concentrations of 7.97, 5.98 and 3.98 mM/L

4.3.4 Effect of cadmium ions on liquid holdup.

Zhang et al (2012) reported that presence of a small fraction of Cd^{2+} (0.03 mmol/l) in the SDS system produced a significant melioration in foam properties. This was ascribed to the formation of adsorption layers of SDS solution were all charged and double electrical layers existed around the surfactant ions. Therefore the electrostatic repulsion of surface-ion hydrophilic head in the surface of single molecule adsorption layer was weakened when anti-ion Cd^{2+} was added in the solution.

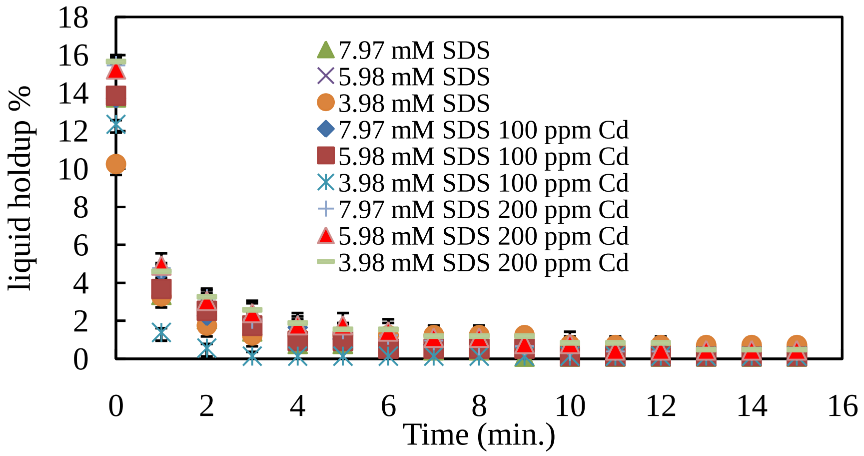


Fig. 4.9: Effect of 100 and 200 ppm cadmium metal ions on liquid holdup in foam for varying SDS concentrations of 7.97, 5.98 and 3.98 mM/L

The effect of presence of cadmium in the feed on the liquid holdup profiles is shown in Fig 4.9. Foam formed with 100 ppm Cd has initial liquid hold up of 13.70%, 13.85% and 12.35% at SDS solution concentration of 7.97, 5.9 and 3.98 mM/L respectively. While at 200 ppm Cd concentration over the entire range of SDS concentration between 7.97 to 3.98 mM/L the initial liquid holdup ranges from 15.65% to 15.24% due to water bridge formation. Moreover, visual inspection of the foam after the measurement revealed that the SDS- Cd^{2+} system formed dry foam with a very thin lamella layer that was highly stable.

Drainage dominates for time t < 10 min. while for t > 10 min. an equilibrium state is reached at which the type of foam film stabilizing the foam comes into play. As the liquid in the plateau border drains due to gravity, the top of the foam becomes drier with a smaller Plateau border cross sectional area and a smaller radius of curvature. With time, there develops a gradient of plateau border suction in the foam as a result of gradient of liquid holdup. This gradient opposes gravity, thus retarding plateau border drainage. Eventually, the foam reaches a mechanical equilibrium thereafter at which point there is no drainage occurs in thin films as well through plateau borders. (Wang and Narsimhan 2004). After t > 10 min. no change in the drainage rates were observed, the foam bed remained of constant height and the process of foam decay was hereafter primarily by coalescence and Ostwald ripening.

4.3.5. Effect of nickel ions on liquid holdup

The presence of nickel ions on the liquid holdup profiles are shown in Fig 4.10. Foam formed with 200 ppm nickel in feed has initial liquid hold up of 11.58%, 12.15% and 13.86% for SDS concentration of 7.97, 5.98 and 3.98 mM/L respectively. While with 100ppm Ni in feed the initial liquid holdup is 9.02%, 9.72% and 11.18% respectively at the above mentioned SDS solution concentrations respectively.

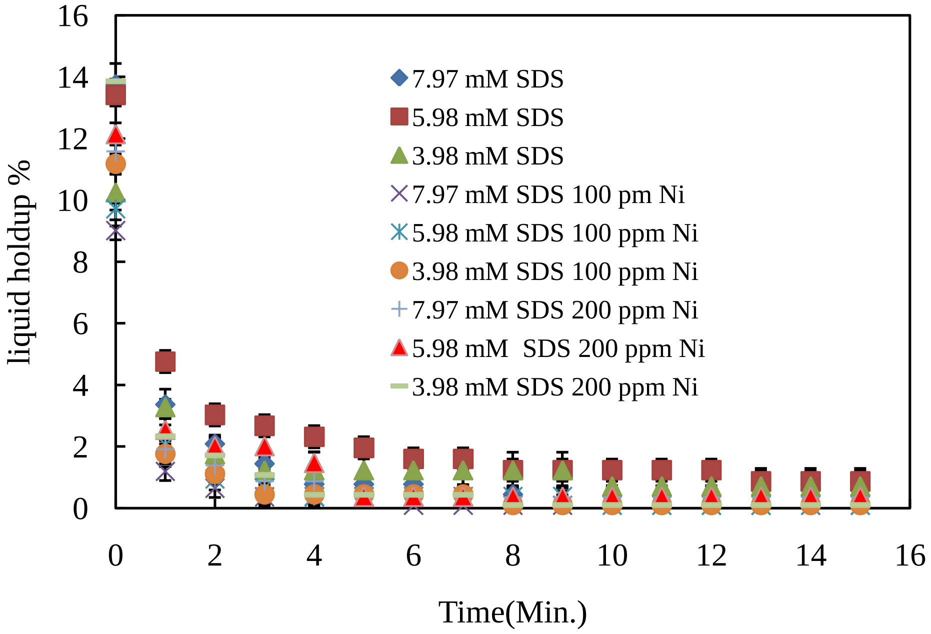


Fig. 4.10: Effect of 100 and 200 ppm nickel metal ions on liquid holdup in foam for varying SDS concentrations of 7.97, 5.98 and 3.98 mM/L

It is noteworthy from visual observation that foam formed is dry in presence of 100 and 200 ppm nickel with SDS concentrations of 7.97, 5.98 and 3.98 mM/L respectively compared to cadmium and zinc of 100 ppm and 200 ppm with SDS concentrations of 7.97, 5.98 and 3.98 mM/L respectively.

4.3.6 Effect of Zinc-Cadmium and Nickel-Cadmium ions on foam bed volume and liquid hold up

The decay of the foam bed volume in the presence of Zn-Cd and Ni-Cd ions at SDS solution concentrations of 7.97, 5.98 and 3.98 mM/L is shown in Fig. 4.11.

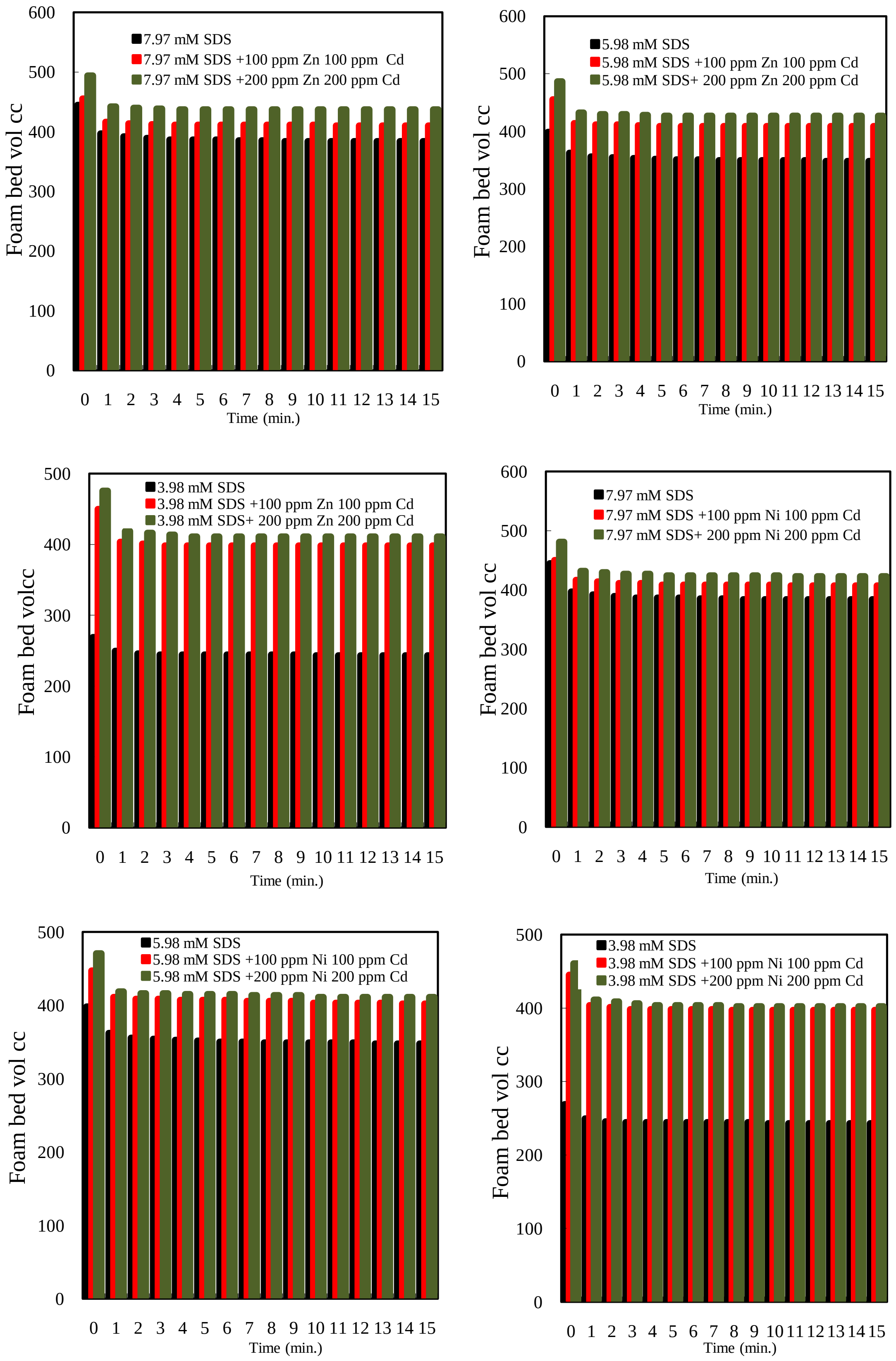
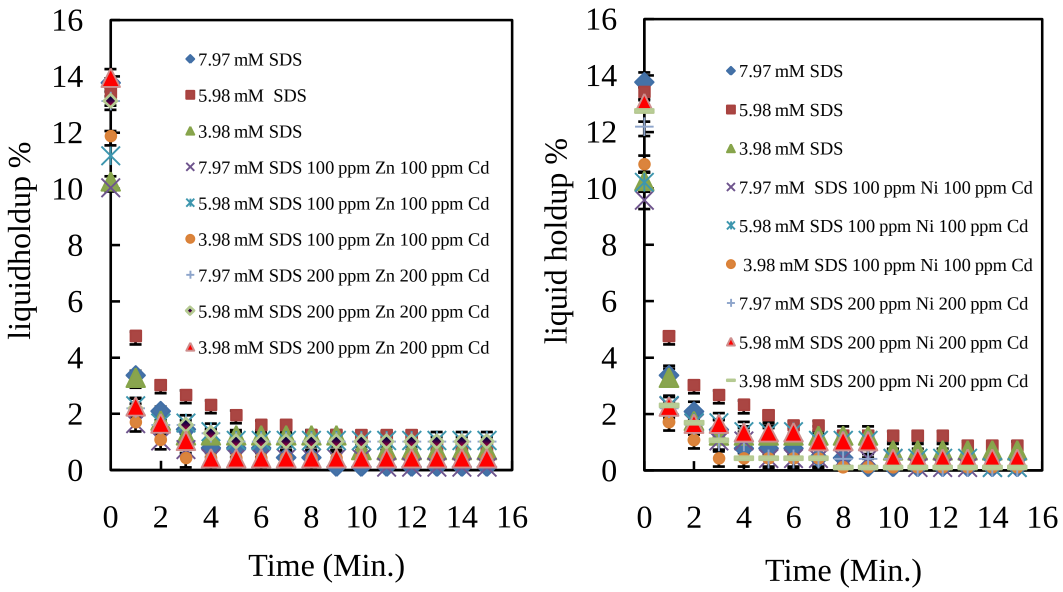


