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## Ion-specific effects on the bubble coalescence in aqueous medium

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Abstract: The flotation froth must have low durability to be useful for the mineral separation process. For this reason, suitable frothers are used. Their role is to suppress the coalescence of the bubbles in the liquid phase of the reactor and to form a short-lasting froth cap above the level of the liquid. Indeed, one could state the question; what makes the bubble coalesce in pure water? They coalesce to decrease their surface energy, which is related to the hydrophobicity of the bubbles. In such a case, why do frothers with very small concentrations, practically not affecting the surface tension value, obstruct their coalescence? The answer, in our opinion, is the hydration repulsion between the bubbles, which are covered by frother with a hydrophilic head pointing outward the bubble. This makes the bubble more hydrophilic even when its surface tension values are practically the same as this one in the absence of a frother. Such a more hydrophilic bubble with a scarce frother adsorption layer has no sufficient Gibbs elasticity to underpin a stable froth cap above the level of the liquid. Some time ago an excellent group from Istanbul Technical University built up a unique setup, able to determine the fraction of bubble coalescence versus the frother concentration. We show in this work that the experimental curve determined by this setup can be converted to an experimental level of hydrophilicity of the bubbles versus the concentration of the frothers. Hundred percent of the primary bubbles coalesce in pure water, where they are the most hydrophobic. At 100% hydrophilicity, the bubbles do not coalesce but form a froth cap, which is short-lasting. Within this context, in this study, the effects of NaCl and CaCl<sub>2</sub> on the coalescence of the bubbles being either frother-free or in the presence of sodium dodecyl sulfate (SDS) were investigated. Their foamability was studied as well. The fraction of the coverage of SDS, NaCl, and CaCl<sub>2</sub> species on the surface of the bubble and the level of hydrophilicity versus their bubble percentage coalescence were determined. The experimental data were related to the adsorption energy of SDS, Na<sup>+</sup>, Cl-, and Ca<sup>2+</sup> on the air/water interface and their Gibbs hydration energy. It was established a linear dependence between the value of CCC and its corresponding level of coverage of the added agent.

Keywords: flotation, SDS, salt, bubble coalescence, CCC, dynamic foam stability

## 1. Introduction

The Bikerman unit of foaminess (Bikerman 1938, Bikerman 1973) (Dynamic foam stability) is a critical aspect of flotation processes, especially in mineral processing. The stability of foam directly affects the flotation recovery, which is based on the separation of hydrophobic particles from hydrophilic ones. The flotation is based on bubbles forming and attaching to the desired particles, allowing them to rise to the surface for collection. The froth should be short-lasting with a low dynamic foam stability. However, this is related to various factors such as the type of reagent, the presence of various ions, concentration, and the physico-chemical properties of the solution.

Various methods have been developed to evaluate foam stability, which can be broadly divided into two categories: dynamic tests and static tests. The dynamic test refers to a scenario where the foam, produced by the sparging of gas through a porous bottom into the frother's aqueous solution, lifts until it reaches either a certain constant stationary height or pulsation of the height up and down with a certain tempo and amplitude. The rate of foam formation and decay are equal in both scenarios. In contrast, a static test is a test in which the foam is produced by shaking the foaming solution (the method of Bartsch (Bartsch 1926); once the foam is generated, it is allowed to decay for a certain time. The dynamic test (Bikerman 1938) is considered more representative of conditions in a real flotation system. In this test, air is continuously supplied to the solution, and foam formation begins at the bottom and then rises to the top. As the liquid flows downward, the quality of foam varies with height. Eventually, the top layer of the foam becomes unstable and collapses. These features are very much like what we see in actual flotation processes, making it more likely that the dynamic method will accurately show how stable the foam is during flotation tests (Farrokhpay and Fornasiero 2017). The Bikerman unit of foaminess (later called dynamic foam stability) was first proposed by Bikerman (Bikerman 1938, Bikerman 1973). It is defined as the ratio of the maximum volume of foam produced to the gas flow rate. In a study conducted by Mackay et al. (Mackay, Mendez et al. 2018), the effects of particle size on dynamic foam stability were investigated, and the relationship between dynamic foam stability and flotation performance was revealed.

The role of foam stability extends beyond supporting the flotation process; it also impacts the overall recovery rates and the quality of the concentrate obtained. It is important to note that improved foam stability can significantly improve water recovery and the entrainment of solid particles, which are critical to maximizing the overall efficiency of the flotation process. Also, managing chemical additives can lower the use of frothers while keeping or boosting flotation performance, showing that foam stability can be improved with careful chemical management (Pashkevich, Li et al. 2023). This highlights the critical role of dynamic foam stability not only in ensuring effective flotation but also in advancing sustainable practices in the industry. By optimizing foam stability, resource consumption can be minimized, leading to more environmentally friendly and cost-efficient operations.

