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A fundamental study of monovalent and divalent ions on froth properties in the presence of terpenic oil

Yubiao Li ^{1,2}, Hongduo Wang ¹, Wanqing Li ¹, Shaoxian Song ¹

¹ School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, 430070, Hubei, China

² School of Natural and Built Environments, University of South Australia, Mawson Lakes, SA 5095, Australia

Corresponding authors : Yubiao.Li@whut.edu.cn (Y. Li)

Abstract: In order to minimize fresh water usage, much attention has been paid to the flotation using saline or sea water. However, the effects of various ions in these waters on froth properties in flotation are not fully understood. In this study, the effects of electrolyte solutions containing NaCl, KCl, CaCl₂, and MgCl₂ at different concentrations in the presence of terpenic oil as a frother were investigated on froth performance, dynamic froth stability (DFS). It was found that KCl had the best synergistic effects with terpenic oil in reducing the solution surface tension. In the presence of terpenic oil, the DFS and half-life time were reduced with the increased ion concentration. Dynamics foamability index measurements (DFI) confirmed that the increased ion concentration increased the foamability, as frother did. In addition, Gibbs adsorption isotherm suggested that the amount of terpenic oil adsorbed at the gas-liquid interface was increased with the increased ion concentration. This study therefore indicated that the presence of ions can reduce the froth stability but not decline foamability due to terpenic oil, enlightening the application of saline or sea water in defoaming process in flotation.

Keywords: surface tension, froth stability, dynamic foamability index, Gibbs adsorption isotherm

1. Introduction

Flotation, as a physico-chemical separation process, is performed based on different surface properties of valuable and gangue minerals (Becker et al., 2009; Kowalczyk et al., 2015). This process is mostly important in mineral processing industry, and requires a variety of reagents, including collectors, modifiers, adjusters, and frothers (Laskowski et al., 2003). Since these reagents can modify the surfaces of air bubbles or mineral particles, thereby they influence flotation efficiency.

According to Leja-Schulman's penetration theory (Leja, 1954; Leja, 1956), frother molecules accumulate preferentially at the gas-liquid interface, and interact with mineral surface resulting in bubble-particle collision and attachment processes which determine mineral recovery significantly (Albijanic et al., 2014). In addition, frothers adsorbed on bubble surface change its surface viscosity and charge, generating and stabilizing fine bubbles (Lee et al., 2005). However, froth in some cases is undesirable due to decreased loading and separation efficiency, loss of target minerals and downstream environmental issues (Oh et al., 2012) if the froth is overstable in the flotation process. Therefore, many defoaming methods including chemical, thermal, and mechanical ones have been attempted, but resultant problems may arise, for instance, high cost, and new pollution (Liu et al., 2013).

Since the flux flotation rate is inversely proportional to bubble size (Jameson, 1977; Gorain et al., 1996; Gorain et al., 1998), bubble size has been widely investigated as an important variable in flotation process (Ahmed and Jameson, 1985; Tao, 2005). Meanwhile, bubble coalescence is one of the most important factors influencing bubble size. It is widely accepted that surface active compounds (frother) and surface inactive compounds (inorganic ions) can prevent bubble coalescence in different manners (Finch et al., 2008; Kracht and Finch, 2009; Kurniawan et al., 2011; Peng and Seaman, 2011; Bournival et al., 2012; Castro et al., 2013; Kowalczyk et al., 2014; Zhang, 2015). Many froth flotation plants apply

recycled water containing dissolved ions of different valences. Although electrolytes like NaClO_3 have no effects on bubble coalescence, most common inorganic electrolytes such as NaCl , and KCl show positive suppression on bubble coalescence (Marrucci and Nicodemo, 1967; Ziemiński and Whittemore, 1971; Gourram-Badri et al., 1998; Craig, 2004). As compared to normal frothers such as terpenic oil in reducing bubble size, the application of inorganic ions is more cost effective (Manono et al., 2013). In addition, the inorganic ions influence the adsorption of surfactant molecules at the air-water interface, thereby altering the interface charge (Kralchevsky et al., 1999; Giribabu et al., 2007; Behera et al., 2014; Yekeen et al., 2017).

Therefore, an increasing research interest is focused on the effects of ions on froth performance (Peng et al., 2012). For instance, Castro et al. (2013) reported that the bubbles in mixed DF-250 (as frother) and inorganic NaCl system were smaller than that without added ions. Laskowski et al. (2014) proposed a similar conclusion in sea water mixed with MIBC. An enhanced flotation of hydrophobic particles was found in electrolyte solution in some studies (Harvey et al., 2002; Kurniawan et al., 2011) as inorganic ion affected the adsorption of frothers on mineral and gas-liquid interface of stabilized froth (Zhang, 2015).

However, the underlying synergistic effects of frother and ions on froth performance are still not fully understood. Therefore, the aim of present work is to investigate the froth performance via investigating the surface tension of the solution, the froth stability, foamability and Gibbs adsorption isotherm in the presence of a common flotation frother of terpenic oil in the solution containing monovalent and divalent ions (e.g. Na^+ , K^+ , Ca^{2+} , and Mg^{2+}), to reveal their synergistic effects in foaming/defoaming performance, thereby presenting the possibility of using sea water or recycled water containing inorganic ions for mineral flotation.