Fig. 4.11: Influence of Zn-Cd and Ni-Cd binary on foam bed volume for SDS concentration 7.97mM, 5.98mM, 3.98mM

Foam bed volumes were in the order 200 ppm Zn-Cd > 100 ppm Zn-Cd > feed without Zn-Cd, for all SDS solution concentrations. The same results were for Ni-Cd system also.

The presence of zinc- cadmium ions on the liquid holdup profiles are shown in Fig 4.12(a). Foam formed with 200 ppm zinc-cadmium in feed has initial liquid hold up of 11.88%, 13.12% and 13.95% for SDS solution concentration of 7.97, 5.98 and 3.98 mM/L respectively. While with 100 ppm zinc-cadmium in feed the initial liquid holdup is 10.04%, 11.17% and 11.88% respectively at the specified SDS solution concentrations.

For zinc- cadmiumn concentration of 200 ppm in feed and SDS concentration 3.98 mM/L the initial liquid holdup is the highest. The same is true with zinc-cadmium concentration of 100 ppm and SDS solution concentration 3.98 mM/L. Initial liquid hold up is more for higher metal concentration. This pattern/behavior is attributed to be mainly due to the formation of water bridge between the metal cations and the dodecyl sulfate anions. The liquid drains more slowly from the foams in presence of zinc-cadmium metals.



(a) **(b)**

Fig. 4.12: Effect of mixture of (a) Zn-Cd and (b) Ni-Cd binary ions on liquid holdup in foam

The presence of nickel- cadmium ions on the liquid holdup profiles are shown in Fig 4.12 (b). Foam formed with 200 ppm nickel-cadmium in feed has initial liquid hold up of 12.19%, 13.00% and 12.73% for SDS concentration of 7.97, 5.98 and 3.98 mM/L respectively. While with 100ppm nickel-cadmium in feed the initial liquid holdup is 9.58%, 10.21% and 10.85% respectively at the above SDS concentrations.

At nickel-cadmiumn concentration of 200 ppm in feed and SDS concentration 5.98 mM/L the initial liquid holdup is maximum. The same is true with nickel-cadmium concentration of 100 ppm and SDS concentration 3.98 mM/L. Initial liquid hold up is more for higher metal concentration. Such an effect is believed to be mainly due to the formation of water bridge between the metal cations and the dodecyl sulfate anions.

4.4 Role of polymeric additive on foaming behaviour

The foaming behavior of the anionic surfactant sodium dodecyl sulfate (SDS) was studied in the presence of nonionic polymer poly(vinylpyrrolidone) (PVP).

Fig. 4.13 shows association of PVP with SDS for various concentrations of surfactant. In general, at low surfactant concentrations, structure B may be obtained with single surfactant molecules or very small surfactant clusters (dimers, trimers, etc.) interacting with one or more hydrophobic modifiers, without causing any conformational changes on the polymer.

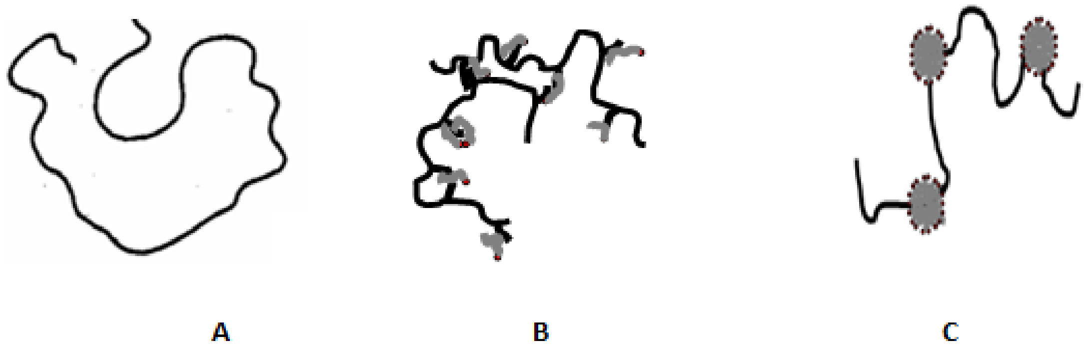


Fig. 4.13: PVP-SDS interactions (a) Polymer PVP (b) Individual SDS molecules associate themselves on a single polymer molecule or multiple polymer molecules (c) clusters of SDS molecules on a single polymer molecule.

When the surfactant concentration is increased, somewhat larger surfactant clusters form co-aggregates with the same polymer molecule, causing the polymer conformation to change significantly. At larger surfactant concentrations, it is possible to obtain the structure C where surfactant aggregates are formed around polymer.

SDS possesses a strong polar group. In aqueous solution they dissociate into ions and therefore electrostatic attractive interaction can appear between PVP and hydrophilic head groups of surfactant SDS. Foam properties are determined not only by the physicochemical properties of the foaming solution but also by the interaction of the SDS with the ambient surroundings.

Interaction between SDS and PVP can change the surface activity of SDS. Surface tension of PVP dissolved in water as well as SDS with PVP in water in various concentration ranges is shown in fig. 4.14. Higher surface tension was noticed for only PVP dissolved in water. Surface tension was reduced in presence of SDS because of PVP-SDS complex formation.