The chemical composition of the flotation medium as well as the physical dynamics of foam significantly influence flotation recovery. The foam's stability is mostly determined by bubble size and distribution, which are affected by frother choice and concentration. Stable foam plays a critical role in keeping floated materials at the water surface, ensuring they are collected at the optimum time. This process is important to ensure effective separation and maximize flotation performance (Szyszka 2018).

One of the primary mechanisms by which salts affect foam stability is through the crystallization of surfactants. Studies have shown that the addition of salts such as NaCl or KCl to aqueous sodium dodecyl sulfate (SDS) solutions induces the formation of surfactant crystals during foam generation (Amani, Karakashev et al. 2021). This phenomenon occurs at moderate salt concentrations where surfactant crystals obstruct the Plateau borders, subsequently reducing liquid drainage and increasing foam stability(Binks and Shi 2020).

Additionally, certain ions can greatly change how surfactants stick to the surface between air and water (Petkova, Ivanova-Stancheva et al. 2024). Studies have shown that magnesium ions can contribute to ultra-stable foams formed by flexible, bipolar-headed surfactants, indicating that certain cations can enhance foam stability by facilitating the formation of a multi-layered surfactant structure within the foam film (Li, Li et al. 2013). Also, the surfactant selection plays an important role in determining the foam stability in saline environments. It has been noticed that anionic surfactants like sodium dodecyl sulfate (SDS) can react with divalent cations when there is a lot of salt, causing solid particles to form. This interaction negatively affects foam stability because the precipitates disrupt the foam structure and reduce its effectiveness (Li, Wang et al. 2021).

Additionally, the interaction between salts and surfactants can result in the formation of more complex foam structures that may be advantageous in certain applications. For example, it has been reported that the addition of high salt concentrations can lead to the precipitation of surfactants on bubble surfaces, resulting in the formation of ultra-stable foams (Ramsden 1903). These foams have the potential to persist indefinitely under certain conditions, highlighting the role of salt-surfactant interactions in enhancing foam stability in targeted contexts (Zhang, Mikhailovskaya et al. 2015). More detailed observation of the flotation froth shows two zones of the froth: (i) liquid zone, in which the bubbles lift driven by the buoyancy force; usually part of the bubbles coalesces in this zone, thus reducing their concentration; (ii) froth cap zone, which is situated on liquid's surface. To supress the bubble coalescence very small frother/surfactant concentration is needed, but to underpin long lasting froth/foam high value of the Gibbs elasticity, at significantly larger frother/surfactant concentrations,

is required. These two scenarios in our opinion should be observed separately. For this purpose, in this study, bubble coalescence measurements using a micro-flotation column based on light adsorption and foam stability measurements using a dynamic foam analyzer were performed to understand the effects of Na<sup>+</sup> and Ca<sup>2+</sup> ions on the stability of the foam formed with sodium dodecyl sulfate (SDS).

## 2. Materials and methods

## 2.1. Materials

In this study, sodium dodecyl sulfate (SDS) ( $\geq$  99.0 C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na, Sigma Aldrich, Japan) as a surfactant, and analytical-grade NaCl (Sigma Aldrich, Denmark) and CaCl<sub>2</sub> (Sigma Aldrich, Germany) salts were used for the bubble coalescence and dynamic foam stability experiments at constant room temperature: (23 ± 1°C). All chemicals were prepared using pure water. All glassware was rinsed with ethylene alcohol (99% purity, MERCK, Kenilworth, New Jersey, USA) and washed with pure water (a total dissolved solid, TDS, 0-3 ppm) followed by drying in a clean oven.

## 2.2. Methods

## 2.2.1. Bubble coalescence measurements

The bubble coalescence measurements were performed using the new method proposed for determining the critical coalescence concentration of frothers (Guven, Batjargal et al. 2020). And, the critical coalescence concentration (CCC) values of SDS and salts were determined as a function of concentrations using a bubble column based on light adsorption (Fig. 1). In this method, a microflotation cell with a volume of 155 cm<sup>3</sup> (30×220 mm) and frit pore diameters ranging from 10 to 16  $\mu$ m was used. Nitrogen gas was introduced into the cell at a flow rate of 50 cm<sup>3</sup>/min. Additionally, a cold light source (Soif Optical Instruments, China), a detector measuring light intensity (Thorlabs, Newton, NJ, USA), and a computer processing data using The Optical Power Monitor (OPM) software (Version: 6.1) were used. As seen in Fig. 1, the experimental setup works on the principle that light emitted from a source passes through a solution within a microflotation cell, some of the light is absorbed by the solution before reaching a detector, and then the intensity of the transmitted light is measured. The light was directed to approximately the middle of the solution column (approximately 10 cm above the frit), and the intensity was recorded. In addition, images of the bubbles formed in the solution were taken using a camera at the same location. The schematic representation of the experimental setup (a) and a photograph of the setup (b) are shown in Fig. 1.



