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An investigation of air/water interface in mixed aqueous solutions of KCl, NaCl, and DAH

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Abstract: Flotation of soluble salts such as borax, potash, and trona is carried out in their saturated solutions. The high ion concentration of the flotation suspension can affect the floatability of the minerals as well as the coalescence behaviors of the bubbles. The bubble coalescence can be inhibited in the presence of dissolved ions at high ion concentrations as well as with the use of surfactants. In this study, the effect of the mixtures of KCl, NaCl, and dodecyl amine hydrochloride (DAH) on air/water interface was investigated with surface tension and bubble coalescence time measurements for potash flotation. The surface tension measurements indicated that lower surface tension values obtained with mixed KCl and NaCl solutions than their single solutions. In addition, the surface tension of the mixed KCl and NaCl solutions increased with the NaCl and the ionic strength of the solution. The dynamic surface tension measurements indicated that while ion adsorption on air/water interface was so fast, DAH molecules required more time for adsorption probably related to the viscosity of the solution. In addition, the bubble coalescence time measurements showed that the bubble coalescence could be inhibited with the use of DAH in the absence and presence of KCl and NaCl. In the absence of DAH, the bubble coalescence time was determined as 100 ms, 270 ms, and 650 ms, respectively for 100% KCl, 100% NaCl, and 50%KCl+50% NaCl salt solutions. Therefore, the trend in the success of the salt solutions for the inhibition of bubble coalescence can be written as 100%KCl<50%KCl+50%NaCl<100% NaCl according to the bubble coalescence time. The results of this study indicated that there was no clear relationship between the surface tension and the inhibition of the bubble coalescence. However, the bubble coalescence time measurements showed that while the bubble coalescence time was 650 ms in the presence of Na⁺ ions, it was 100 ms in the presence of K⁺ ions 100 ms. It can be concluded from the results obtained from this study that the bubble coalescence phenomena may be managed by the specific ion pairing types in solutions which significantly affect the flotation recovery of minerals.

Keywords: bubble coalescence, surface tension, KCl, NaCl, DAH

1. Introduction

In flotation process, air is pumped into the suspension in the form of small bubbles. Hydrophobic particles are attached to air bubbles, and rise to the surface of the suspension, while hydrophilic particles remain in the suspension. Therefore, the success of the flotation process is strongly related to the behaviors of the bubbles, when they meet a mineral particle or another bubble. Since air bubbles are extremely hydrophobic, and the repulsion forces between them are very weak, when two bubbles approach to each other, they tend to coalesce in order to form a larger bubble to decrease their surface area, which is called bubble coalescence (Ahmed and Jameson, 1985; Tao, 2005). Bubble coalescence is usually detrimental to the flotation process (Yoon and Luttrell, 1986; Laskowski et al., 2003; Ata, 2009; Zhu et al., 2018). In general, the bubble coalescence is controlled by frothers which adsorbed at the air/water interface, and decreased the surface tension of the air bubble (Bournival et al., 2012). In addition, although most of the inorganic electrolytes increase the surface tension of pure water, bubble coalescence can be inhibited above a certain critical concentration (transition concentration) of some

specific dissolved ions, while others have no effect (Craig et al., 1993; Christenson and Yaminsky, 1995; Deschenes et al., 1998; Craig, 2004; Henry et al., 2007). The effect of electrolytes on bubble coalescence has been investigated by various researchers (Kim et al., 1990; Craig et al., 1993; Pashley and Craig, 1997). Bournival et al. (2012) investigated bubble behaviors in the presence of an inorganic electrolyte (NaCl) and a frother (MIBC) in terms of bubble coalescence. Although a small amount of MIBC was enough for the inhibition of bubble coalescence, NaCl at high concentrations can be as effective as MIBC in a dynamic environment. Gungoren et al. (2018) reported that CaCl_2 was more effective on the surface tension of MIBC than that of NaCl. Moreover, the size of bubbles is also an important parameter for the coalescence. The transition concentration increases with the bubble size (Tsang et al., 2004).

Flotation is a widely used method for the separation of soluble salts such as trona, borax, and potash (Hancer et al., 2001; Celik et al., 2002; Titkov, 2004; Ozdemir et al., 2011; Wang et al., 2014; Wu et al., 2016). Flotation of these soluble minerals must be carried out in their saturated solutions where the flotation suspension contains ions at high concentrations (Monte and Oliveira, 2004). Dissolved ions in flotation affect flotation success in many ways. For instance, they suppress the electrical double layer, and therefore decrease the zeta potential of the particles (Ozdemir et al., 2011). Furthermore, dissolved ions can change the bulk, interfacial water structure, and the colloidal interactions among the particles, bubbles, and surfactants, and hence affect the adsorption of flotation reagents at the particle/water and air/water interfaces in flotation (Burdukova et al., 2009; Ozdemir et al., 2010).