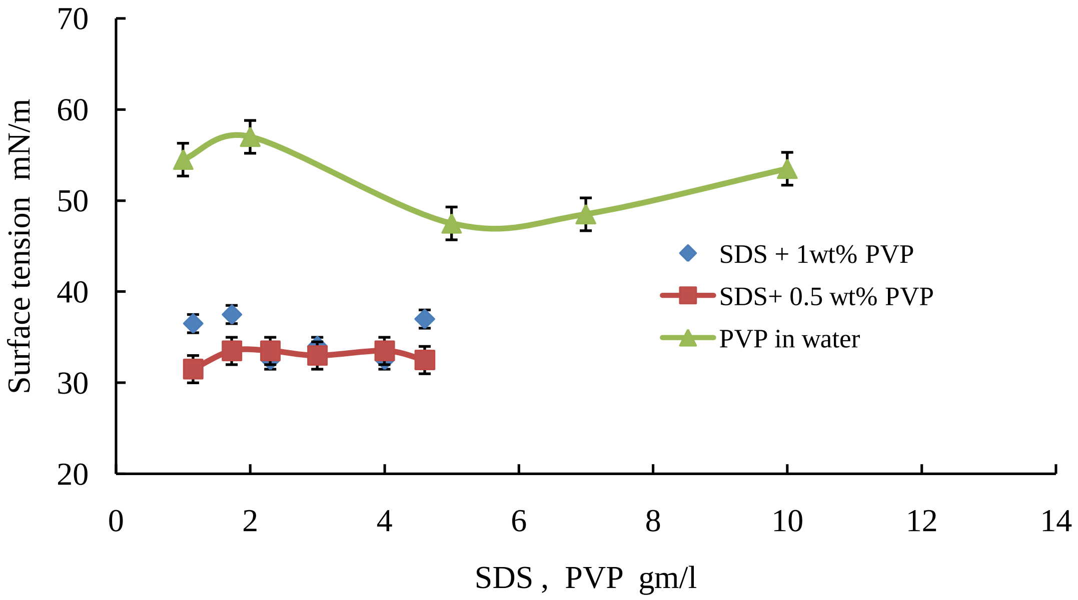
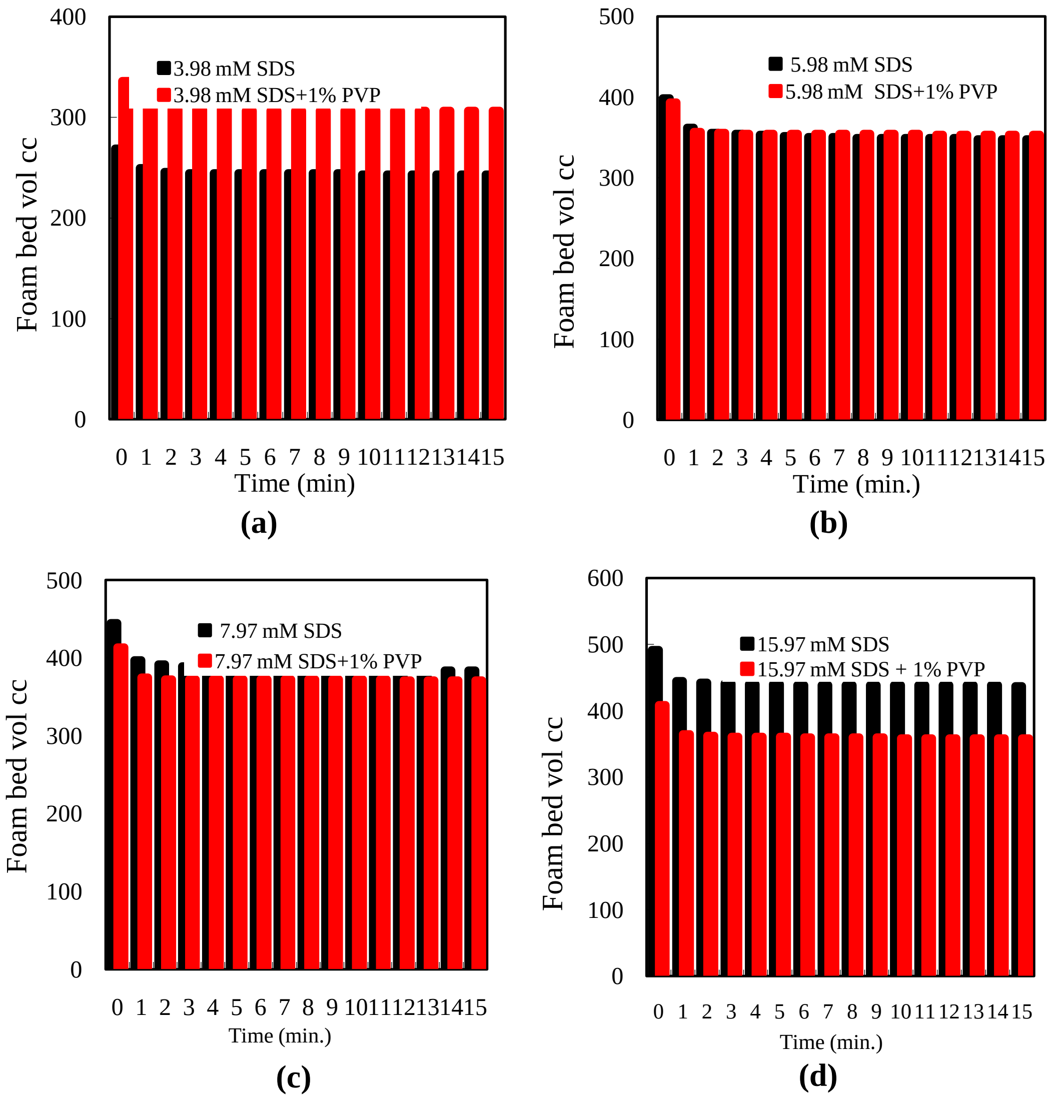


Fig. 4.14: Effect of PVP and PVP- SDS concentrations on surface tension

4.5 Effect of presence of polymer

The foam bed volume in the presence of 1% PVP by weight at SDS concentration of 3.98, 5.98, 7.97 and 15.97 mM/L is shown in Fig. 4.15(a), (b), (c) & (d) respectively. Foam bed volumes follow the order 7.97 mM SDS + 1% PVP > 15.97 mM SDS + 1% PVP > 5.98 mM SDS + 1% PVP > 3.98 mM SDS + 1% PVP.

For the surfactant only, the foam bed volume increases as surfactant concentration increases. For SDS concentrations of 7.97 mM/L and 15.97 mM/L initial foam bed volume was more for 15.97 mM/L SDS.



(a) **(b)**

(c) **(d)**

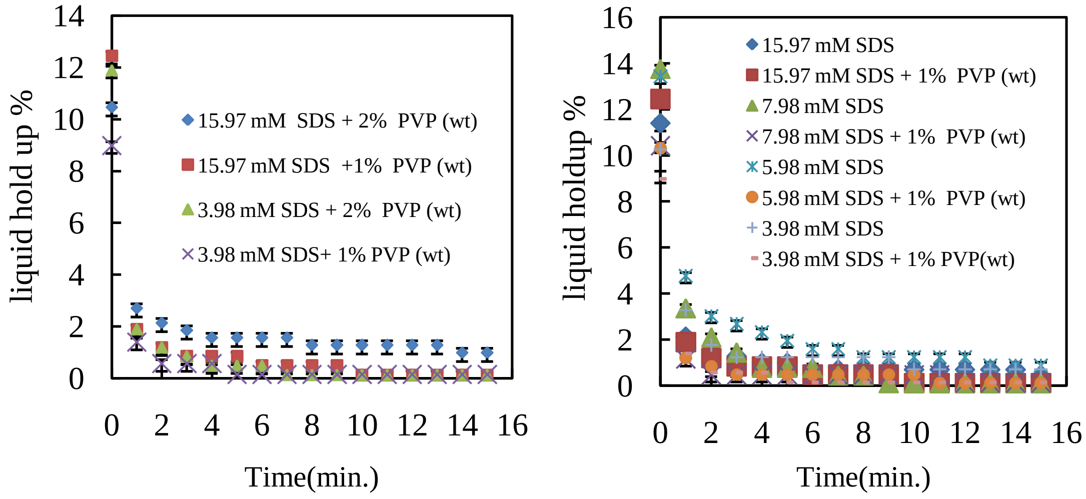
Fig. 4.15: Effect of PVP on foam bed volume at SDS concentrations of (a) 3.98, (b) 5.98mM, (c) 7.97mM, (d) 15.97mM/L

The polarizable pyrrolidone side group in the polymer PVP can acquire positive charge on the ring nitrogen wherein an anionic group of sodium dodecyl sulfate

(SDS) can interact. (Prasad M. 2006). When the PVP is connected with surfactant via electrostatic interaction, reactive groups of surfactant are complex or hidden, followed by a decrease of hydrophilicity, foamability.

The presence of PVP on the liquid holdup profiles are shown in Fig 4.16. Initial percentage liquid hold up is 12.45, 10.42, 10.31 and 8.98 for 15.97 mM/L, 7.97 mM/L , 5.98 mM/L and 3.98 mM/L SDS respectively with addition of 5 gm pvp (1% PVP by wt)in 500 ml SDS solution. PVP has the ability to induce surfactant aggregation and binding of the aggregates to the polymer. Water associated with SDS-PVP complexes result in higher initial liquid hold up.

The presence of 2% wt and 1% wt by PVP on the liquid holdup profiles are shown in Fig 4.16 (a) and (b). Foam formed with 2 % and 1% by wt PVP has initial percentage liquid hold up of 10.46 and 12.45 respectively for fixed surfactant concentration of 15.97 mM/L SDS.



(a) **(b)**

Fig. 4.16: Effect of (a) PVP (b) PVP and SDS on liquid hold up (%)

Foam formed with 2 % and 1% by wt PVP has initial percentage liquid hold up of 11.89 and 8.98 respectively for fixed surfactant concentration of 3.98 mM/L. Micelle formation at higher SDS concentration resulted less availability of free surfactant hence less percentage liquid hold up for 2% by wt PVP 15.97 mM/L SDS.

Availability of free SDS at lower concentration enhances the chance of PVP attachment in solution that results in higher initial liquid hold up for 2% PVP along with 3.98 mM/L SDS. Liquid drainage was found to be the slowest for 2% PVP while the liquid holdup profiles differed significantly.

Visual observations show that foam was found to be the most stable for 1% PVP and 3.98 mM/L SDS. The difference between the percentage liquid hold ups for 2% PVP and 1% PVP after 10 min. was not significant for 3.98 mM/L SDS. PVP-SDS complex adsorption at the air–water interface is expected to occur because of the minimum electrostatic energy barrier for adsorption, resulting increased stability of thin liquid films. It is, therefore, not surprising that the foam was found to be most stable for 1% wt PVP.

The presence of 100 ppm cadmium on the percentage liquid holdup profiles is shown in Fig 4.17 below. Foam formed with 100 ppm cadmium, 1% PVP and 3.98 mM SDS has initial percentage liquid hold up of 12.85% while for 1% PVP and 3.98 mM SDS has initial percentage liquid hold up of 8.98%. This indicates that metal addition increased percentage liquid hold up which may be attributed to water bridge formation.