Fig. 1. Bubble coalescence measurements experimental setup (a) photograph of the experimental setup (b) schematic of the experimental setup

## 2.2.2. Dynamic foam stability measurements

Foam stability measurements were conducted using a dynamic foam analyzer (DFA100, KRÜSS GmbH, Hamburg, Germany). This device measures foam generation and decaying in liquids as a function of time. The device essentially consists of a cell made of a tempered glass column with a diameter of 40 mm and a height of 250 mm, optical sensors monitoring the cell, and a computer for data collection. In

this method, firstly, the prepared solution (100 cm<sup>3</sup>) is placed into the cell, and foam formation is initiated by supplying air ( $0.2 \text{ dm}^3/\text{min}$ ) through a filter plate with a pore size of 12-25 µm at the bottom of the cell. After the foam generation, the foam height in the system is measured as a function of time up to 60 s, and then, the airflow is stopped automatically at 60 s, and the foam decaying is measured for 40 s. The experimental setup used in the tests is shown in Fig. 2.



Fig. 2. Dynamic foam stability measurements experimental setup (a) photograph of the experimental setup (b) schematic of the experimental setup

Subsequently, using the measured foam heights, the dynamic foam stability for systems with different concentrations of SDS and SDS+salt concentrations was calculated using Eq. 1:

$$\Sigma = \frac{H_{max}A}{Q} \tag{1}$$

where  $\Sigma$  is the dynamic foam stability factor (min),  $H_{max}$  is the maximum foam height (cm), A is the cross-sectional area of column (cm<sup>2</sup>), and Q is the gas flow rate (cm<sup>3</sup>/min).

#### 3. Theoretical concepts

It is well-known that the sparging of gas through a porous filter into a pure water leads to the immediate coalescence of the small bubbles into big bubbles, which lift up driven by the buoyance force. The addition of any frother suppresses the coalescence resulting in myriads of lifting up bubbles, which might either form or not form a froth cap (Guven, Batjargal et al. 2020). The molecule of the frother contains a hydrophilic head and hydrophobic tail. When they adsorb on the surface of the bubble their hydrophilic heads point outwards from the surface of the bubble and toward the bulk (see Fig. 3).



Fig. 3. Sketch on our concept for partially (a) hydrophobic and (b) bubbles (not to scale)

A bubble covered with hydrophilic heads of the frother molecules/ions is certainly more hydrophilic than a bubble with a free surface (see Fig. 4). The collision of two hydrophobic bubbles ends up in coalescence, while the collision between two hydrophilic bubbles ends up with retraction. Yet, there is a scope between 100% hydrophilic and 100% hydrophobic. How to know how much hydrophilic are

the bubbles in every particular case? It is logical to accept (by the setup in Fig. 1) that if 100% of the bubbles coalesce they are 0% hydrophilic and if 100% of the bubbles do not coalesce they are 100% hydrophilic. Every other particular case with bubble coalescence (%) value situated between these two limits regards partially hydrophilic bubbles.



Fig. 4. Bubble percentage coalescence and level of bubble's hydrophilicity versus SDS concentration

Fig. 4 shows the bubble percentage coalescence and the level of the bubble's hydrophilicity versus SDS concentration. One can see that both curves are inverted to each other in accordance with our definition of the level of hydrophilicity of the bubble. It is evident that the increase of the occupied area of the bubble by the SDS species increases the level of its hydrophilicity. To estimate how the adsorption of SDS affects the hydrophilicity of the bubbles we applied the adsorption model of Ivanov (Ivanov, Ananthapadmanabhan et al. 2006, Slavchov, Karakashev et al. 2014) on the surface tension isotherm of SDS produced by Hines (Hines 1996), which is known as one of the most experimentally accurate surface tension isotherms for SDS. It consists of the following set of adsorption isotherm and equation of state:

$$KC^{2/3} = \frac{\Gamma}{(1 - \alpha\Gamma)^{1/3}} \left(\frac{2}{1 + R_{\beta}}\right)^{\frac{1 + 8\beta}{12\beta}} \times exp\left[\frac{\alpha\Gamma(4 - 3\alpha\Gamma)}{3(1 - \alpha\Gamma)^{2}} \times \frac{2}{1 + R_{\beta}}\right]$$
$$R_{\beta} = \sqrt{1 + 16\beta\frac{\alpha\Gamma}{1 - \alpha\Gamma}}$$
(2)

$$\frac{\sigma_0 - \sigma}{\Gamma kT} = \frac{1}{(1 - \alpha \Gamma)^2} \times \frac{2}{1 + R_\beta} + 2 \tag{3}$$

where *K* is the equilibrium adsorption constant of the frother (dimensionless),  $C = \sqrt{C_s(C_s + C_{salt})}$ (mol/m<sup>3</sup>) is mean concentration taking into account the frother concentration  $C_s$  and the concentration of the added salt  $C_{salt}$ ,  $\alpha(m^2)$  is the cross-sectional area per molecule on the air/water interface,  $\Gamma$ (mol/m<sup>2</sup>) is its adsorption,  $\beta$  (dimensionless) is the attraction coefficient,  $\sigma_0$  (N/m) is cohesion constant of the SDS species on the air/water interface,  $\sigma$  (N/m) is the surface tension value, k (J/K) and T (K) are Boltzman constant and the absolute temperature.

The coincidence between the experimental and the theoretical surface tension isotherms of SDS is shown in Fig.5.

The adsorption parameters of SDS presented in Table 1 are used by us to calculate the fraction of the occupied surface of the bubbles by the SDS species versus the concentration of SDS. The experimental data of bubble percentage coalescence versus SDS concentration allow us to build up a correlation between the bubble percentage coalescence and the fraction of the occupied surface of the bubble by the SDS species. In addition, we defined here above the level of the bubble's hydrophilicity as an inverted dependence of the bubble percentage coalescence. Hence, we can follow how the level of the hydrophilicity of the bubble depends on the bubble percentage coalescence.

Another interesting point is how the presence of either only NaCl or only CaCl<sub>2</sub> affects the coalescence of the bubbles. It was reported in the literature(Craig, Ninham et al. 1993, Craig 2004) that there exists a specific for each salt short concentration range of many salts in which they start suppressing the coalescence of the bubbles from 0% to 100%. There exists a number of salts, which do not affect the coalescence of the bubbles at any concentration.



Fig. 5. Experimental (Hines 1996)and theoretical (Ivanov, Ananthapadmanabhan et al. 2006) surface tension isotherm

Table 1. Cross-sectional area per molecule  $\alpha$  on the air/water interface, the equilibrium adsorption constant K, the attraction constant  $\beta$  and the cohesion constant  $\sigma_0$  of SDS according to the model of Ivanov et. al.

| α (Å) | К      | β    | $\sigma_0 (mN/m)$ |  |
|-------|--------|------|-------------------|--|
| 20.30 | 103.26 | 1.90 | 79.19             |  |

Table 2. Combination of cations and anions, which when being combined in the form of salt either suppress or not suppress the coalescence of the bubbles. Printed from (Henry, Dalton et al. 2007) with the permission of the ACS

| Ions                 |     | Li+          | Na+          | K+           | Cs+          | Mg <sup>2+</sup> | Ca <sup>2+</sup> | NH4 <sup>+</sup> | H+           | (CH <sub>3</sub> )NH <sub>3</sub> + | (CH3)2NH2+ | (CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup> | (CH3)4N+     |
|----------------------|-----|--------------|--------------|--------------|--------------|------------------|------------------|------------------|--------------|-------------------------------------|------------|---|--------------|
| Assignme             | ent | α            | α            | α            | α            | α                | α                | a                | β            | β                                   | β          | β   | β            |
| OH-                  | α   |              | $\checkmark$ | ~            |              |                  |                  |                  | ×            |                                     |            |   |              |
| Cl-                  | α   | $\checkmark$ | $\checkmark$ | $\checkmark$ |              | $\checkmark$     | $\checkmark$     |                  | ×            | ×                                   | ×          | ×   | ×            |
| Br-                  | α   |              | $\checkmark$ | $\checkmark$ | $\checkmark$ |                  |                  |                  | ×            |                                     |            |   | ×            |
| NO3-                 | α   | $\checkmark$ | $\checkmark$ | ~            |              |                  | $\checkmark$     |                  | ×            |                                     |            |   |              |
| SO42-                | α   | $\checkmark$ | $\checkmark$ | ~            |              | $\checkmark$     |                  |                  | ×            |                                     |            |   |              |
| (COO)2 <sup>2-</sup> | α   |              |              | $\checkmark$ |              |                  |                  |                  | ×            |                                     |            |   |              |
| 1O3-                 | α   |              | $\checkmark$ |              |              |                  |                  |                  |              |                                     |            |   |              |
| ClO3-                | β   |              | ×            |              |              |                  |                  |                  |              |                                     |            |   |              |
| ClO <sub>4</sub> -   | В   |              | ×            |              |              | ×                |                  | ×                | $\checkmark$ |                                     |            |   |              |
| CH <sub>3</sub> COO- | β   |              | ×            | ×            | ×            | ×                |                  | ×                | $\checkmark$ |                                     |            |   | $\checkmark$ |
| SCN                  | β   |              | ×            |              |              |                  |                  |                  |              |                                     |            |   |              |