2. Experimental

2.1 Materials

Technical grade of terpenic oil ($\text{C}_{10}\text{H}_{17}\text{OH}$) that normally used for sulfide mineral flotation was used as a frother in this study while analytical grade NaOH was used to adjust solution pH to avoid contamination from $\text{Ca}(\text{OH})_2$ that normally used in mineral processing industry for pH adjustment. Analytical grade NaCl , KCl , CaCl_2 , and MgCl_2 were used to prepare electrolyte solutions, e.g., 1×10^{-2} mol/dm³ to 1 mol/dm³ for NaCl , and KCl , 1×10^{-4} mol/dm³ to 1×10^{-2} mol/dm³ for CaCl_2 , and MgCl_2 . The concentration level of NaCl and CaCl_2 were referred to those in sea water (Na^+ and Ca^{2+} ions in sea water are 0.47 mol/dm³ and 0.01 mol/dm³, respectively) while the KCl and MgCl_2 concentrations were set at the same levels of NaCl and CaCl_2 , respectively for comparison purpose (Millero et al., 2008; Suyantara et al., 2018). In addition, the concentrations of divalent ions of Mg^{2+} and Ca^{2+} greater than 1×10^{-2} mol/dm³ would result in precipitation when the pH of flotation pulp was greater than 9 (Hirajima et al., 2016; Suyantara et al., 2016). Therefore, the concentration of monovalent and divalent ions were set at 1×10^{-2} mol/dm³ to 1 mol/dm³ and 1×10^{-4} mol/dm³ to 1×10^{-2} mol/dm³, respectively. All the reagents used in this study were purchased from Sinopharm Chemical Reagent CO., LTD, China except the terpenic oil which was purchased from the Chengchao Iron Mine, Ezhou, Hubei Province, China. In addition, the concentration of terpenic oil was varied from 0~1000 mg/dm³. Millipore® (Billerica, MA, USA) ultrapure water with a resistivity of 18.2 MΩ cm was employed in all measurements.

2.2 Methods

2.2.1 Surface tension measurements

Surface tension measurements were carried out according to the Wilhelmy Pt plate method (Su et al., 2004), by using KRUSS Tension meters K100, Germany. The instrument was calibrated against ultrapure water. Prior to the measurements, the Pt plate was fixed to the force sensor of tensiometer. Then, a vessel containing 50 cm³ testing solution was placed on the platform which was placed under Pt plate. Subsequently, the platform was moved up at a rate of 0.09 mm/min until the solution surface touched the Pt plate. Thereafter, the surface tension was determined. This procedure was repeated at least five times, and the average value was reported with an accuracy of ± 0.1 mN/m or less. It should be noted

that the Pt plate was burned by absolute ethyl alcohol blast burner and washed using ultrapure water to avoid contamination (Scholz et al., 2018).

2.2.2 Froth stability

The modified Bikermann's method (Iglesias et al., 1995; Beneventi et al., 2001) was used to generate bubbles in the electrolyte solution system. The glass column (with a height of 70 cm and an internal diameter of 4 cm) was pre-washed by the solution to be tested. Subsequently, 150 cm³ prepared electrolyte solution was poured into the glass column. The froth air bubbles was produced by a glass sand filter (pore size of 50 μm) at a certain gas flow of 667 cm³/min (*i.e.* 40 dm³/h) adjusted by a glass rotor flowmeter while the distance between the solution-froth interface and the top of the froth was considered as the steady-state froth height.

According to Eq.1, the dynamic froth stability (DFS) method was used to evaluate froth stability (Gourram-Badri et al., 1998).

$$DFS = \frac{V_f}{Q} = \frac{H \times A}{Q} \quad (1)$$

where, V_f is the maximum steady-state froth volume (cm³), Q is the gas flow rate (cm³/min), H is the maximum steady-state froth height (cm), A is the cross-sectional area of the experimental apparatus (cm²). As both gas flow rate and cross-sectional area of the experimental apparatus are constants, the froth stability can be determined by the maximum steady-state froth height. In addition, the half-life (min) of froth decay was also investigated to evaluate the froth stability (Barbian et al., 2005; Farrokhpay and Zanin, 2012; Liang et al., 2015).

2.2.3 Dynamic foamability index

The dynamic foamability index (DFI) method (Malysa et al., 1981; Czarnecki et al., 1982) was used to test the foamability of solution with various ions, via investigating the total height of solution and froth phase using the same instrumentation as for froth stability. The DFI values were determined using Eqs.2 and 3.

$$rt = \frac{\Delta V}{\Delta Q} \quad (2)$$

$$DFI = \left(\frac{\partial rt}{\partial C} \right)_{C \rightarrow 0} \quad (3)$$

where rt is the retention time (min), V is the total gas volume (cm³); Q is the gas flow rate (cm³/min), C is the frother concentration in mol/dm³. DFI (min·dm³/mol) value can be defined as the limit slope of retention time when $C \rightarrow 0$.

2.2.4 Gibbs adsorption isotherm

According to the Blankschtein isothermal adsorption equation (Mulqueen and Blankschtein, 2002), the main factors affecting the adsorption loading are: (a) frother concentration; (b) electrical repulsion between ionic head-groups; (c) interaction between hydrophobic groups; (d) cross-sectional area of frother; and (e) hydrophilic/lipophilic balance (HLB). The addition of ions can influence the above mentioned factors, and consequently affect the adsorption loading.