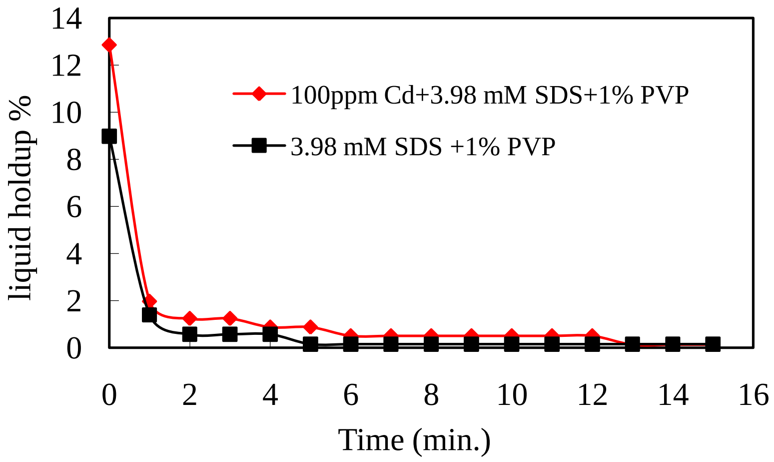


Fig. 4.17: liquid holdup (%) in presence of SDS, Cd and PVP

4.6 Foam formed by bubbling air in surfactant solutions

In the earlier section the pattern of foam formation, foam bed height and foam drainage reported were based on the Ross – Miles pour test that is inherently a static method for foam generation and evaluation of foam stability. Foam generation could also be achieved by continuously bubbling air in surfactant solution, this method is a semi continuous and dynamic procedure to generate foam till the surfactant exists in the aqueous feed. Foam was generated by bubbling gas continuously in surfactant solutions at varying flow rates over a period of time with the objective to establish the amount of foamate volume that could be collected over the time interval and the surfactant concentration in the foamate thus collected. This information becomes valuable in identifying the various parameters that affect the removal of metallic ions / precipitates using foam separation.

The foam column (FC-1) having multiple outlets as described in Chapter 3 was used to study the foaming patterns in this semi continuous mode of operation. In all the runs this column was filled with 450 ml of feed that filled the column up to a height of 38 cm above the gas sparger. Foam could be collected from outlets at heights 47 cm, 92.5 cm , 157.5 cm and 203 cm above the liquid surface denoted as O-1, O-2, O-3 and O-4 respectively. At any time only one outlet was kept open to collect the foam, moreover in the concentration range of the surfactant, as well as the gas rates used the foam bed height could not be reached outlet O-4.

4.7 Effect of air flow rate on foamate volume

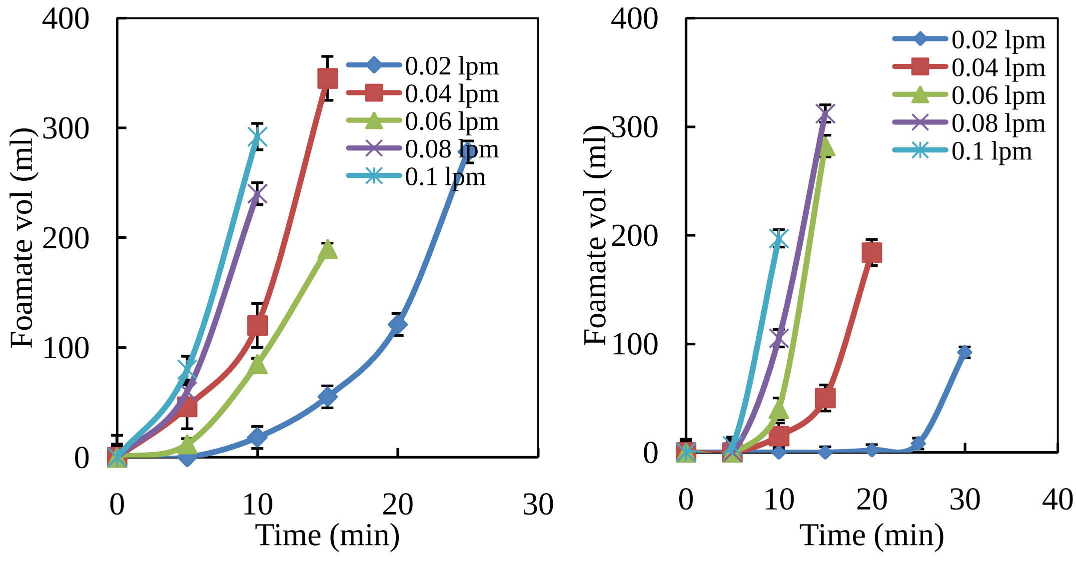
Experiments were conducted to generate foam by bubbling air through a surfactant solution and to collect the foam from one of the outlets. Subsequently the foam was broken and the foamate volumes were measured. At constant surfactant concentration of 0.882 gm/lit (0.00306 gmoles/lit) the air flow rates were varied in the range of 0.02-0.1 lpm corresponding to superficial air velocities of $1.06 \text{x} 10^{-7}$ to $5.30 \text{ x} 10^{-7}$ m/s and mass flux of $1.35 \text{x} 10^{-7}$ to $6.75 \text{x} 10^{-7}$ $\text{kg/m}^2\text{s}$

It was observed that except for very low air flow rates (0.02 lpm) there was acute inconsistency in the amount of foamate volume collected at different time intervals. There was abrupt and inexplicable change in the amount of foam formed at different flow rates at different time intervals.

There is scope for large scale circulation, bubbles group into clusters which are swirled upwards by turbulent eddies. At high gas rate, transient high speed channels are formed by chains of large bubbles. Outside these channels the bubbles move up slowly or are carried down by draining liquid. The top layer void fraction is higher because the large gas bubbles carry less liquid to the top. Turbulence disrupts the stable bubbles, the total foam height decreases sharply and hence foamate volume.

Fig 4.18(a) and (b) present the profile pictures of the foamate volume collected from O-1 and O-2 outlets respectively at different time intervals. The experiments were continued till the liquid level in the column declined to a height of 5cm above the distributor.

Experimental planning was to study removal of 100 ppm Zn using SDS keeping Zn:SDS 1:2 on mole basis. The same amount of calculated surfactant (0.8820 gm/lit) was used for experimental runs.



(a) **(b)**

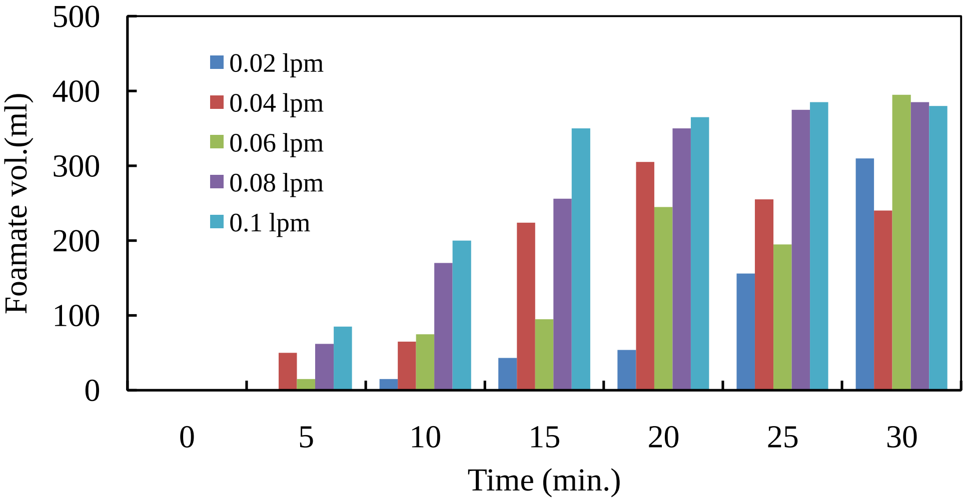
Fig. 4.18: Foamate volumes obtained at different flowrates

For higher air flow rate i.e. 0.06-0.1 lpm the amount of foamate collected is more in the initial few minutes and within 10-15 minutes almost half of the feed came out as foamate therefore the column could not be operated for longer time.

4.7.1 Foamate volume collected in fixed time intervals

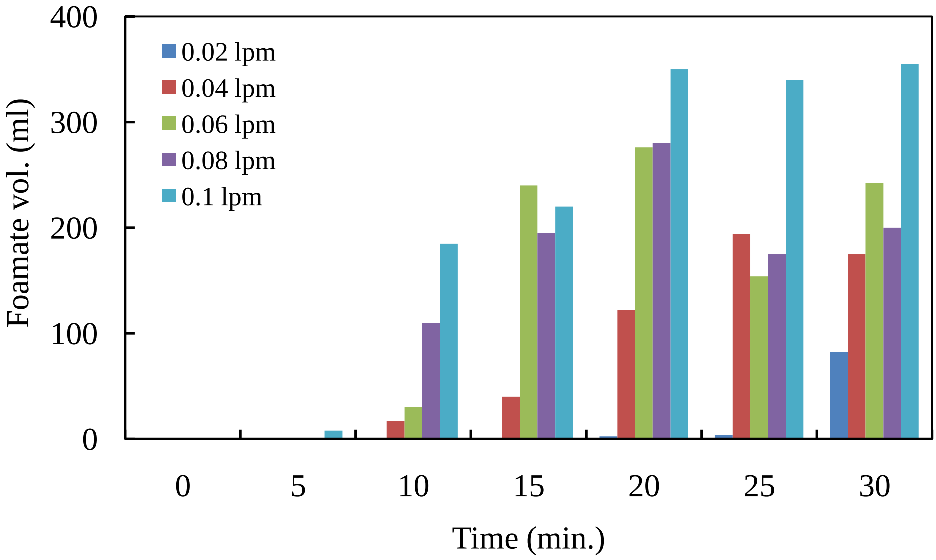
In view of the inconsistencies of the foaming operation and the amount of foamate generated at different time periods, it was decided to feed the column with specified surfactant solution and run the experiments for a fixed time ranging from 5 min. up to 30 min while collecting the foam generated from a specified outlet over the entire period of time and investigate the effect of air rate on the foamate collected. Implying that every point of the data reporting foamate volume, was the outcome of an independent experiment.