✓=inhibit coalescence ×=no inhibition

*αα, ββ* = √

αβ, βα =×

Table 2 shows which combinations of cations and anions in the form of salt can suppress the coalescence of the bubbles and which are not able to do the same. There is a critical concentration specific for each active salt, at which it starts to inhibit the coalescence of the bubbles (Firouzi, Howes et al. 2015). The values of these critical concentrations are in the range of 0.01 mol/dm<sup>3</sup> to 0.2 mol/dm<sup>3</sup>. The inactive salts do not inhibit the bubbles' coalescence in this concentration range but they start to inhibit it above 1 mol/dm<sup>3</sup> (Christenson, Bowen et al. 2008). The accepted explanation for this effect is the Gibbs –

Marangoni stress on the surface of the bubbles, which decreases the speed of thinning of the foam films upon clashing if the bubbles in the aqueous phase (Firouzi, Howes et al. 2015, Palliyalil, Mohan et al. 2024). According to (Marcelja 2006) and (Jungwirth and Tobias 2006) the active salts exhibit spatial separation of cations and anions near the air/water interface, thus initiating the Gibbs-Marangoni stress effect, while the inactive salts do not exhibit such separation. At larger concentrations, the physical picture of their locations is significantly more complex.

We have studied in the present work the effect of NaCl and  $CaCl_2$  alone and being mixed with SDS on the bubble percentage coalescence. So, we exploited the theory of Ivanov et al. (Ivanov, Marinova et al. 2007) to calculate the specific adsorption energies of Na<sup>+</sup>, Ca<sup>2+</sup>, and Cl<sup>-</sup> ions on the air/water interface. Thus, we have calculated their equilibrium adsorption constants and calculated the fractions of the ions on the bubble's surface versus the concentration of each one of these salts.

Table 3. Specific adsorption energies of Na<sup>+</sup>, Cl<sup>-</sup> and Ca<sup>2+</sup> ions on the air/water interface according to the theory of Ivanov (Ivanov, Marinova et al. 2007); The ionic parameters for this calculation are taken from ref. (Marcus 1997)

| Ions               | Na+    | Cl⁻    | Ca <sup>2+</sup> |
|--------------------|--------|--------|------------------|
| u <sub>0</sub> /kT | - 0.33 | - 1.43 | 0.36             |

The specific adsorption energies of the Na<sup>+</sup>,  $Cl^-$  and  $Ca^{2+}$  ions on the air/water interface are presented in Table 3. One can see that Na<sup>+</sup> and Cl<sup>-</sup> ions have negative values of the specific adsorption energy, which indicates positive adsorption on the air/water interface with Cl<sup>-</sup> being more adsorbed. Surprisingly, our calculation shows a positive value of the specific adsorption energy of Ca<sup>2+</sup> ions, which indicates weak repulsion between Ca<sup>2+</sup> and the air/water interface. It is generally accepted that all the inorganic ions are repelled by the air/water interface due to the image repulsion force (Heydweiller 1910, Onsager and Samaras 1934, Randles 1957, Israelachvili 1992, Markin and Volkov 2002) resulting in an increase of the surface tension of their aqueous solutions. More precise measurements conducted by Jones and Ray (Jones and Ray 1935, Jones and Ray 1937, Jones and Ray 1941, Jones and Ray 1941) report that at relatively small concentrations of the inorganic salts in the scope of  $0.001 \text{ mol}/\text{dm}^3 - 0.002$ mol/dm<sup>3</sup> the salts decrease the surface tension and at higher salts concentration begins un onset of increase, which can be measured by the conventional setups at significantly higher concentrations. The operational concentrations of NaCl and CaCl<sub>2</sub> in this work are higher than the above mentioned scope. The change of the slope of the surface tension versus concentration in dilute salt solutions from decrement to increment is slight, so we can assume that the theory of Ivanov is valid at this concentration range. Here the question is (see Fig. 2) why do many inorganic salts, including NaCl and CaCl<sub>2</sub> suppress the coalescence of the bubbles? The reason in our opinion is the same as in the presence of frother – the bubble becomes more hydrophilic, thus exhibiting hydration repulsion when they clash. The only difference is that the frother is a much stronger surface-active agent than the inorganic salt. As far as we know the specific adsorption energy and the hydration radius of each ion we can calculate its equilibrium adsorption constant, its adsorption on the surface of the bubble the fraction of the occupied area, and finally to correlate with the level of its hydrophilicity.