Frothers are a class of substances containing amphoteric groups, giving rise to a particular tendency to be adsorbed onto two or three phase interfaces. The Gibbs adsorption isotherm (Eq. 4) was used to evaluate the adsorption capacity of frother in the gas-liquid interfaces (Tan et al., 2005; Gupta et al., 2007).

$$\Gamma = -\frac{1}{2.303RT} \left(\frac{d\gamma}{d \log C} \right) \quad (4)$$

where, Γ is the adsorption loading (μmol/m²), γ is the static surface tension (mN/m), T is the absolute temperature (K), R is the ideal gas constant while C is the bulk frother concentration (mol/dm³). The ratio, $d\gamma/d \log C$, was obtained from the maximum slopes of γ versus $\log C$. Since Γ corresponds to the amount of surfactant per unit surface area, the adsorption area per molecule A_{exp} of each molecule can be calculated according to Eq.5.

$$A_{\text{exp}} = \frac{1}{T \times N_A} \quad (5)$$

where A_{exp} is the adsorption area per molecule (\AA^2) while N_A is the avogadro constant.

3. Results and discussion

3.1 Surface tension measurements

Fig. 1 shows the surface tension of solutions containing monovalent and divalent ions in the presence of terpenic oil. The surface tension of ion solutions without terpenic oil (71.3~73.4 mN/m) was slightly greater than that of ultrapure water (71.2 mN/m), probably due to the positive and negative ions dissociated from salts. Therefore, the magnitude of surface tension was highly depended on the extent of ion hydration (Weissenborn and Pugh, 1996). In contrast, a significant decrease in surface tension was observed upon the terpenic oil addition. Specifically, with the increased terpenic oil concentration, the surface tension of all four ion solutions showed a gradual decrease, attributing to the adsorption of terpenic oil at the gas-liquid interface (Tan et al., 2005; Ozdemir et al., 2009; Samanta and Ghosh, 2011).

Compared to control experiment (ultrapure water), a clearly lower surface tension was observed in the solution containing different valent ions in the presence of terpenic oil. For instance, the surface tensions of monovalent ion solutions were lower than that of ultrapure water when terpenic oil was added, with a gradual decrease being observed with the increased NaCl and KCl concentrations, e.g. the surface tension of NaCl solution was decreased from 48.41 mN/m at 10^{-2} mol/dm³ NaCl to 47.19 mN/m at 1 mol/dm³ NaCl when terpenic oil was 10 mg/dm³, while the surface tension of KCl solution was decreased from 48.38 mN/m at 10^{-2} mol/dm³ KCl to 47.16 mN/m at 1 mol/dm³ KCl when terpenic oil was 10 mg/dm³. In addition, with the increase of monovalent ion concentration from 10^{-2} mol/dm³ to 1 mol/dm³, the surface tension of the solution containing the same NaCl or KCl was concentration gradually declined. This might be a fact that the ions influenced the terpenic oil adsorption at the air-water interface.