The flotation of potash ore is carried out in its saturated solution of about 5 mol/dm^3 of sylvite (KCl) and halite (NaCl). KCl can be floated with both of the cationic and anionic collectors. On the contrary, NaCl cannot be floated with either of them (Cao et al., 2010). In practice, cationic long-chain primary amines are preferred as a collector in potash flotation (Monte and Oliveira, 2004). In the flotation of KCl, generally, the amine is melted at $70\text{-}90^\circ\text{C}$, and then added into the flotation suspension at room temperature, which is much lower than the Krafft point of the amine which is 26°C for dodecyl amine hydrochloride (DAH) (Du et al., 2014). The amine precipitates immediately and attaches to the surfaces of KCl particles (Laskowski, 2013). They may also accumulate at the surfaces of the purged air bubbles, followed by spreading into molecular films. The existence of amine films on the bubble surfaces enables the bubbles to pick up the KCl particles more easily. There are three important parameters in the flotation of water-soluble minerals: (i) the adsorption of the collectors onto bubble surfaces, (ii) association of collectors with water-soluble minerals, (iii) association of water-soluble mineral particles with bubbles (Wu et al., 2016).

It is important to understand how the dissolved ions behave in bulk solutions and at the air/water interfaces of salt flotation (Ozdemir et al., 2011). Titkov (2004) reported that the surface hydration of KCl is dependent upon the temperature and chemistry of the salt solution. Monte and Oliveira (2004) enhanced the KCl flotation recovery by adding long-chain hexyl and octyl alcohols on the dodecylamine flotation of KCl. Weedon et al. (2007a; b) studied the effects of high magnesium concentration on KCl-amine flotation. They found that magnesium addition can cause the precipitation of fine NaCl particles on the surface of coarse KCl particles, reduced their hydrophobicity, and caused depression. Burdukova et al. (2009) reported that dodecyl amine (DDA) particles attach to KCl surfaces, while no attachment took place on the surfaces of NaCl. Cao et al. (2010) investigated the surface chemistry of KCl for flotation process using various collectors (octadecyl amine (ODA), dodecyl amine (DDA), and sodium dodecyl sulfate (SDS)). They reported that both of cationic and anionic collectors make KCl surface hydrophobic with a contact angle between 30° and 60° , while the contact angle of NaCl, which is a structure making salt, was remained zero in all cases. Recently, Huang et al. (2019) used a novel gemini surfactant (N,N'-bis (octadecyl dimethyl)-1,4-butane diammonium dibromide (BOBD)) in bench scale flotation tests of potash ores. Their results indicated that BOBD has a good collecting power for sylvite. They obtained higher recoveries with more selectivity compared to a traditional monomeric surfactant (octadecyl amine hydrochloride (OAH)).

Although there are several studies in literature on the effect of a single salt on potash flotation, the studies on the effect of the mixed salts are quite limited. In addition, it is well-known that dissolved ions and surfactant molecules considerably affects the stability of bubbles which has a crucial role in the success of flotation. Therefore, this study was aimed to investigate the effect of the mixture of KCl and NaCl salts in flotation via investigating the changes at air/water interface in the presence of a widely

used surfactant (DAH) for improving the flotation technology. Since the experiments on the ion adsorption on air/water interface are very difficult because of the surface-active contaminants, surface tension measurements allow to directly gain information of the surface activity of salts (Horinek et al., 2009). Therefore, contact angle measurements were carried out as a function of time in this study. In addition, bubble coalescence time was determined with a novel method using a modified bubble-particle attachment timer in order to observe the changes in the stability of bubbles in the presence of KCl, NaCl, and DAH.

2. Materials and methods

2.1. Materials

Reagent grade KCl and NaCl samples purchased from Merck (Germany) were used in this study. In order to remove possible organic contaminants from the samples, the salts were heated at 300°C in an oven (Electromag M3025P, Turkey) for 24 h. All solutions were prepared using de-ionized (DI) water (18.2 MΩcm) (Millipore Milli-Q, Merck, Germany), freshly. The solutions were stored, and experiments were carried out at room temperature (23±1°C). In the mixed salt solutions, KCl and NaCl solutions at the proper saturation percent were mixed in 1:1 ratio by volume. The concentration equivalents of saturation percents are presented in Table 1 in mol/dm³. In the case of the salt solutions with dodecyl amine hydrochloride (DAH), DAH with 99% purity (Arcos Organics, USA) was added directly to the salt solution.

Table 1. Concentration (mol/dm³) equivalents of saturation percents of KCl and NaCl

Saturation (%)	Concentration (mol/dm ³)	
	KCl	NaCl
25	1.0025	1.3
50	2.05	2.6
75	3.075	3.9
100	4.1	5.2

The glassware used in the experiments was cleaned with a solution of ethanol, KOH, and DI water at the ratios of 75.5%, 14%, 10.5% by weight, respectively, then with 1% HCl solution. Finally, they were rinsed with DI water for several times, and dried upside down to protect them from dust. The metallic apparatus such as spatulas and the needle of the micro-syringe were cleaned with reagent grade ethanol, and then rinsed with DI water.