In this mode of experimentation also it was found that the overall behavior of foamate volume collected in an span of time was certainly chaotic, however there was some reproducibility in the pattern of foamate generated. Foamate volume increases with increase in gas flowrate and time for air flow rates i.e 0.02 to 0.1 lpm till 30 min. Foam levels generally increase in height with increasing gas flow rate since more bubbles erupt from the liquid surface and then are converted into foam as shown in Fig. 4.19.



(a)

Fig.4.19 (a): Foamate volumes obtained at varying volumetric flowrates between 0.02-0.1 lpm for O-1



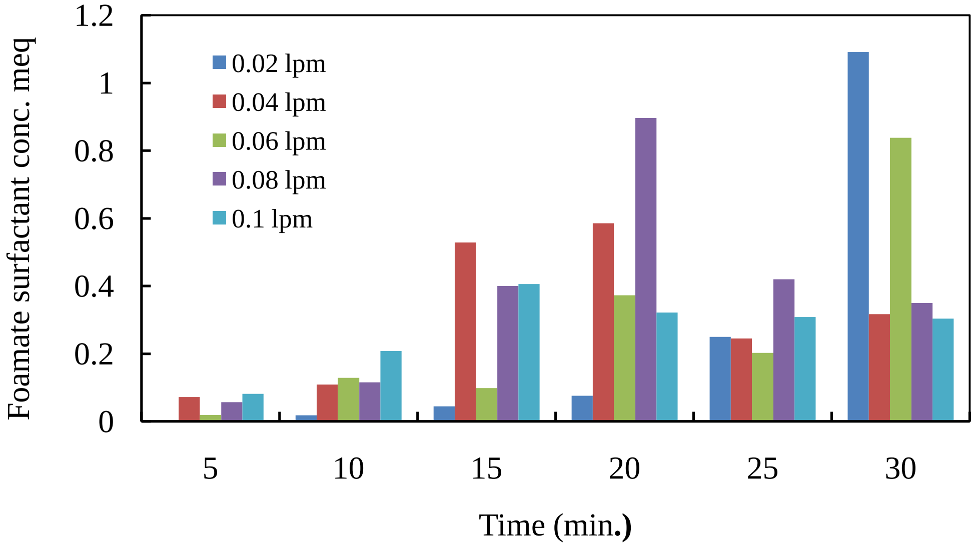
(b)

Fig.4.19 (b): Foamate volumes obtained at varying volumetric flowrates between 0.02-0.1 lpm for O-2 outlet from bottom

At higher flowrate and foaming time intervals up to 30 minutes, foamate volume collected was higher. The number and velocity of large gas bubbles increases resulting in higher foamate volume at top. The foamate volume obtained increases with time because in presence of surfactant, bubble size decreases, and hence more surface area crosses the foam-water interface per unit time and hence more water is also entrained in the foamate. This then leads to an increase in liquid fraction at the top of glass column and hence higher foamate volume.

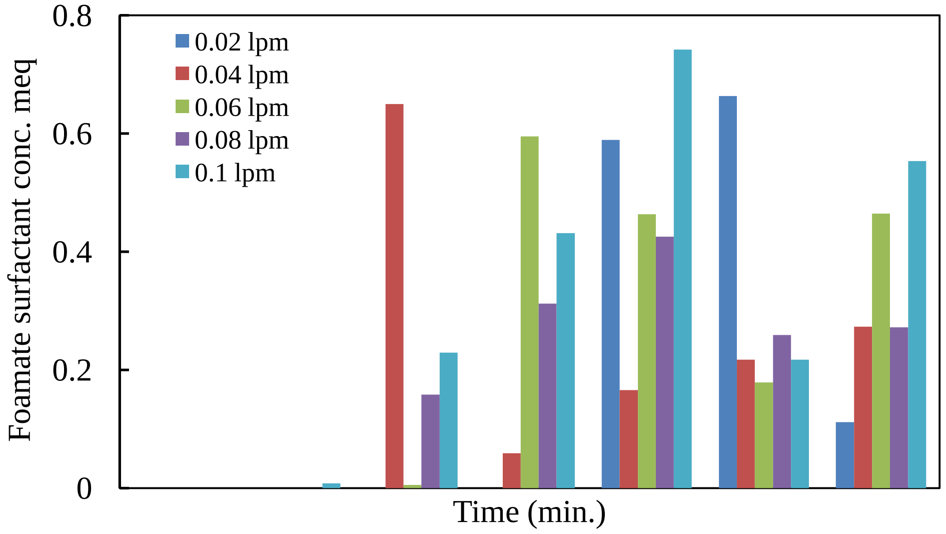
Surfactant concentration increases in the initial time intervals (up to 15 min.), it decreases in intermediate time intervals (20-25 min.) and then it increases again till 30 minutes as shown in Figure 4.20 (a) and (b) for both O-1 and O-2 outlet of glass column.

Under the conditions used in the experiments the Na^+ ---dodecylsulfate and Me^{2+}----dodecyl sulfate combinations at the gas/solution interface can be expressed in the form of hydrated ion pairs, in a general way as $[Me(H_2O)n\text{-}q,(RSO_4)q]m\text{-}q$ where Me^{m+} can be Na^+ or Me^{2+} , n is the number of water molecules in relation to a metal, and q is the number of dodecyl sulfate anions. The above expression of the hydrated ion pairs results from the competition for metal cations between water molecules and surfactant anions.



(a)

Fig.4.20: (a) Foamate surf conc. at varying volumetric flowrates between 0.02-0.1 lpm for O-1outlet.



(b)

Fig.4.20: (b) Foamate surf conc. at varying volumetric flowrates between 0.02-0.1 lpm for O-2 outlet

On the basis of analysis of intermolecular interaction in aqueous solutions it can be supposed that dodecyl sulfate hydration results from two kinds of hydrogen bonds, namely among water molecules (H_2O---H_2O) as well as between dodecyl sulfate anion and water molecules (OH_2----OSO_3R). Also hydration can result from the formation of a donor-acceptor bond between a metal cation and water oxygen (Me^{2+}…OH_2). Therefore, the water acts a bridge between the metal cation and the dodecyl sulfate anions. Electrostatic model of ion pairs which are based on the electric double layer was also suggested by many researchers. In this view layer of anionic surfactant adsorbed at gas/solution interface is associated with a layer of oppositely charged colligend ions in order to maintain electrical neutrality. (Jurkiewicz 1990)

4.7.2 Foaming behaviour of SDS in presence of metal ions.

In order to study the effect of the presence of metal experiments were carried out using 100 ppm zinc retaining concentration of SDS that gave a metal to surfactant molar ratio of 1:2 at varying flowrates of 0.02- 0.08 lpm.

Foamate volume was collected from O-2 outlet of column. Foamate volume collected vs time is plotted which is shown in Fig.4.21 for volumetric flowrates of 0.02, 0.04, 0.06 and 0.08 lpm respectively.

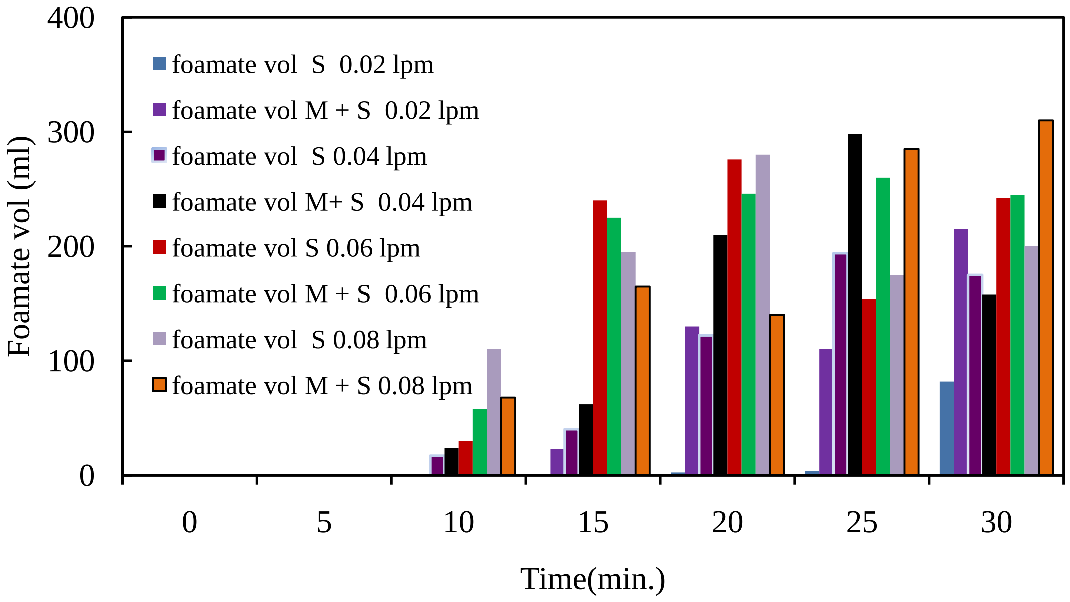


Fig. 4.21: Foamate volume for SDS and SDS along with 100 ppm zinc for various flowrates

Higher foamate volume was obtained when zinc was present along with SDS at gas flowrates of 0.02, 0.04 and 0.06 lpm in column. At air rate of 0.08 lpm the foamate volume obtained for SDS alone was higher for 10,15 and 20 min. Higher flowrate affects the bubble motion, the bubbles are not of uniform size. The vigorous circulation patterns in the liquid cause a net increase in rise velocity, which influences adsorption of metal-surfactant complex on bubble surface.