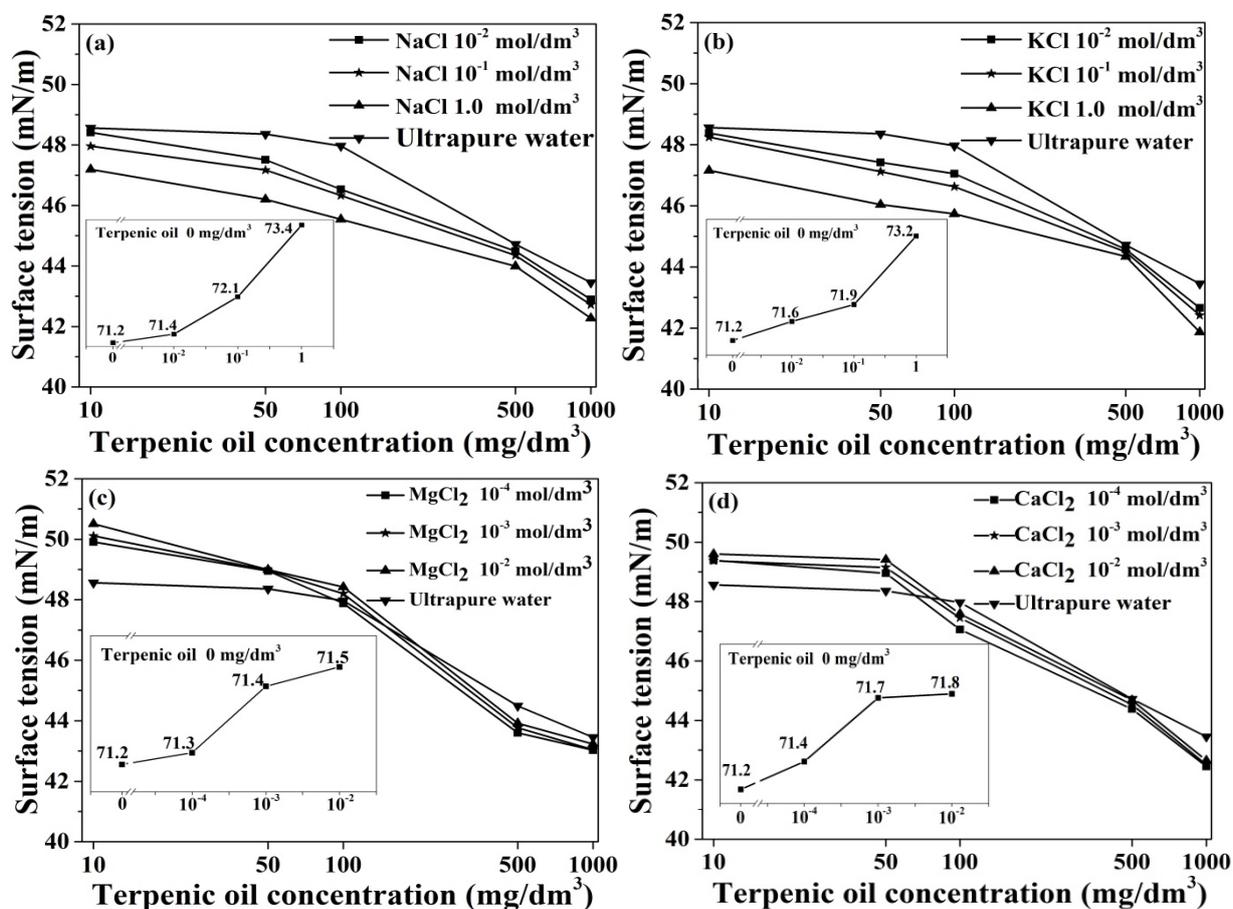


Fig. 1 Effects of terpenic oil on surface tension in the presence of (a) NaCl, (b) KCl, (c) MgCl₂, and (d) CaCl₂

However, the surface tensions of divalent ion solutions were greater than that of ultrapure water with the terpenic oil concentrations lower than 70~86 mg/dm³ and 100~260 mg/dm³ for CaCl₂ and MgCl₂, respectively. A further increase in the terpenic oil concentration decreased the surface tension of divalent electrolytes, resulting in a surface tension lower than that of ultrapure water. Therefore, there is a critical point considered as the surface tension switch point (s.t.s.p) (Castro et al., 2013) to divide the terpenic oil concentration into two parts. In other words, when the terpenic oil concentration was lower than the s.t.s.p., the surface tension was dominated by surface-inactive compound (*i.e.*, CaCl₂ and MgCl₂), giving rise to an increased surface tension with the increased ion concentration. In contrast, when the terpenic oil concentration was greater than the s.t.s.p., the surface tension was dominated by terpenic oil, leading to a decreased surface tension with the increased terpenic oil concentration (Wang and Peng, 2014). In addition, when the ion concentration was 1×10⁻² mol/dm³, the most significant decrease in surface tension was observed in the solution with KCl (42.66 mN/m), indicating that KCl had a better synergistic effect with the terpenic oil in reducing solution surface tension.

3.2 Froth stability

Fig. 2 shows the effects of terpenic oil concentration on froth stability of aqueous solutions in the presence of different ions. The DFS of solution without terpenic oil (0 mg/dm³) was slightly increased with the increased ion concentration, indicating that these ions had a positive effect on froth stability, similar to that observed in Bournival et al. (2012).