2.2. Dynamic surface tension measurements

The surface tension measurements for the solutions were carried out using Attension Theta Lite tensiometer (Finland) with the pendant drop technique. In the measurements, a backlighted solution droplet was formed at the end of a glass micro-syringe and observed with a CCD camera. The images of bubbles taken during surface tension measurements at different salt concentrations are shown in Fig. 1. As seen in Fig. 1 that the size of the bubbles decreased with the increased salt concentration.

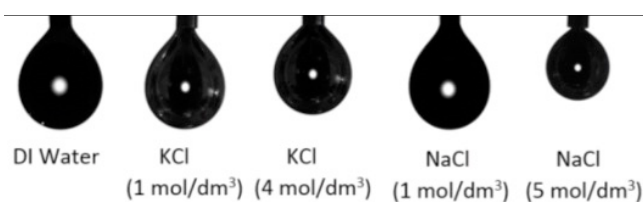


Fig. 1. Bubble images at different salt concentrations

The shape of the droplet silhouette was recorded by a computer at every 15 sec for 3 min, and automatically analyzed by the software of the tensiometer to calculate the surface tension. The

measurements were carried out two times, and the average values were obtained as the mean of two measurements.

First, the surface tension measurements were carried out with KCl and NaCl solutions at various saturation ratios (25%, 50%, 75%, and 100%) to control the reliability of the salts and the measurement system. Then, the effect of mixing ratios of KCl and NaCl on the surface tension was investigated. In this purpose, the salt solutions at various saturation percents were mixed to obtain 100% saturation (25% KCl+75% NaCl, 50% KCl+50% NaCl, and 75% KCl+25% NaCl), and the surface tension measurements were performed. Finally, in order to investigate the effect of *DAH* on the surface tension, $1 \cdot 10^{-6}$ mol/dm³, $1 \cdot 10^{-5}$ mol/dm³, and $1 \cdot 10^{-4}$ mol/dm³ *DAH* solutions were prepared with 100% saturated KCl, 100% saturated NaCl, and 50% KCl+50% NaCl mixed salt solutions.

2.3. Bubble coalescence time measurements

The bubble coalescence time measurements were carried out with a novel technique using a modified bubble-particle attachment timer. In this technique, a glass container was placed under the glass capillary tube and filled with the desired salt solution. Then, a glass syringe with a U-shaped needle was located beneath the glass capillary tube. Two bubbles at close sizes (~1 mm) were formed both of at the end of the glass capillary tube and micro-syringe. Then, the upper bubble was moved towards the bottom bubble, and contacted for a predetermined time (1, 10, 100, and 1000 ms), and moved back to its original position. Finally, the bubbles were observed on the computer screen via a CCD camera if the coalescence occurred. The coalescence time was determined if 50% of the observations resulted in coalescence. The experimental setup and steps of the bubble coalescence time measurements is seen in Fig. 2. The details of the measurement process were explained before by Gungoren et al. (2018). In this study, the bubble coalescence time was determined for $1 \cdot 10^{-6}$ mol/dm³, $1 \cdot 10^{-5}$ mol/dm³, and $1 \cdot 10^{-4}$ mol/dm³ *DAH* solutions in addition to the same *DAH* concentrations in various salt solutions (100% KCl, 100% NaCl, and 50%KCl+50% NaCl).

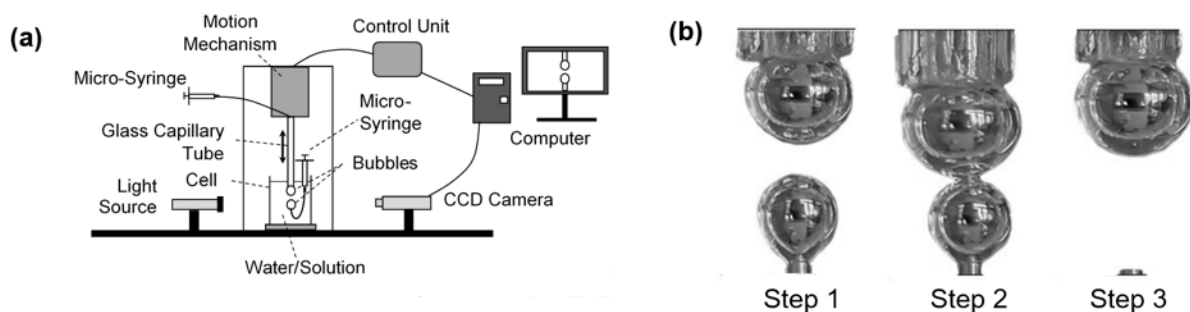


Fig. 2. (a) Experimental set up for bubble coalescence time measurements, (b) steps of a bubble coalescence time measurement (Gungoren et al., 2018)

3. Results and discussion

3.1. Dynamic surface tension measurements

The results of the surface tension measurements of KCl and NaCl solutions at various saturation percents are shown in Figs. 3(a) and (b), respectively. As can be seen from Fig. 3 that the ions adsorbed on the air/water interface very fast (less than 15 sec), and the surface tension of the KCl and NaCl solutions showed no significant change as a function of bubble age. Therefore, the average of the surface tensions in 3 min was calculated for the determination of the equilibrium surface tension of each saturation value and salt type.