Table 4 presents the adsorption energy of SDS, NaCl, and CaCl<sub>2</sub> on the air/water interface, their equilibrium adsorption constants, the cross-sectional area per molecule, and the Gibbs hydration energy of Na<sup>+</sup>, Cl<sup>-</sup>, and Ca<sup>2+</sup> ions. The adsorption energies of the salts were calculated from the specific adsorption energy of the ions (see Table 3), excluding Ca<sup>2+</sup>, which is repelled by the air/water interface, so the adsorption energy of CaCl<sub>2</sub> was calculated by doubling the adsorption energy of Cl<sup>-</sup> ions. The cross-sectional area per molecule of the salts was calculated from the tabulated data (Marcus 1997) of the hydration radii of their ions (excluding Ca<sup>2+</sup> as mentioned here above). To hydrophilize qualitatively the bubble, one substance should have both high adsorption energy and high Gibbs hydration energy, which is an indication of the affinity of the ion/functional group to the water. SDS has both high adsorption energy of SO<sub>4</sub><sup>-</sup> functional group attached to the frother's molecule. For this reason, is the most effective among the three substances to suppress the bubble coalescence. The adsorption of the salt on the surfaces of the bubble was calculated by Davies adsorption isotherm (Slavchov, Karakashev et al. 2014):

| Substance         | Ea       | К         | α                 | ΔG <sub>h</sub> |
|-------------------|----------|-----------|-------------------|-----------------|
|                   | (kJ/mol) |           | (A <sup>2</sup> ) | (kJ/mol)        |
| SDS               | 176.62   | 103.26    | 20.3              | —               |
| NaCl              | 4.29     | 6.00x10-9 | 14.8              | _               |
| CaCl <sub>2</sub> | 6.97     | 8.65x10-9 | 14.8              | _               |
| $SO_4^{2^-}$      | -        |           | -                 | -1090.0         |
| Na <sup>+</sup>   | -        | _         | _                 | - 375.0         |
| Cl-               | -        |           | _                 | - 131.2         |
| Ca <sup>2+</sup>  | _        |           | _                 | -1515.0         |

Table 4. Adsorption energy Ea of SDS, NaCl, and CaCl<sub>2</sub> on the air/water interface, their equilibrium adsorption constants K, cross-sectional area per molecule  $\alpha$ ; the Gibbs hydration energy of Na<sup>+</sup>, Cl<sup>-</sup>, and Ca<sup>2+</sup> ions (Marcus 1997)

| $\Gamma = KC^{2/3}$ | (4 | 1)  |
|---------------------|----|-----|
|                     | 1. | ~ / |

where  $C = \sqrt{C_s(C_s + C_{salt})}$  is the mean frother concentration,  $C_s$  is the frother concentration, and  $C_{salt}$  is the concentration of the added salt.

## 4. Results

#### 4.1. Determination of CCC values of salts and SDS

First, the bubble coalescence experiments were carried out with each chemical, SDS, NaCl, and CaCl<sub>2</sub>, and the results obtained from the experiments are shown in Fig. 6 for both salts and SDS. As seen in Fig. 6, the bubble coalescence percentages for all chemicals decrease as a function of each chemical concentration. In the case of SDS, it sharply decreased with the increased concentration, and the CCC value of SDS was determined as 6.10<sup>-6</sup> mol/dm<sup>3</sup>. In the case of salts, the bubble coalescence percentages for both salts showed slight changes to a certain concentration. After that concentration, the bubble coalescence values for both salts considerably decreased. And, the results indicated that the CCC values of NaCl and CaCl<sub>2</sub> were determined as 2.10<sup>-1</sup> mol/dm<sup>3</sup> and 7.10<sup>-2</sup> mol/dm<sup>3</sup>, respectively as shown in Table 5. Table 5 shows the fraction of the occupied area of the bubbles by the SDS, NaCl, and CaCl<sub>2</sub> species at CCC value. One can see that they are in the same order of magnitude corresponding to the scarce adsorption layer, but able to hydrophilize the bubbles.