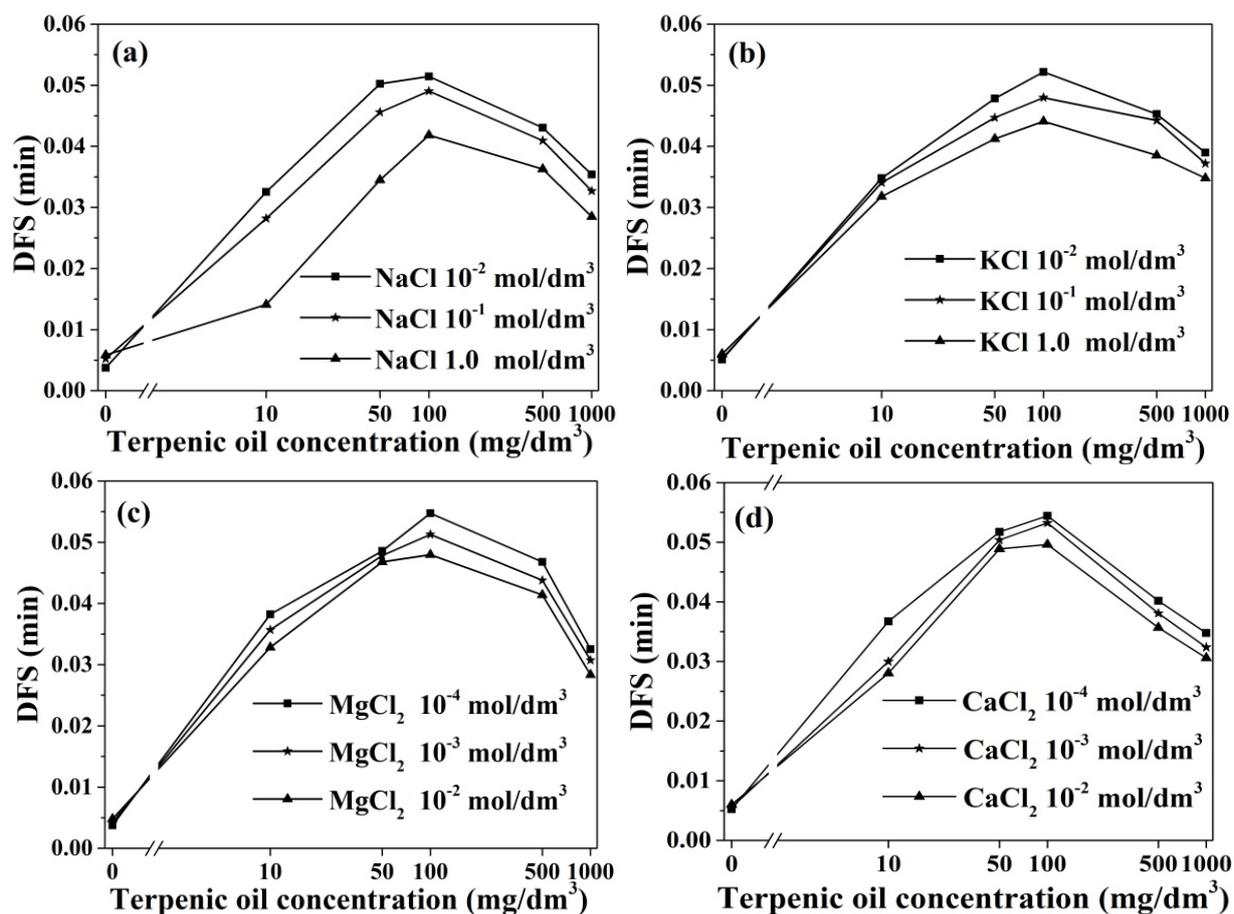


Fig. 2 Effects of terpenic oil concentration on DFS in the presence of (a) NaCl, (b) KCl, (c) MgCl₂ and (d) CaCl₂

The DFS increased significantly in the presence of terpenic oil, due to its positive role in stabilizing froths, consistent with many other studies. Comley et al. (2002) reported that frothers can reduce bubble size by inhibiting bubble coalescence. However, DFS decreased with the increased ion concentration greater than 10 mg/dm³, probably due to the decreased bubble stability in the presence of ions, *e.g.*, thinner bubble layer and easier bubble breakage (Fuerstenau et al., 1983; Arnold and Aplan, 1986). Once

the film on the bubble is sufficiently thin, the bubbles rupture due to the instability mechanisms, resulting in bubble coalescence (Kracht and Finch, 2009). Therefore, the decreased *DFS* value is due to the increased ion concentration. In addition, when the terpenic oil concentration was increased from 0 to 100 mg/dm³ but at a constant ion concentration, the *DFS* values increased significantly. However, further increase in terpenic oil concentration showed a gradual decrease in *DFS*, indicating a negative role of high terpenic oil concentration, similar to that found in Tan et al. (2009). This might be because the increased terpenic oil concentration decreased the Marangoni effects, resulted in the collapse of froth (Tan et al., 2005).

On the other hand, froth stability can also be indirectly represented by the half-life time of froth. A longer half-life time indicates a more stable froth. Fig. 3 shows that the half-life time of froth was increased with the increased terpenic oil concentration, revealing that the presence of terpenic oil was beneficial to froth stability. However, the half-life time of froth decreased with the increased ion concentration. The half-life time experiments agree well with the *DFS* results, suggesting that the increasing ion concentration played a negative role on froth stability in the presence of terpenic oil.