In addition, the ionic strength of the solutions calculated using Eq. 1, and they are shown with the surface tension values in Fig. 4.

$$I = \frac{1}{2} \sum_{i=1}^n c_i (z_i)^2 \quad (1)$$

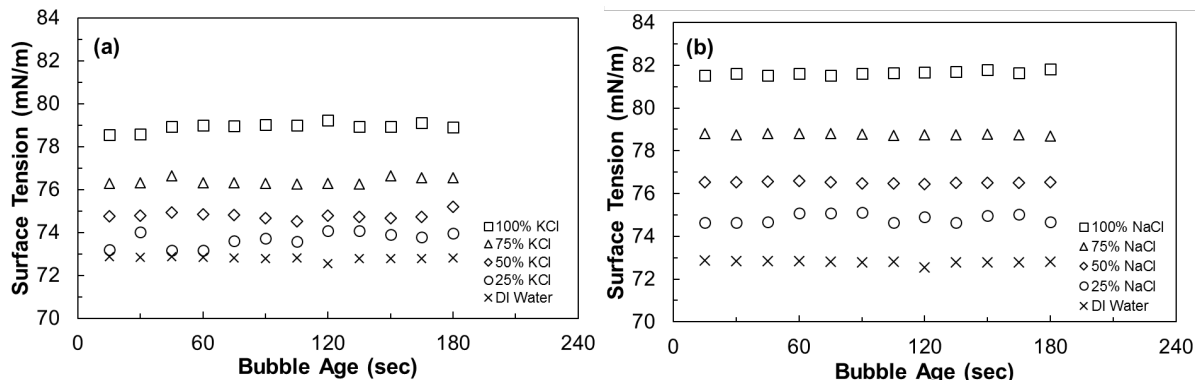


Fig. 3. Dynamic surface tension results of (a) KCl and (b) NaCl solutions at various saturation percent

where I is ionic strength, c is the concentration of the solution, and z is the valance of the ions (adapted from Ozdemir et al. (2009)).

As seen in Fig. 4, the surface tensions of KCl and NaCl solutions increased with the ion concentration up to the saturation concentration of each salt linearly, which are about 4.1 and 5.2 mol/dm³ for KCl and NaCl, respectively. In accordance with Ozdemir et al. (2009), a direct proportion was found between the saturation and surface tension of KCl and NaCl solutions. NaCl has higher solubility and higher ionic strength, and therefore gives higher surface tension values at a given level of saturation than KCl. Most of the ions including KCl and NaCl increase the surface tension of water with the increasing concentration. This increase in the surface tension can be explained by the negative absorption of ions at the air/water interface.

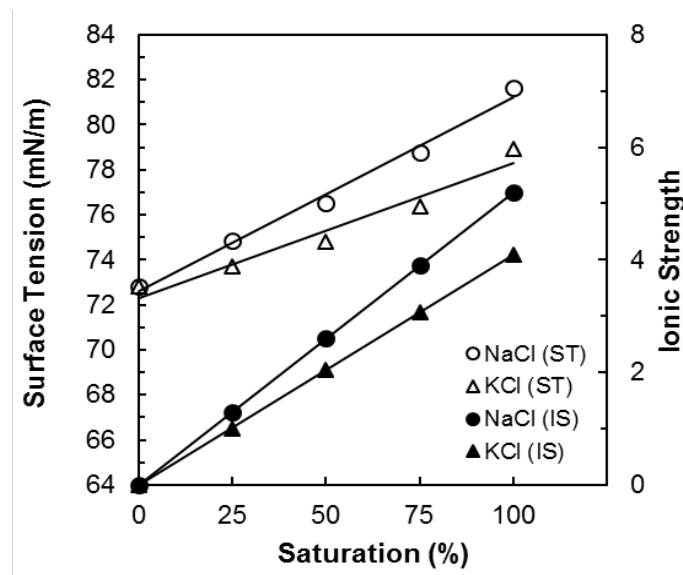


Fig. 4. Surface tension and ionic strength of KCl and NaCl solutions with respect to saturation percent

In the aqueous solutions of salts, dissolved ions interact strongly with surrounding water molecules in an ion-specific manner. Since water molecules are asymmetrical, they interact with cations and anions in different ways. Furthermore, ion charge densities may govern the interactions between the ions and water molecules. Small ions with a high charge density cause a strong electrostatic ordering of nearby water molecules. On the contrary, large ions with low charge density lead the surrounding water molecules being largely hydrogen bonded. Therefore, salt ions are classified as chaotropic (water structure breakers) or kosmotropic (water structure makers) according to their hydration behavior, which comes from the relative strength of the ion-water interactions compared to water-water interactions (Wu et al., 2016).