| Chemicals                | SDS    | NaC1 | CaCl <sub>2</sub> |
|--------------------------|--------|------|-------------------|
| CCC, mol/dm <sup>3</sup> | 6.10-6 | 0.20 | 0.07              |
| θ (CCC), %               | 0.48   | 1.83 | 1.2               |

Table 5. Chemicals and their corresponding values of CCC



Fig. 6. CCC values of salts and SDS

Fig. 7 shows our experimental and theoretical data on the dependence of the level of the bubble's hydrophilicity and the occupied area of the bubble's surface versus the concentration of SDS, NaCl, and CaCl<sub>2</sub>. One can see that the most effective is SDS, requiring only 0.48% occupation of the bubble surface by  $SO_4^-$  functional groups attached to hydrophobic tails, whose only role are to hold them tightly to the surface of the bubble. The difference between the required occupied areas to achieve CCC of NaCl and CaCl<sub>2</sub> is small with CaCl<sub>2</sub> being more effective.



Fig. 7. Level of hydrophilicity of the bubbles and the occupied part of the bubble's surface versus the concentration of each one of the chemical agents – (a) SDS (b) NaCl, and (c) CaCl<sub>2</sub>

#### 4.2. Determination of CCC values of salt+SDS mixed system

Then, the effect of each salt on the bubble coalescence behaviour of SDS was investigated, and the results are presented in Figs. 8 and 9. The experiments were carried out at the CCC values of each salt,  $2.10^{-1}$  mol/dm<sup>3</sup> and  $7.10^{-2}$  mol/dm<sup>3</sup> for NaCl and CaCl<sub>2</sub>, respectively. As seen in Fig. 8, the CCC value of SDS decreased from  $6.10^{-6}$  mol/dm<sup>3</sup> to  $3.10^{-7}$  mol/dm<sup>3</sup> in the presence of NaCl. A similar situation was observed for the CCC value of SDS in the presence of CaCl<sub>2</sub>. As seen in Fig. 9, the addition of  $7.10^{-2}$  mol/dm<sup>3</sup> CaCl<sub>2</sub> reduced the CCC value of SDS from  $6.10^{-6}$  mol/dm<sup>3</sup> to  $5.10^{-7}$  mol/dm<sup>3</sup>.



Fig. 9. CCC values of CaCl2 + SDS mixed system

The latter results are not surprising because it is well known that the addition of salts to ionic surfactants increases their energy of adsorption (Ivanov, Ananthapadmanabhan et al. 2006). Yet it is interesting to assess the increase in this particular case. Yet, the hydrophilization of the bubbles suppresses their coalescence in the liquid phase, but as far as their adsorption layer is scarce their Gibbs elasticity is small and the bubbles cannot form a froth cap lasting for some time.

#### 4.3. Dynamic foam stability measurements

Fig. 10 shows the foam stability of salts and SDS individually, and their mixture. As seen in Fig. 10, no stable foam was formed in the presence of NaCl and CaCl<sub>2</sub> salts even at  $1 \text{ mol}/\text{dm}^3$  concentration. It is no surprise because stable foam requires a high Gibbs elasticity value, while NaCl and CaCl<sub>2</sub> cannot

underpin it. Meanwhile,  $5.10^{-5}$  mol/dm<sup>3</sup> SDS solution showed a steady increase over time, reaching a foam height of about 50 mm. Furthermore, the addition of 1 mol/dm<sup>3</sup> NaCl to the  $5.10^{-5}$  mol/dm<sup>3</sup> SDS solution significantly increased the foam height from 50 mm to approximately 160 mm, indicating that NaCl positively affects the foam stability of SDS. In contrast, the same effect was not observed for CaCl<sub>2</sub>. When 1 mol/dm<sup>3</sup> CaCl<sub>2</sub> was added to the  $5.10^{-5}$  mol/dm<sup>3</sup> SDS solution, the foam height decreased from approximately 50 mm to 20 mm indicating that CaCl<sub>2</sub> had a negative effect on the foam stability of SDS. This result can be attributed to the precipitation of SDS in the presence of high concentrations of Ca<sup>2+</sup> ions (Zhang et al., 2015).