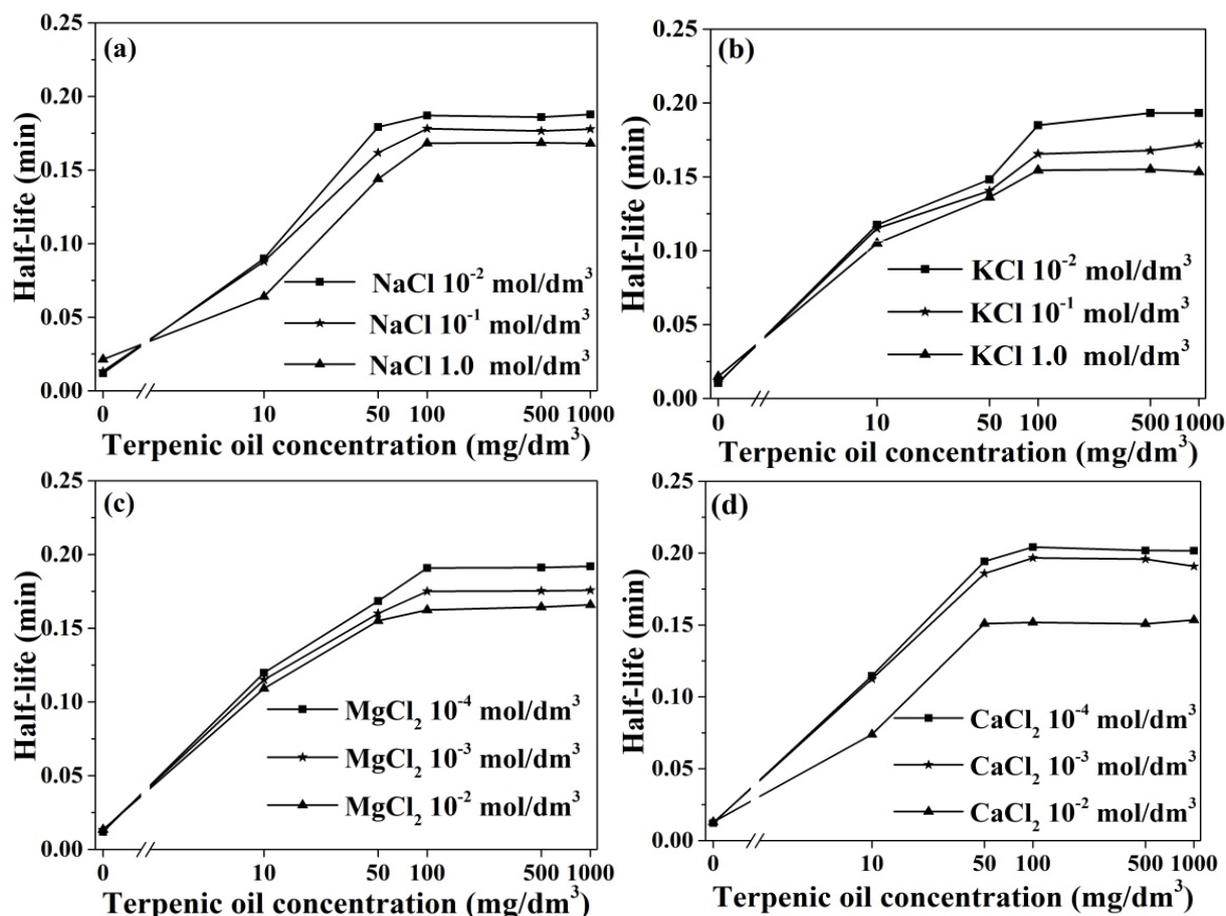


Fig. 3 Effects of terpenic oil concentration on half-life of aqueous solution in the presence of (a) NaCl, (b) KCl, (c) MgCl₂ and (d) CaCl₂

3.3 Foamability

DFI has been used extensively to characterize the foamability of frother efficiency (Małysa et al., 1987; Laskowski et al., 2003; Laskowski et al., 2003; Gupta et al., 2007). Fig. 4 shows that *DFI* values of four ions were increased with the increased ion concentration from 1×10^{-4} mol/dm³ to 1×10^{-2} mol/dm³, suggesting that higher ion concentration is beneficial to bubble foamability in the presence of terpenic oil due to the screening effects on electrostatic charge (Behera et al., 2014). As compared to other three ions, the *DFI* value of NaCl solution was significantly lower, especially compared with its monovalent counterpart KCl which showing a much higher *DFI* at the same concentration, indicating that K⁺ played a more important role than that of Na⁺ in enhancing bubble foamability. No apparent difference was

observed in DFI between CaCl_2 and MgCl_2 solution when at $1 \times 10^{-4} \text{ mol/dm}^3$, although CaCl_2 showed a slightly greater DFI than that of MgCl_2 when concentration was greater than $1 \times 10^{-3} \text{ mol/dm}^3$. It should be noted that the foamability of CaCl_2 and MgCl_2 was greater than that of KCl at $1 \times 10^{-2} \text{ mol/dm}^3$, giving rise to an order of $\text{CaCl}_2 > \text{MgCl}_2 > \text{KCl} > \text{NaCl}$ at $1 \times 10^{-2} \text{ mol/dm}^3$, further indicating that divalent ions had stronger ability in enhancing bubble foamability than that of monovalent ions.