4.8 Bubble size distribution in foams

Gas flow rates (bubbling rates) affect the bubble motion, the bubbles are no longer of uniform size because of bubble coalescence and breakage, and the bubble shape changes rapidly. The vigorous circulation patterns in the liquid cause a net increase in rise velocity and hence results in higher foamate volumes (Darton and Sun 1999). Surfactant causes some retardation in coalescence and hence a change in hold-up and other properties. With increasing gas flow rate and time the bubble size and velocity increases.

These bubbles coalesce frequently and burst almost immediately at the top of the foam. To measure average bubble size the behaviour of air bubbles in dilute aqueous surfactant solution was studied**.** Bubble size distribution effects foamate volume and hence metal removal associated with it. Average bubble size was studied in water and surfactant solution in foam column (FC-2) as discussed in Chapter 3. To study the bubble size distribution air was bubbled in 0.1 gm/l SDS solutions.

Image analysis software Image J was used to measure the size of bubbles generated and getting bubble size distribution in foams. Image J is a powerful image analysis program that was created at the National Institute of Health USA. It is in the public domain, runs on a variety of operating systems and is updated frequently. It can calculate area and pixel value statistics of user-defined selections. It can measure distances and angles. It can create density histograms and line profile plots. (Ferreira 2011)

It was observed that clean bubble rises faster because its entire surface is mobile. However, for a bubble in surfactant contaminated water, the situation is very different. Gradient of surface tension has the important effect of decreasing surface mobility, bubbles in such contaminated water rise slower. A digital single lens reflex camera (DSLR NIKON D90), equipped with a proper macro lens in order to attain appropriate magnification was employed to photograph the bubble formation in the column and from this data the bubble size distribution was inferred.

Coalescence is the merging of two bubbles as a result of the rupture of the film between the bubbles. Larger bubbles appear in the foam and the number of bubbles decreases. Disproportionation is inter bubble gas diffusion, also called Ostwald ripening. As a result of gas diffusion larger bubbles grow at the expense of smaller bubbles. Smaller bubbles shrink and may finally disappear. These processes effect the distribution of the liquid and gas phase and thus alter the foam properties.(Bisperiak et.al**.**1992)

Initially the bubble-size distribution is almost monodisperse and all bubbles have a spherical shape. The initial average bubble size in water is 0.36, 0.513, 0.746, 1.135 and 1.433 mm^2 for 0.02, 0.04, 0.06, 0.08 and 0.1 lpm respectively.

Fig. 4.22 shows average bubble size at varying air flowrates for different water pool depths in the column.

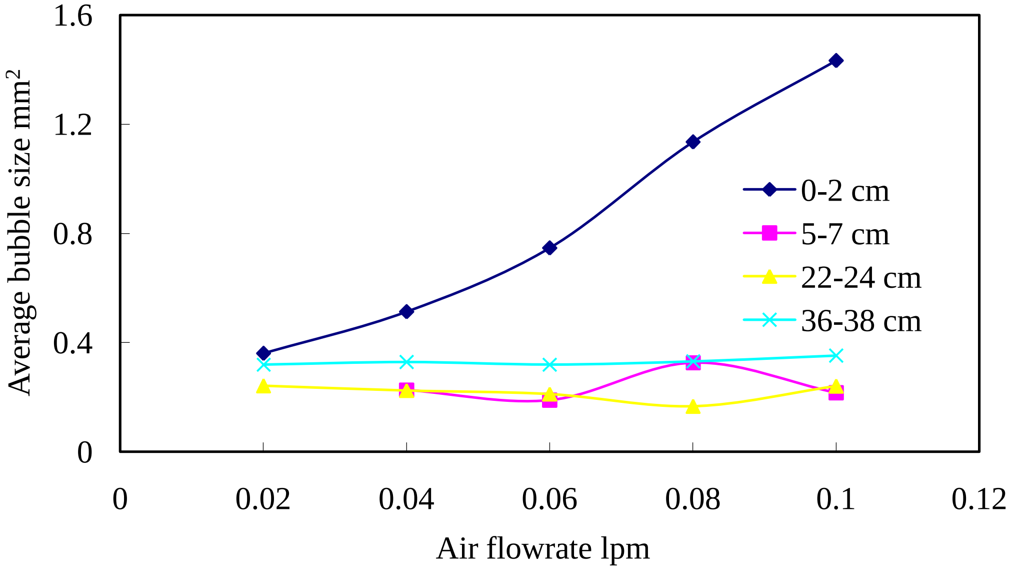


Fig. 4.22: Average bubble size for various air flowrates in water column of different depths

Fig. 4.23 shows counts at varying flowrates for water pools of different depths. Fig.4.23 indicates that for a particular air flowrate in column bubble counts increases though their size decreases which is indication of disproportion. At 0.02, 0.04, 0.06 lpm bubble size increases and counts also increase after 24 cm height which indicates coalescence dominates at upper level.

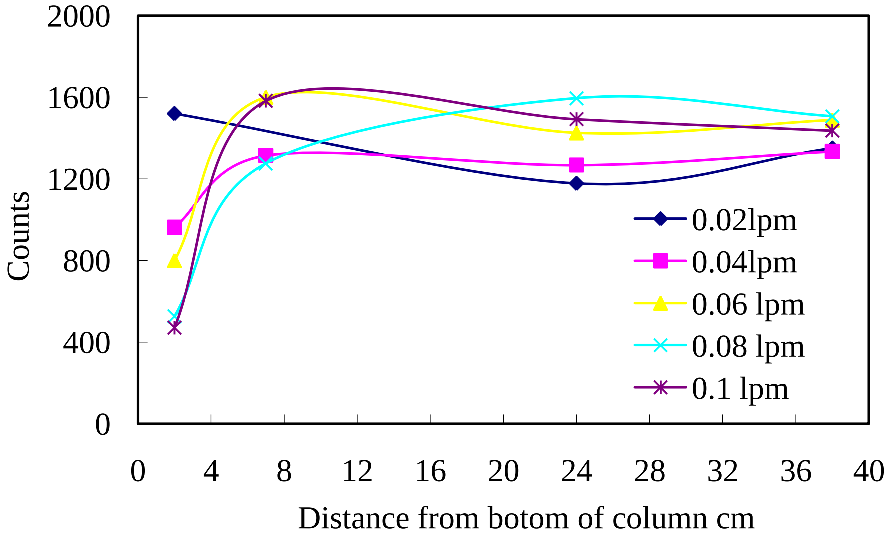
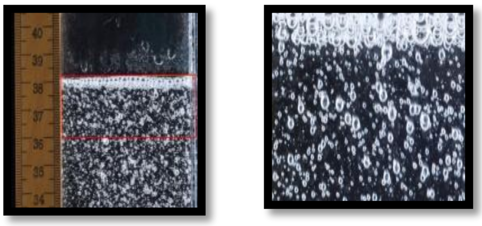


Fig. 4.23: Counts in water at various distance of column for different flowrates

Air bubbles in water at different heights moving in upward direction of column were analysed. Average bubble size decreased for 5-7 cm. Average bubble size decreased to 0.227, 0.189, 0.327 and 0.216 mm^2 for 0.04, 0.06, 0.08 and 0.1 lpm respectively. Average bubble size was 0.242, 0.225,0.212, 0.167 and 0.241 mm^2 for 0.02, 0.04,0.06, 0.08 and 0.1 lpm respectively for 22-24 cm. Average bubble size was 0.32, 0.329,0.32, 0.331 and 0.352 mm^2 for 0.02, 0.04,0.06, 0.08 and 0.1 lpm respectively for 36-38 cm in foam glass column (FC-2).

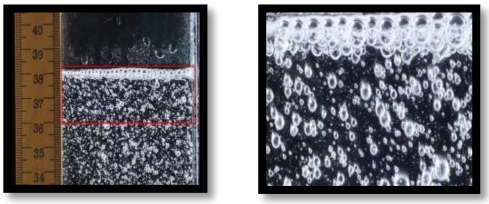
Coalescence and disproportionation both have contributed to coarsening of the bubbles. Large number of bubbles become smaller giving evidence of the fact that disproportionation occurred. Lemlich (1968) showed that the initial bubble-size distribution has a major influence on the progress of disproportionation. In 36-38 cm bubbles became larger. This is attributed to coalescence because none of the bubbles became smaller.

Photographic images of bubbles observed in the rectangular foam column FC-2 is shown in Fig.4.24 for (a) bubbles in water (b) bubbles in surfactant solution, both at 0.02 lpm air flow rate. Similarly Fig. (c) and (d) are for 0.04 lpm flow rate , Fig (e) and (f) are for 0.06 lpm, Fig. (g) and (h) are for 0.08 lpm and finally Fig. (i) and (j) are for air flow rate of 0.1 lpm .