The ordering of several ions according to their interactions with water molecules in terms of their chaotropicism and kosmotropism, which is also known as "Hofmeister Series" is given in Fig. 5. The ions

on the left side of the two sequences have weaker interactions with water relative to those on the right side (Zhao et al., 2015). According to Fig. 5, the effect of K^+ and Cl^- ions are negligible. On the contrary, Na^+ indicates a kosmotropic effect.

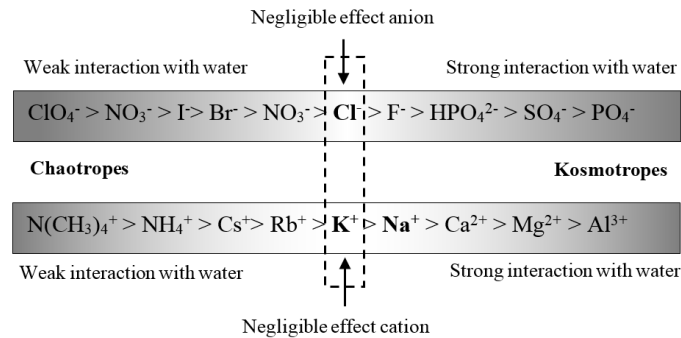


Fig. 5. Ordering of several ions according to their interactions with water molecules in terms of their chaotropism and kosmotropism (Zhao et al., 2015)

Although the specific cation-anion pairing determines the actual change in the surface tension (Weissenborn and Pugh, 1996), generally speaking, kosmotrope ions prefer to be fully hydrated in the bulk solution and considerably increase the surface tension of the solution, while chaotrope ions are partially hydrated at the interface and do not contribute significantly to increase surface tension of the solution (Du et al., 2008). In similar, in this study, the surface tension of NaCl, which is more kosmotrope, was found higher than that of KCl.

The effect of the mixing ratios of KCl and NaCl on the surface tension of the salt solutions is seen in Fig. 6 along with the ionic strength of the solutions. It is clearly seen in Fig. 6 that in similar with the single salt solutions, the surface tension increased with the ionic strength in the mixed solutions. Therefore, the increase in the surface tension may be related to the ionic strength of the mixed KCl and NaCl solutions.

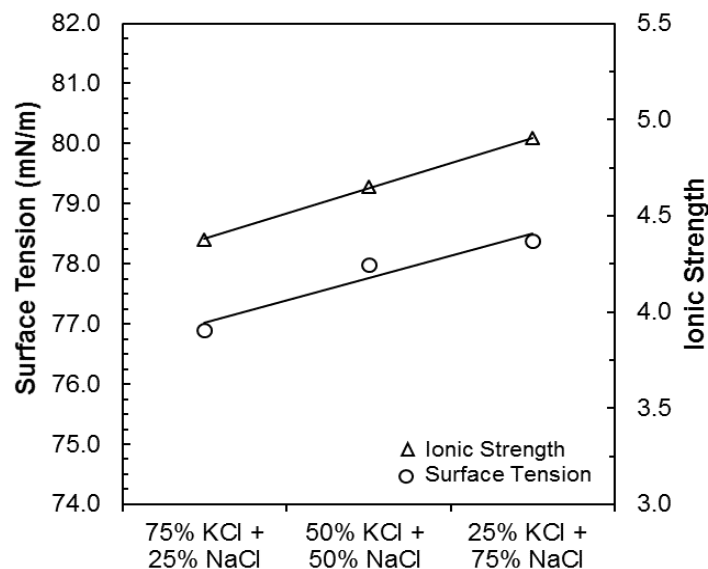


Fig. 6. Surface tensions and ionic strengths of the mixed salt solutions

Table 2 presents the dynamic surface tension results for DAH solutions at various concentrations without salt and with 100% saturated KCl, 100% saturated NaCl, and 50%KCl+50%NaCl solutions). As seen in Table 2, the surface tension of DI water decreased with DAH concentration. However, it did not change significantly with respect to bubble age because of the fast adsorption of DAH molecules to the air/water interface. On the contrary, the surface tension decreased with time in the presence of salt. The biggest decrease was observed in $1 \cdot 10^{-4}$ mol/dm³ DAH concentration.