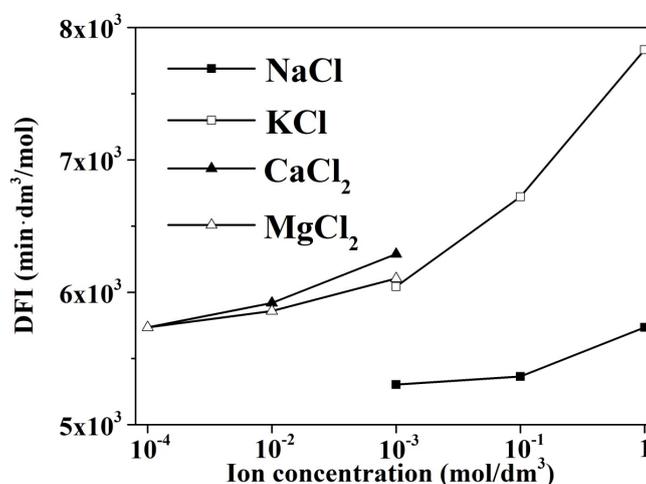


Fig. 4 Effects of ion concentration on DFI

3.4 Gibbs adsorption isotherm

Fig. 5(a) showed that the adsorption loading was increased with increased ion concentration in the presence of terpenic oil, but in different extents, probably due to different compression of electric double layer from various ions (Fuerstenau et al., 1983). Specifically, KCl showed a much higher adsorption loading than that of NaCl within $1 \times 10^{-2} \text{ mol/dm}^3 \sim 1 \text{ mol/dm}^3$ while the adsorption loading due to CaCl_2 was greater than that of MgCl_2 from 1×10^{-4} to $1 \times 10^{-2} \text{ mol/dm}^3$, showing an order of $\text{CaCl}_2 > \text{MgCl}_2 > \text{KCl} > \text{NaCl}$ at $1 \times 10^{-2} \text{ mol/dm}^3$. This indicates that divalent ions played a more significant role in enhancing adsorption loading of terpenic oil on bubbles due to stronger ability in increasing the repulsion force than that of monovalent ions (Samanta and Ghosh, 2011). Actually, once upon the addition of ions, the mutual repulsion force between the ionic head-groups of terpenic oil was decreased, giving rise to a denser adsorption of terpenic oil molecules on bubble surface. In addition, the hydration of cations derived from ion reduced the liquid film on bubble surface, resulting in increased activity of terpenic oil molecules. Therefore, the adsorption loading of terpenic oil on bubble surface was improved with increased ion concentration.

Fig. 5(b) shows that the adsorption area per molecule of NaCl was apparently greater than that of KCl , indicating that terpenic oil molecules on the gas-liquid interface in KCl solution were closer than that in NaCl solution, therefore terpenic oil in KCl solution showed a slightly better foamability than that in NaCl , consistent with the surface tension shown in Fig. 1. Similarly, MgCl_2 presented a higher adsorption area per molecule than that of CaCl_2 , suggesting that a better foamability can be from CaCl_2 rather than MgCl_2 . In other words, the terpenic oil molecules adsorbed on the bubble surface in the CaCl_2 solution were closer than that in the MgCl_2 solution.

Generally, ions dissolved from salts can be either a water structure maker or a water structure breaker (Ozdemir et al., 2009; Wang and Peng, 2014). For instance, Na^+ and Mg^{2+} can be regarded as the water structure maker. More water molecular clusters can be found on the hydrated surface in the presence of Na^+ and Mg^{2+} , therefore preventing the adsorption of frothers on the bubble surface. Differently, K^+ and Ca^{2+} have been considered as the water structure breaker, thereby improving the adsorption of frothers. Therefore, the water structure breaker ions such as K^+ and Ca^{2+} are capable of loading more frother molecules on the bubble surface, as compared to the water structure maker ions such as Na^+ and Mg^{2+} .

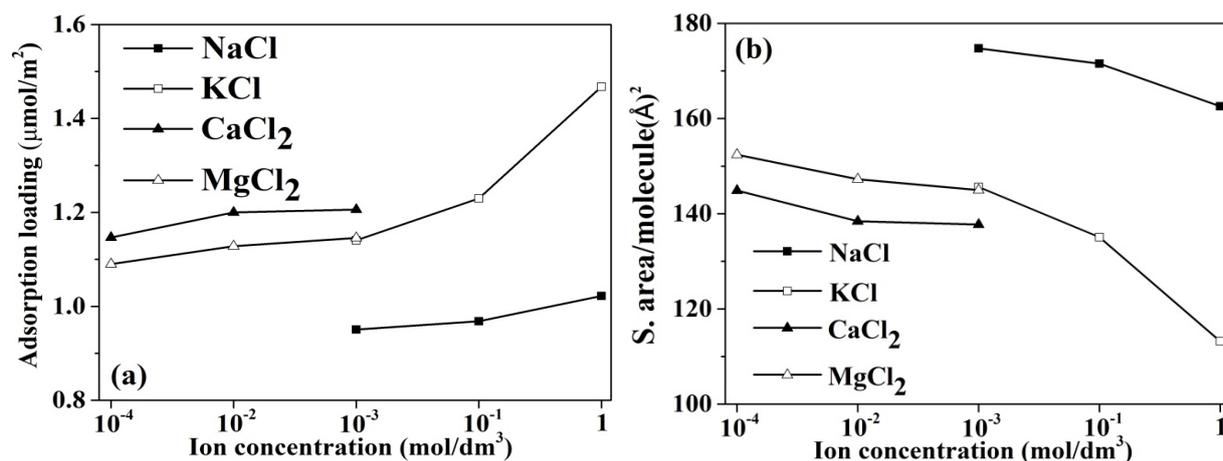


Fig. 5 Effects of ion concentration on (a) adsorption loading, and (b) adsorption area per molecule