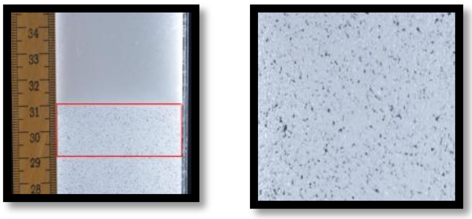


(a)

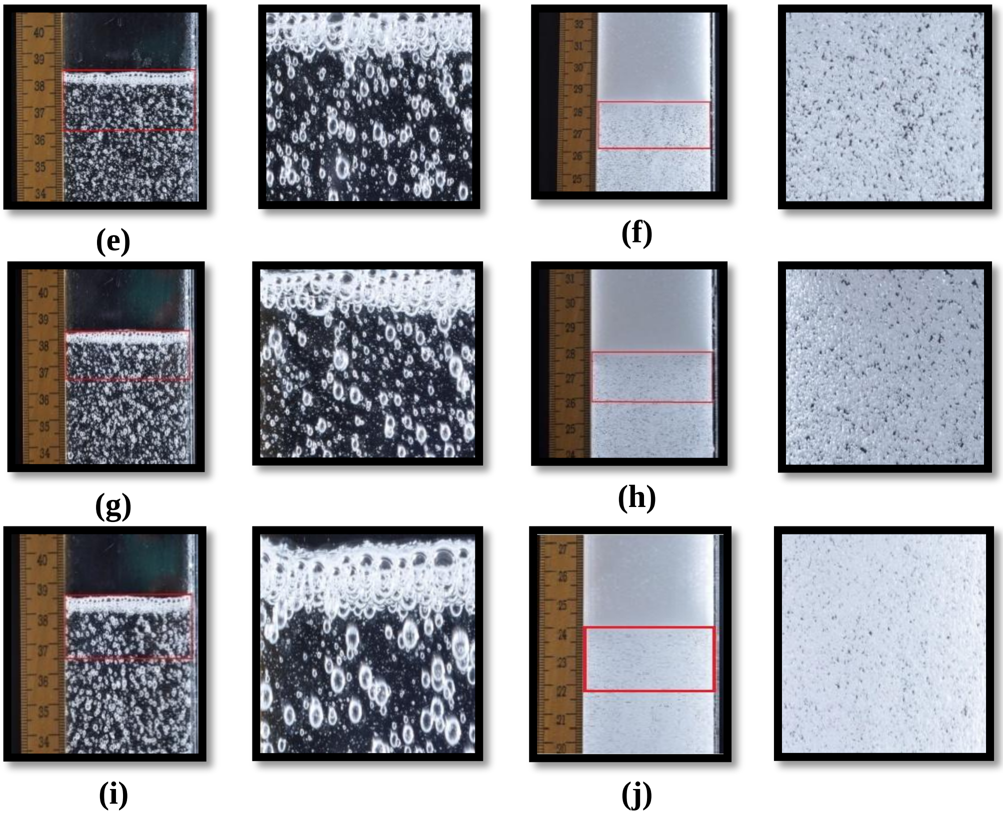
(b)



(c)



(d)



(e) (f)

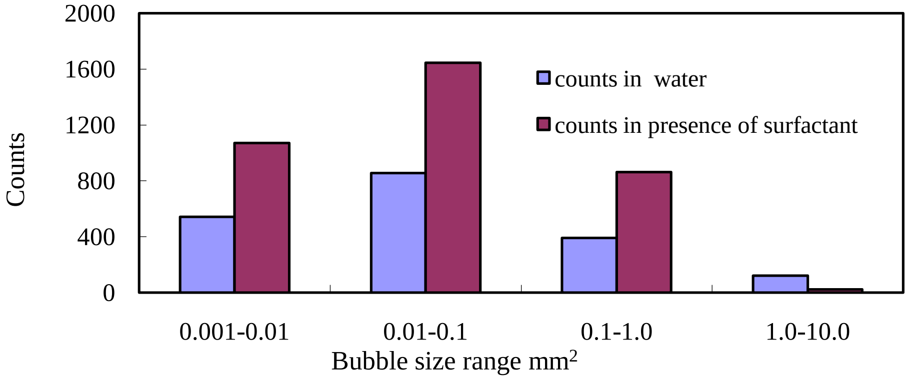
(g) (h)

(i) (j)

Fig.4.24: Bubbles in water and surfactant solution at different air flow rates

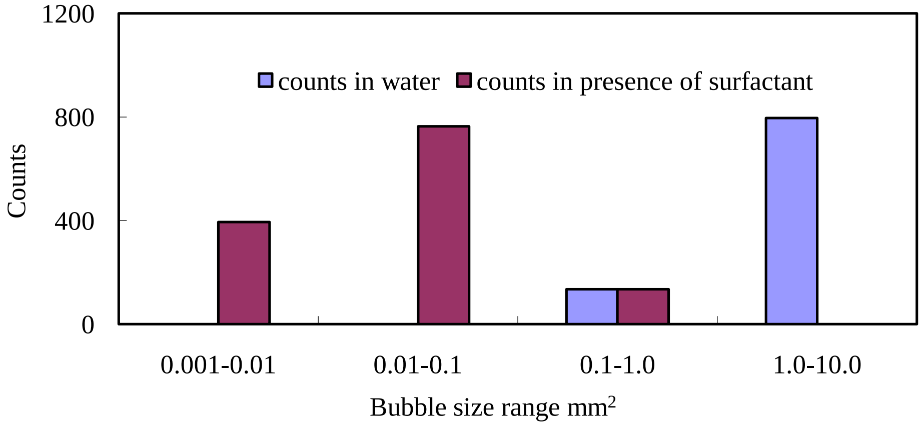
In the pictures shown in Fig 4.24 the foam interface between the bubbly mixture and foam is clearly identified, the interface between the foam and the bubbly mixture is quite sharp. The foam and bubbly mixture are strictly segregated by gravity, foam above and bubbly mixture below.

As foaming continues and the surfactant is progressively removed from the liquid into the foam the foam interface becomes more distinct. Enlarged view of the foam interface at different air flow rates is also shown. It was observed that the density of bubbles has considerably reduced after 15 min. Fig.4.25 (a to e) shows bubble count histograms in water and in surfactant solution at different air flow rates.



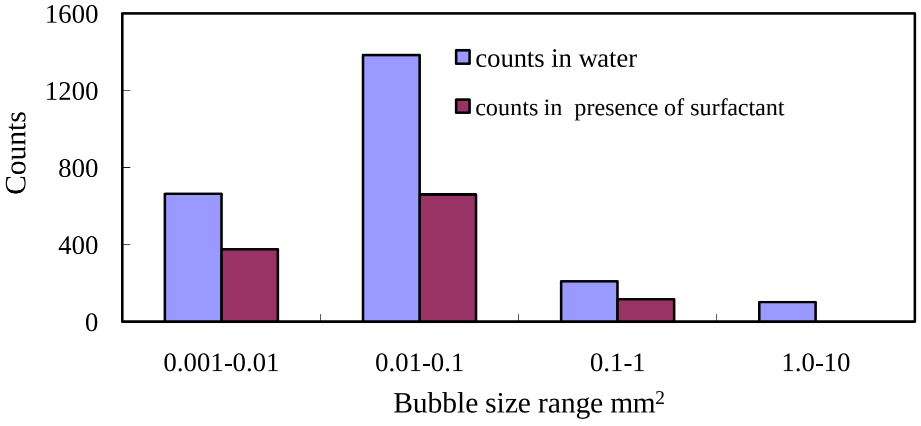
(a)

Fig. 4.25 (a): Histograms of counts vs bubble sizes for 0.02 lpm in water and surfactant solution after 15 min.



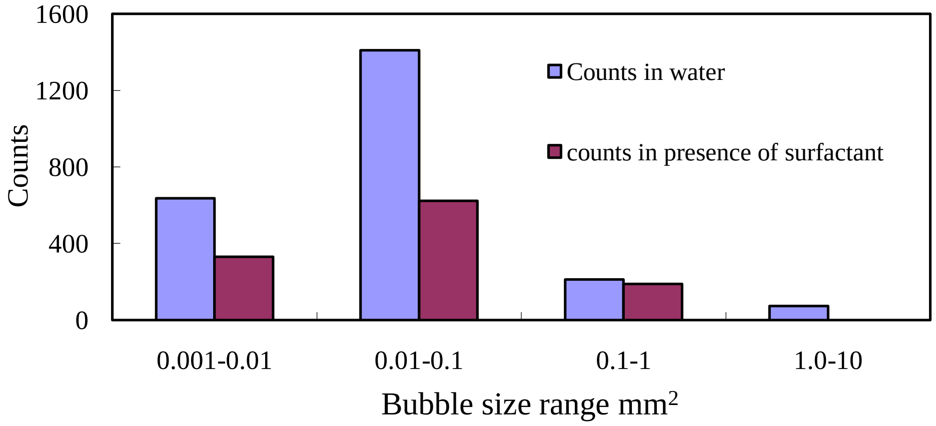
(b)

Fig. 4.25 (b): Histograms of counts vs bubble sizes for 0.04 lpm in water and surfactant solution after 15 min.