Because of the time dependence of the surface tension in salt and *DAH* mixtures, the surface tension values at the end of 3 min was accepted as the equilibrium surface tension value. The surface tension of solutions as a function of *DAH* concentration is shown in Fig. 7 which indicates that *DAH* decreased the surface tension slightly with the increasing concentration in the absence of salt. On the other hand, the decrease in the surface tension became more significant in the presence of salt. The minimum surface tension was obtained using 50% KCl+50% NaCl mixture with $1 \cdot 10^{-4}$ mol/dm³ *DAH* as 50.32 mN/m.

Table 2. Dynamic surface tension results of *DAH* solutions at various concentrations ($1 \cdot 10^{-6}$, $1 \cdot 10^{-5}$, and $1 \cdot 10^{-4}$ mol/dm³) with DI water, 100% saturated KCl, 100% saturated NaCl, and 50%KCl+50%NaCl solutions

Time (sec)	No Salt			100% KCl			100%NaCl			50% KCl+50% NaCl		
	DAH Conc. (mol/ dm ³)			DAH Conc. (mol/ dm ³)			DAH Conc. (mol/ dm ³)			DAH Conc. (mol/ dm ³)		
	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴
15	72.56	72.30	70.37	78.43	77.76	76.69	81.34	81.02	78.28	78.01	77.77	74.51
30	72.54	72.23	70.31	78.21	77.47	76.09	81.16	80.96	77.76	77.72	77.12	72.02
45	72.53	72.22	70.28	78.04	77.20	75.51	81.12	80.89	77.48	77.35	76.26	70.38
60	72.53	72.19	70.26	77.95	77.01	75.16	81.05	80.79	77.18	76.94	75.83	68.62
75	72.51	72.19	70.23	77.88	76.79	73.78	81.01	80.70	76.73	76.51	74.83	66.89
90	72.51	72.18	70.21	77.80	76.52	73.13	80.98	80.60	76.48	76.22	74.14	64.83
105	72.50	72.18	70.18	77.73	76.20	71.73	80.95	80.42	75.56	75.83	73.54	62.71
120	72.50	72.18	70.17	77.66	76.03	70.38	80.92	80.22	75.04	75.62	72.81	60.46
135	72.50	72.17	70.15	77.60	75.71	69.01	80.88	80.07	74.42	75.41	72.16	57.82
150	72.49	72.16	70.12	77.53	75.52	67.31	80.85	79.88	73.46	75.32	71.20	55.46
165	72.49	72.15	70.09	77.45	75.37	66.42	80.74	79.52	72.83	75.08	70.52	52.94
180	72.48	72.14	70.07	77.31	75.21	65.25	80.70	79.30	72.00	75.40	70.02	50.32

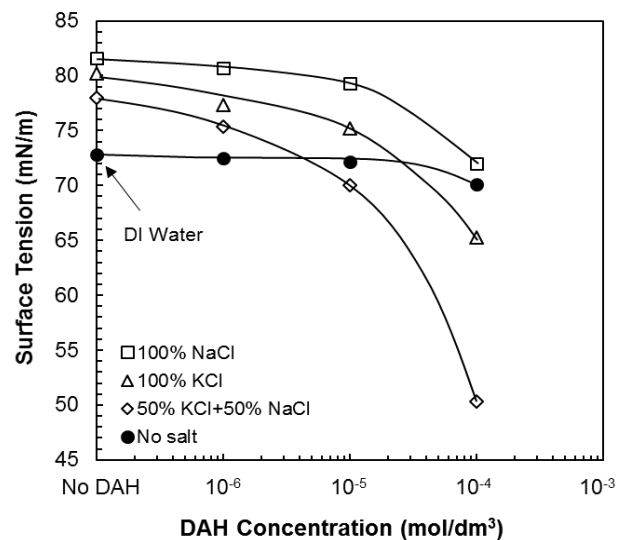


Fig. 7. Surface tension of KCl and NaCl solutions as a function of *DAH* concentration

3.2. Bubble coalescence time measurements

Bubble coalescence percents of salt and *DAH* solutions are given in Fig. 8. As seen in Fig. 8, while 100% of the experiments resulted in coalescence in DI water, the bubble coalescence could be inhibited completely with almost all solutions with *DAH*, except 50% KCl+50%NaCl+ $1 \cdot 10^{-6}$ mol/dm³ *DAH* solution, which several bubble coalescences were observed. Even in this case, the coalescence percent remain under 25%. On the other hand, bubble coalescence percents exceed 50% limit, and the bubble

coalescence time was determined as 100 ms, 270 ms, and 650 ms, respectively for 100% KCl, 100% NaCl, and 50%KCl+50% NaCl salt solutions.