Fig. 10. Foam height of salts, SDS, and salt + SDS mixed system



Fig. 11. Activity coefficients of NaCl and CaCl<sub>2</sub> according to the theory of Pitzer (Pitzer 1973)

Fig. 11 shows the activity coefficients of NaCl and CaCl<sub>2</sub> according to the theory of Pitzer (Pitzer 1973). One can see that the activity coefficient of CaCl<sub>2</sub> is significantly lower than that of NaCl. This is an indication of the stronger reactivity of CaCl<sub>2</sub> compared to NaCl.

Finally, the dynamic foam stability (DFS) values for salts and SDS were calculated and the results are presented in Fig. 12. The data presented in Fig. 12 reveal the significant effects of NaCl and CaCl<sub>2</sub> addition on the DFS of a 5.10<sup>-5</sup> mol/dm<sup>3</sup> SDS solution. For example, when NaCl and CaCl<sub>2</sub> are added in the absence of SDS, the DFS remains low at all concentrations, indicating that these salts alone are not

effective in stabilizing foam. However, the addition of NaCl leads to a concentration-dependent increase in foam stability. No considerable change was observed at 1.10<sup>-3</sup> mol/dm<sup>3</sup> NaCl in the presence of SDS. Then, the DFS values for NaCl increased gradually as a function of salt concentration. This shows that NaCl significantly increases the foam stability of SDS. In contrast, the addition of CaCl<sub>2</sub> appeared to have a negative effect on the foam stability of SDS. While the DFS value showed a sharp decrease at 1.10<sup>-3</sup> mol/dm<sup>3</sup> CaCl<sub>2</sub>, and then gradually decreased as the concentration increased, dropping to almost zero at 1 mol/dm<sup>3</sup> CaCl<sub>2</sub>. These findings demonstrate that NaCl has a positive effect on the foam stability of SDS, whereas CaCl<sub>2</sub> reduces foam stability at higher concentrations. A similar effect was found with KCl (Amani, Karakashev et al. 2021). As seen above the salts affect the physical properties of the frothers. The latter ones are often collectors as well. Finding a chemical agent, which is both a good collector and a good frother is a difficult task. For this reason, the knowledge of the salt-specific effects on the frothers can be used to tune them to achieve such dual activity on an industrial scale.



Fig. 12. Foam stability of salts, SDS, and Salt+SDS mixed system

## 5. Conclusions

This study shows that the suppression of the bubble coalescence in the liquid phase is due to partial hydrophilicity of the bubbles due to hydrophilic functional groups or ions pointing out towards the liquid phase – being either attached to hydrophobic tails (SDS) or adsorbed at the air/water interface. Our calculations show that if a small area of the surface of the bubble (less than 10%) is occupied by these hydrophilic entities, the bubbles practically do not coalesce in the liquid phase but they are not able to form a lasting froth cap. This is due to the small value of the Gibbs elasticity. Long-lasting foams require large values of Gibbs elasticity. Thus, we studied the effects of different ions (Na<sup>+</sup> and Ca<sup>2+</sup>) on the stability of sodium dodecyl sulfate (SDS) with bubble coalescence and foam stability measurements. The results obtained from this study showed that the salts alone were unable to form stable foam, even at concentrations up to 1 mol/dm<sup>3</sup>. The addition of NaCl to a 5.10<sup>-5</sup> mol/dm<sup>3</sup> SDS solution does not significantly affect the foam formation of SDS at low concentrations. However, as NaCl concentration increases, there is a significant increase in foam height. In contrast, the effect of CaCl<sub>2</sub> shows the opposite trend. At low concentrations, CaCl<sub>2</sub> increases foam height, but as the concentration increases, it negatively affects foam height, leading to a decrease in foam formation. The presence of NaCl significantly increases the foam stability of SDS as its concentration increases. In contrast, the effect of CaCl<sub>2</sub> on SDS shows an opposite trend reverse trend; foam stability decreases as the concentration increases. At a concentration of 1 mol/dm<sup>3</sup> CaCl<sub>2</sub>, foam stability almost disappears. It was also observed that when NaCl and CaCl<sub>2</sub> were used alone in the absence of SDS, the foam stability remained very low and did not show a significant increase despite changes in concentration.

These findings suggest that NaCl positively affects the foam stability of SDS, while CaCl<sub>2</sub> has a negative effect on this stability at higher concentrations. Furthermore, this may be related to the CCC values of these salts on the foamability of surfactants, and hence flotation efficiency. Therefore, additional studies are needed to understand this effect, especially on the flotation process.

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