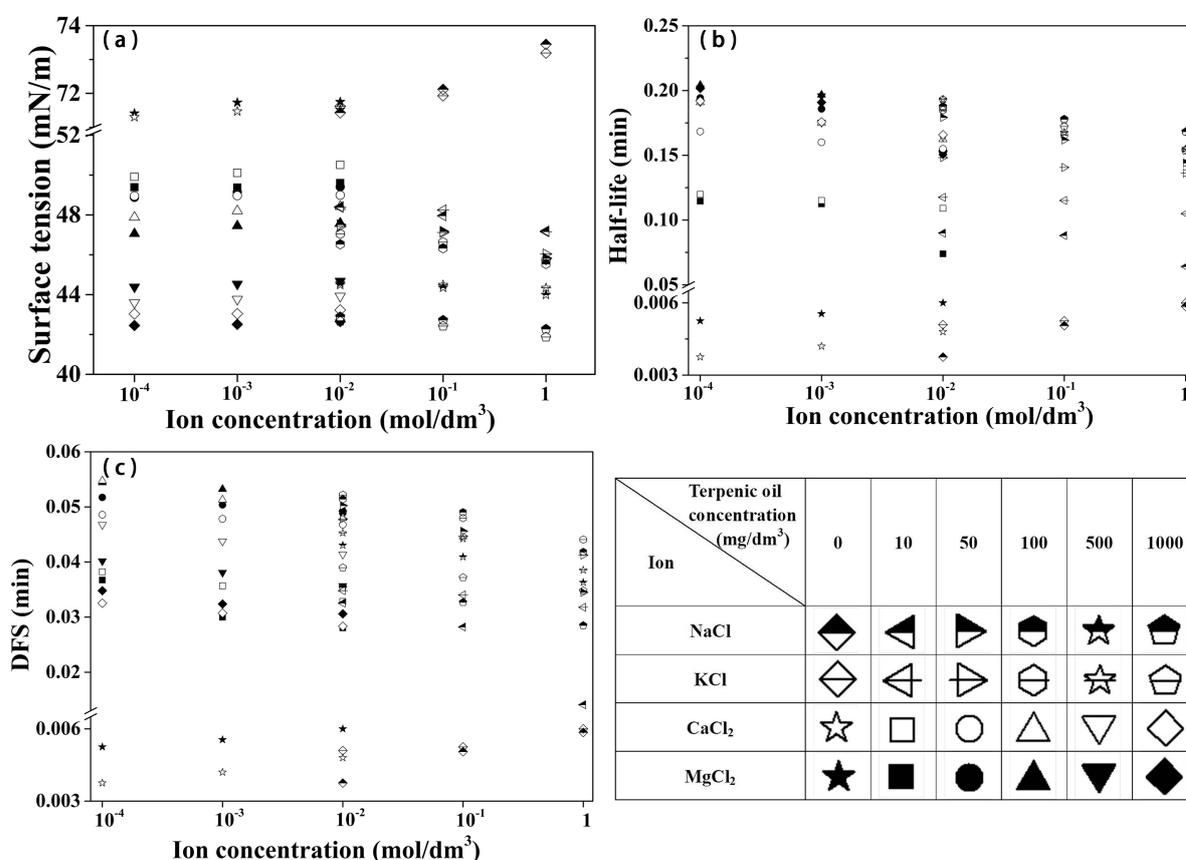


Fig. 6 (a) surface tension, (b) half-life time, and (c) DFS as a function of ion concentration

Specifically, the highest adsorption area per molecule was observed in NaCl solution (approximately 175 Å²) while the lowest value was found for CaCl₂ solution (approximately 138 Å²) at 1×10⁻² mol/dm³. Based on the molecular structure, terpenic oil molecules occupy from approximately 6 Å² to 10 Å² when lying while upright situation occupies only about 2.0 Å² (Gupta et al., 2007). The adsorption area per molecule in four electrolyte solutions (113~174 Å²) were apparently larger than that of terpenic oil molecules. Therefore, the terpenic oil molecules are more likely to lie flat on the gas-liquid interface and lead to a weak foamability. In addition, the terpenic oil molecules in CaCl₂ solution had a closer arrangement than other solutions due to smaller adsorption area per molecule observed in CaCl₂ solution. This may be the reason why terpenic oil worked better in CaCl₂ solution than the others at the same concentration. Jachimiska et al. (1995) reported that the DFI value had a positive correlation with

the adsorption loading of frother. The increased amount of frother adsorbed on the gas-liquid interface improved frother foamability. From the above Gibbs adsorption isotherm results, KCl and CaCl₂ solution showed better adsorption loadings, compared with NaCl and MgCl₂ solution, consistent with the DFI results.

Furthermore, Fig. 6 summarises the surface tension, half-life and *DFS* of the ion solution in the absence and presence of terpenic oil. Specifically, Fig. 6(a) shows that the monovalent ions reduced surface tension more significantly as compared to that of divalent ions at the same concentration of 1×10^{-2} mol/dm³. In addition, as compared to Na⁺, K⁺ showed a more apparent role in reducing the solution surface tension (Fig. 6(a)).

4. Conclusions

The effects of four salts (*i.e.* NaCl, KCl, CaCl₂, and MgCl₂) on froth performance were investigated in the presence of terpenic oil. KCl showed the most beneficial effects in decreasing solution surface tension, compared to that of NaCl, CaCl₂, and MgCl₂. The excessive addition of terpenic oil decreased froth stability, but foaming ability was increased. As compared to the monovalent ions, divalent ions had a better synergistic effect with terpenic oil based on the *DFI* and Gibbs adsorption experiments. There is a positive correlation between *DFI* and adsorption capacity. Moreover, the higher valence of ions, a higher adsorption load can be obtained. In addition, when terpenic oil concentration was lower than the s.t.s.p., the surface tension was dominated by surface-inactive compound (*i.e.*, CaCl₂ and MgCl₂). In contrast, when terpenic oil concentration was greater than the s.t.s.p., the surface tension was dominated by terpenic oil, leading to a decreased surface tension with increased terpenic oil concentration. Therefore, the presence of ions in the flotation system contributed to less stable froths, but not affecting the foamability due to frothers, thereby giving new ways to solve the overstable froth issues in the plants, *e.g.* by using saline water or sea water for defoaming.

5. Acknowledgements

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