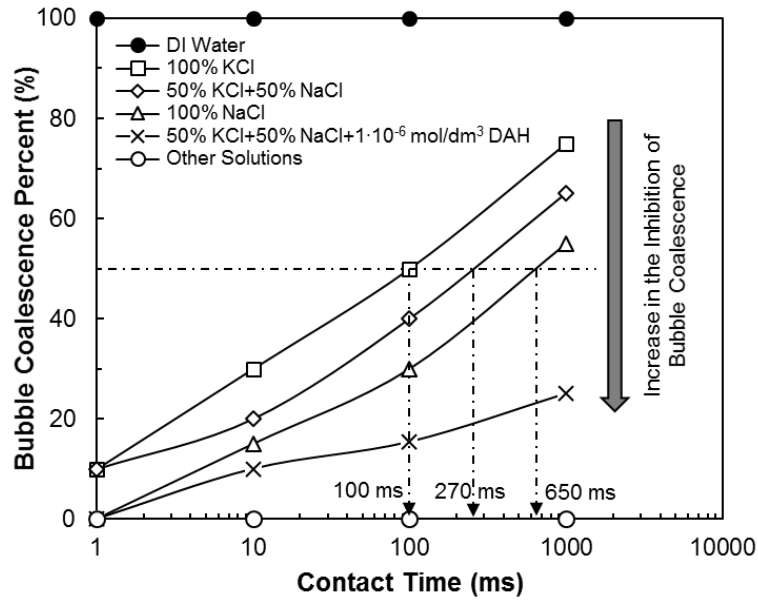


Fig. 8. Bubble coalescence time of various solutions (“Other solutions” include the individual solutions of 100% KCl+1.10⁻⁶ mol/dm³ DAH, 100% KCl+1.10⁻⁵ mol/dm³ DAH, 100% KCl+1.10⁻⁴ mol/dm³ DAH, 100% NaCl+1.10⁻⁶ mol/dm³ DAH, 100% NaCl+1.10⁻⁵ mol/dm³ DAH, 100% NaCl+1.10⁻⁴ mol/dm³ DAH, %50NaCl+%50KCl+1.10⁻⁵ mol/dm³ DAH, %50NaCl+%50KCl+1.10⁻⁴ mol/dm³ DAH, 1.10⁻⁶ mol/dm³ DAH, 1.10⁻⁵ mol/dm³ DAH, and 1.10⁻⁴ mol/dm³ DAH)

Bubble size can change with salt concentration (Nguyen et al., 2012). In general knowledge, since the bubble coalescence reduced in the presence of dissolved ions at high concentrations, the bubble size should reduce. Kurniawan et al. (2011) was measured the froth bubble size in the presence of various salts, and reported that while some salts reduced the froth bubble size, others showed no effect. Tsang et al. (2004) stated that the transition concentration increased with decreasing in the bubble size. On the other hand, frothers have a dominant role in the stability and the size of froth bubbles.

In addition to bubble size, the surface tension is another phenomenon for the bubble coalescence process. The results of the surface tension measurements, which can be seen together with the bubble coalescence time results in Fig. 9, indicated that there was no strong relationship between the surface tension and the bubble coalescence time of the salt solutions. On the other hand, the results also showed that the bubble coalescence time in the presence of Na⁺ ions (650 ms) was longer than that of K⁺ ions (100 ms) which indicates that there is a specific ion effect on bubble coalescence phenomena.

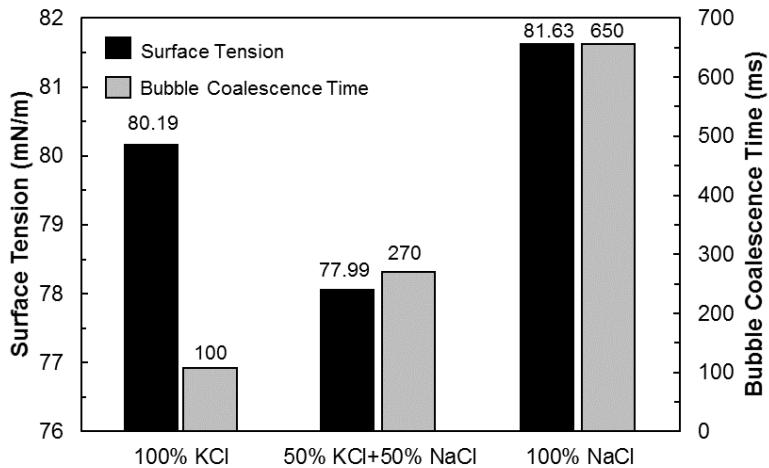


Fig. 9. Surface tension and bubble coalescence times of the salt solutions

The electrolytes may not change the equilibrium interaction forces between the bubbles, but instead, alter the dynamic processes leading to film thinning and rupture (Craig, 2011; Wu et al., 2016). It was also reported by Wang and Peng (2014) and Wu et al. (2016) that the surface tension gradient resulting from the thinning process immobilizes the gas/liquid interface between coalescing bubbles at high salt concentrations, and therefore bubble coalescence time increases.