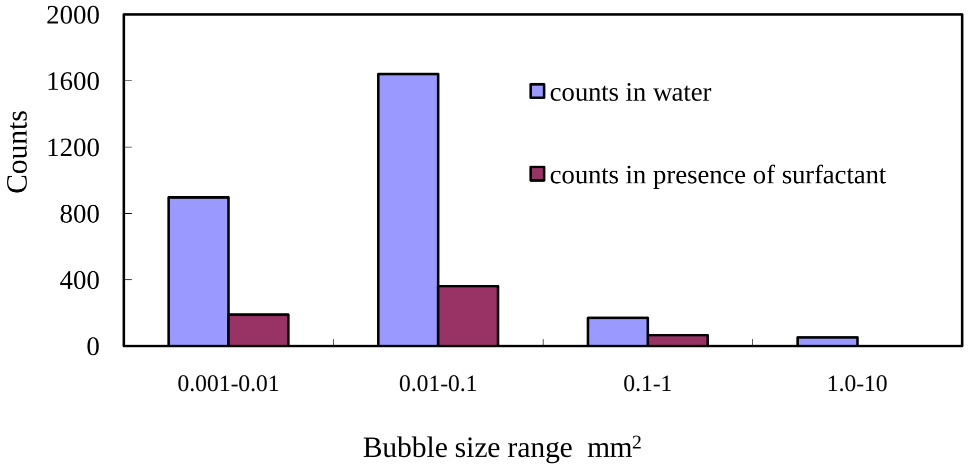
(c)

Fig. 4.25 (c): Histograms of counts vs bubble sizes for 0.06 lpm in water and surfactant solution after 15 min.



(d)

Fig. 4.25 (d): Histograms of counts vs bubble sizes for 0.08 lpm in water and surfactant solution after 15 min.



(e)

Fig. 4.25 (e): Histograms of counts vs bubble sizes for 0.1 lpm in water and surfactant solution after 15 min.

Histograms of counts and bubble size in water and in dilute surfactant solution are shown in Fig.4.25. More number of smaller bubbles in the range of 0.001-0.01 mm^2 are present in surfactant solution at interface. It is observed that even small amount of surfactant can drastically reduce bubble size and hinder coalescence between bubbles.

4.8.1 Effect of Gas flowrate on Bubble size distribution

Gas flow rate has a significant effect on the resultant bubble size distributions. As the gas flow rate increases the number of bubbles with larger sizes increases. The increase of gas flow rate yields more bubbles from the sparger and thus their population in the column increases. Consequently, the frequency of collisions between bubbles increases and bubble coalescence increases.

As the air flow rate is increased, turbulence in the liquid also increases, enhancing collisions and coalescence between bubbles, which in turn favours the formation of larger bubbles. Less number of counts indicates coalescence. The attachment process is selective and the difference in attachment probability of different particles determines the selectivity of flotation. The attachment process is determined by hydrodynamic and surface forces of particles and bubbles.

The prediction of particle–bubble interaction in a real system depends on the gas holdup effect, the interaction between neighboring bubbles, and the presence of multilayers of bubbles, all of which tend to straighten the liquid streamlines around a bubble and thus increase the overall probability of collection. The behavior of the foam phase is another important aspect of foam separation that affects performance. Separation efficiency can be improved if foam stability is properly controlled.

With low gas flow rates, higher retention times are needed. On the other hand high gas flow rates result usually in the formation of large amounts of wet foam, indicating a volume of entrained water, which is difficult to handle. The bubble size and gas flow rate have been found to influence significantly the rate of removal.

4.9 Interfacial area measurement

Interfacial areas available in the foam column were attempted to be measured experimentally using the chemical techniques of interfacial area measurement. Sulfite oxidation method using depletion of sodium sulfite concentration was measured for different time intervals. To study effect of presence of metal on interfacial area, 50 ppm Zn, 50 ppm Zn with Zn:SDS 1:2 molar ratio, 100 ppm Zn, 100 ppm Zn with Zn :SDS 1:2 molar ratio were charged in foam glass column and sulphite depletion was measured. The same was repeated for cadmium and nickel as well.

The interfacial areas obtained by sulfite oxidation technique did not show any significant change in the presence of metals such as cadmium, nickel and zinc. In presence of surfactant with metal to surfactant molar ratio of 1:2 the interfacial area increased for zinc and nickel as their concentration increased. This was attributed to the presence of free surfactant in the aqueous system. The behavior of cadmium was contrary to this behavior and is attributed to clustering tendency of Cd –SDS complexes.

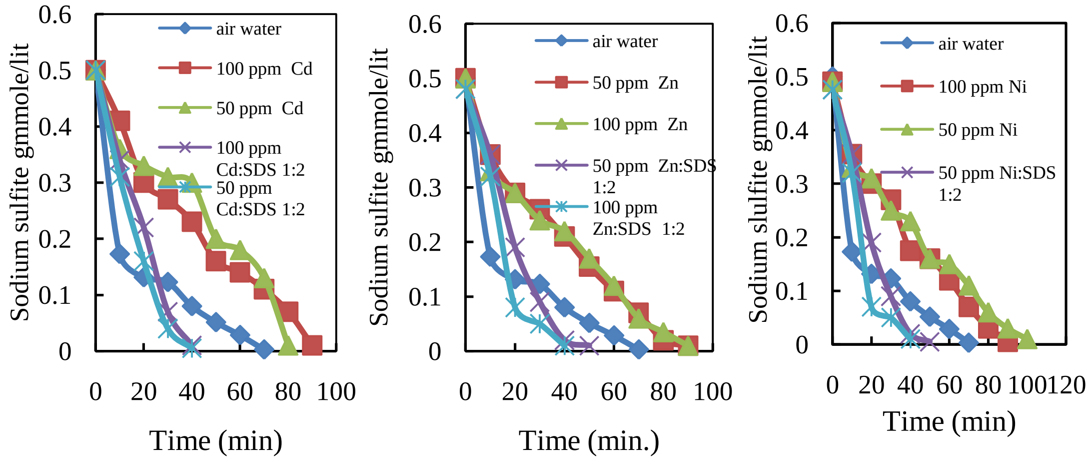


Fig. 4.26: Depletion of Sodium sulfite concentration with time for metals and metal:surfactant system

The resulting interfacial areas in the foam column obtained under different conditions are listed below in Table 4.1

Table 4.1: Interfacial area

Sr. No.	System	Surfactant conc.mg/l	Surfactant conc.mM/l	Metal conc.mg/l	Metal conc.mM/l	Interfacial area cm^{-1}
1	50 ppm Zn	-	-	50	0.76	2.06
2	100 ppm Zn	-	-	100	1.53	2.15
3	50 ppm Zn :SDS 1:2	443.52	1.54	-	-	3.16

4	100 ppm Zn:SDS 1:2	881.28	3.06	-	-	4.07
5	50 ppm Cd	-	-	50	0.45	1.86
6	100 ppm Cd	-	-	100	0.89	1.82
7	50 ppm Cd :SDS 1:2	256.32	0.89	-	-	4.18
8	100 ppm Cd:SDS 1:2	512.6	1.78	-	-	3.71
9	50 ppm Ni	-	-	50	0.85	1.90
10	100 ppm Ni	-	-	100	1.7	1.98
11	50 ppm Ni :SDS 1:2	489.6	1.7	-	-	3.14
12	100 ppm Ni:SDS 1:2	979.2	3.4	-	-	4.02
13	Only SDS (0.13gm/450ml)	288.88	1	-	-	3.61
14	Air water					3.71

4.10 Conclusions

The salient conclusions drawn from this work are as follows:

Liquid hold up in foams generated by aeration of aqueous SDS solutions was determined by Ross-Miles method. Liquid hold up in foam was determined at different metal concentration of 100 mg/l , 200 mg/l and varying SDS concentration in the range of 3.98 milimole to 7.97 milimoles. Liquid hold up of foam was also measured in the presence of PVP.

The presence of single metal ions such as zinc, cadmium, nickel on the foaming patterns of SDS solutions and in combinations of zinc-cadmium and nickel-cadmium were also investigated. Liquid holdups were also determined for the case of polymer PVP being present in the SDS solution and with SDS-Cd-PVP systems.

It was observed that for the same surfactant concentration liquid hold up in foam was more in presence of metal. This is attributed to the formation of water bridge between the metal cation and the dodecyl sulfate anions. Liquid drains more slowly from the foams in presence of metal, especially at the later stages of drainage. Foam bed volume was measured in presence of 100ppm, 200ppm metal with SDS concentration ranging between 3.98-7.97mM. Foam bed volume and percentage liquid hold up is more at 200 ppm metal concentration compared to 100ppm metal concentration.

With increase of the surfactant concentration the drainage rate of foam decreases this can be attributed to the increasing immobilization of the surfaces by the adsorption monolayers resulting in an increase in liquid hold up in the foams.

Interfacial areas of air-water system, in the foam column were determined by sulfite oxidation method at optimum conditions. The interfacial areas obtained by sulfite oxidation technique did not show any significant change in the presence of metals such as Cd, Ni and Zn. In presence of surfactant with metal to surfactant ratio of 1:2 the interfacial area increased for Zn and Ni as metal concentration increased this was attributed to the presence of free surfactant in the aqueous system.

Effect of air flow rate on foamate volume for different outlets was also discussed. Higher foamate volume was obtained when metal zinc was present along with SDS for gas flowrates of 0.02, 0.04 and 0.06 lpm in column. While for 0.08 lpm the foamate volume obtained for SDS alone was higher. Higher flow rate affect the bubble motion, the bubbles are no longer of uniform size because of bubble coalescence and breakage, the bubble shape changes rapidly. The vigorous circulation patterns in the liquid cause a net increase in rise velocity which influences adsorption of metal-surfactant complex on bubble surface.

Behavior of air bubbles in water and in dilute aqueous surfactant solutions was also observed**.** It was observed that clean bubble rises faster because its entire surface is mobile. However, for a bubble in surfactant contaminated water, the situation is very different. Gradient of surface tension has the important effect of decreasing surface mobility. Bubbles in contaminated water rise slower. As foaming continues and the surfactant is progressively removed from the liquid into the foam the foam interface becomes more distinct .It was observed that the density of bubbles has considerably reduced. Bubble size distribution was measured using Image J software. Confocal microscopy was used to study structure of foam.