According to Craig et al. (1993) and Craig (2004), the effect of the salts on bubble coalescence is controlled by the proper combination of specific cations and anions classified as α and β (Table 3). They asserted that the salts consisted of same type cations and anions ($\alpha\alpha$ or $\beta\beta$) inhibit bubble coalescence. On the contrary, the salts containing a mixture of these ion types ($\alpha\beta$) have no effect. According to Table 3, it is seen that the combination of K^+ and Cl^- inhibits the bubble coalescence as well as Na^+ and Cl^- combination.

Table 3. Effect of several anions and cations on bubble coalescence

Anions	Cations	H ⁺	Li ⁺	Na ⁺	K ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	(CH ₃) ₄ N ⁺	(CH ₃) ₄ NH ⁺	(CH ₃) ₄ NH ₂ ⁺	(CH ₃) ₄ NH ₃ ⁺
	Type	β	α	α	α	α	α	α	α	β	β	β	β
OH ⁻	α	x		✓	✓								
Cl ⁻	α	x	✓	✓	✓		✓	✓		x	x	x	x
Br ⁻	α	x		✓	✓	✓							
NO ₃ ⁻	α	x	✓	✓	✓			✓					
ClO ₃ ⁻	β			x									
ClO ₄ ⁻	β	✓		x			x		x				
CH ₃ COO ⁻	β	✓		x	x	x	x	x	x				
SO ₄ ²⁻	α	x		✓			✓					✓	
(COO) ₂ ²⁻	α	x			✓								

Combining rules:

$\alpha\alpha$ or $\beta\beta$ salts inhibit bubble coalescence (✓)

$\alpha\beta$ or $\beta\alpha$ salts do not inhibit bubble coalescence (x)

The results of this study showed that the bubble coalescence can be inhibited more successfully with NaCl than 50%KCl+50% NaCl mixture. On the other hand, the KCl is not as effective as these two salts in the inhibition of bubble coalescence. Therefore, the following trend can be written for the inhibition of bubble coalescence: 100%KCl < 50%KCl+50%NaCl < 100% NaCl

Weissenborn and Pugh (1995) reported that the solubility of oxygen decreased exponentially with increasing electrolyte concentration and a good correlation was observed between the transition concentration and the gas solubility (represented by the exponential decay coefficient of O₂ solubility with increasing electrolyte concentration). This trend is in accordance with the correlation between the transition concentration and the exponential decay coefficients for oxygen solubility given by Weissenborn and Pugh (1995). Therefore, the inhibition of bubble coalescence may be linked with the decreased dissolved gas concentration in the electrolyte solution.

4. Conclusions

In this study, the air/water interface in the mixed solutions of KCl, NaCl, and DAH was investigated in terms of surface tension and bubble coalescence time measurements. The surface tension measurement results indicated that while the surface tension of single KCl and NaCl solutions increased linearly with the saturation percent, in case of mixed KCl and NaCl solutions, the surface tension increased with NaCl percent which increased the ionic strength of the solution. The increase in the surface tension is in accordance with the ionic strength of the solution for both single and mixed solutions. Therefore, the increase in the surface tension of salt solutions may be related to the ionic strength of the salt solutions in some cases. In addition, lower surface tension values were obtained with the mixed solution of 50%KCl+50%NaCl than single salt solutions (100%KCl and 100% NaCl) in the absence and presence of DAH.

The effect of ions on the surface tension of salt solutions is related to the chaotropic and kosmotropic effects of the ions which are identified in the Hofmeister series. In general, while the chaotropic ions do not contribute significantly to increase the surface tension of the solution, the kosmotropic ions increase it. In accordance, in this study, the surface tension of NaCl, which is more kosmotrope, found higher than that of KCl.

The results of this study also showed that the absorbance of the ions an air/water interface was so fast that the surface tension did not change as a function of time (bubble age). However, since the surfactant (*DAH*) molecules were larger than ions, the completion of the adsorption process took time.

Bubble coalescence time measurement results of this study showed that the bubble coalescence could be inhibited with the use of *DAH* in the absence and presence of KCl and NaCl. However, bubble coalescence may occur with the saturated KCl and NaCl solutions in the absence of *DAH*. Additionally, the bubble coalescence time was determined as 100 ms, 270 ms, and 650 ms, respectively for 100% KCl, 100% NaCl, and 50%KCl+50% NaCl salt solutions in the absence of *DAH*. The success of the salt solutions in the inhibition of bubble coalescence can be written as 100%KCl<50%KCl+50%NaCl<100% NaCl in terms of obtained bubble coalescence time values. There is no strong relationship can be found between the surface tension and bubble coalescence time of the salt solutions. Therefore, the inhibition of bubble coalescence by salts may be controlled by the specific ion pairing types and the solubility of oxygen in salt solutions.

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