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Study on the foam behavior of amine reagents adsorbed at gas-liquid and gas-liquid-solid interfaces

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Abstract: Alkyl amines are widely used as cationic collectors in flotation. In this work, the flotation foaming behaviors of alkyl amines, including dodecylamine (DDA), di-n-hexylamine (DHA), octadecylamine (ODA), oleylamine (OLA), in the presence or absence of quartz were investigated by a new approach, "foam analyzer". The effects of pH, reagent dosage, concentration of quartz powder, and particle size on foaming property and stability of bubble were explored, and the physical model of foam structure evolution was established. The adsorption mechanism of amines on quartz surface was studied from molecular structure, surface tension, zeta potential, charging mode, and adsorption form. The results show the foam stability of four amine collectors as follows: OLA > ODA > DHA > DDA. In the range of pH=6-10, the foam properties of the four amines are better. Under the same conditions, the longer carbon chain of aliphatic amine, the more unsaturated bonds, the fewer hydrogen atoms of the amine group, and the corresponding foam properties are better. When the concentration of quartz powder is 8-10%, the foaming and stability of the foam of four kinds amines are the best, The finer quartz powder particle size, the more stable the amine foam and the stronger the foamability.

Keywords: foam, amine kind, stability, foaming property, foam structure

1. Introduction

Flotation has been considered to be the most technologically and economically effective solution to separate mineral particles based on their wetting properties (Filippov, et al. 2014; Liu, et al. 2018; Wang, et al. 2014). During this process, the key to the recovery of valuable minerals from gangue is the selective adsorption of collectors on desired mineral surface (Liu, et al. 2016b). Today, with the increase in demand and the lack of rich ore, the exploitation of middle and low grade ore has attracted a lot of attention, among which about 40% of common minerals are silicate minerals (Tian, et al. 2019). Quartz is the main gangue of siliceous and silicate minerals, many studies have confirmed that reverse flotation of the gangue mineral quartz is the most widely used method for the separation of these minerals (Cao, et al. 2013; Huang, et al. 2020; Li, et al. 2017a; Liu, et al. 2019; Teng, et al. 2018).

Alkyl amine along with their derivatives, due to their low cost, high efficiency, strong foaming properties and high temperature resistance (Liu, et al. 2015b), has been broadly applied as cationic collectors in the reverse flotation of quartz from different types of minerals, such as phosphate and iron oxides (Sis and Chander 2003; Wang and Ren 2005; Zawala, et al. 2017). The head groups of alkyl amines

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can be physically adsorbed on the mineral surface, while their non-polar hydrocarbons form a hydrophobic monolayer on surface of the particle, resulting particles hydrophobic (Kou, et al. 2010), and bubbles are indispensable in the flotation process as a result of they act as the carrier of hydrophobic minerals to the foam (Wang, et al. 2016; Wang and Tao 2017; Xing, et al. 2017) and then rise to the top of the containing vessel to form a froth that flows over the lip of the vessel(Ata and Jameson 2005).

Therefore, when considering the separation processes, understanding the adsorption properties and foaming properties of amine reagents at the solid/liquid interface is a crucial step to improve mineral recovery and reduce costs associated with reagent production, transport, and utilization (Xu, et al. 2014). Zhu et al. (2018) investigated the bubble aspect ratios and rising velocities of dodecylamine (DDA), methyl isobutyl carbinol (MIBC), sec-octylalcohol (2-octanol), DDA-MIBC blend, and DDA-2-octanol blend for different concentrations. Corona-Arroyo, M.A. (2015) studied the effect of the cationic surfactant dodecylamine (DDA) and the frothers MIBC and polyglycol F507 on the bubble size and gas holdup in a downflow system, the results showed that frother-DDA blends gave the lowest gas holdup in the downflow column. Li E. Z. (2017b) investigated the adsorption kinetics and adsorption isotherm of the collector, octadecylamine hydrochloride (ODA), on the surface of KCl crystals, the results suggested that the bubbles could promote the adsorption of ODA on the surface of KCl crystals, and the micro-flotation tests indicated that the flotation recovery rate could be effectively improved by increasing the gas flow rate.

Until now, extensive research has focused on the flotation theory of amine reagents and flotation recovery, especially on the study of DDA (Deng, et al. 2019; Shen, et al. 2017; Smith and L Scott 1990; Wu, et al. 2013; Xu, et al. 2015; Zhang, et al. 2018; Xie, et al. 2020; Scott and Smith 1993; Takeda and Usui 1987; Vieira and Peres 2007). However, few studies have been carried out to explain the flotation behavior of amines in the solid/liquid interface from the perspective of foam production and foam stability (Abdollahy 2018; Eskanlou, et al. 2019; Eskanlou, et al. 2020). In this study, a new device was employed to accurately and automatically measure the height and half-life of foam before and after the addition of quartz in the four amine solutions, respectively. We studied the foam behavior of amine reagents at gas-liquid and gas-liquid-solid interfaces through molecular structure, surface tension, charging mode, and zeta potential, so as to gain a detailed understanding of the hydrophobization mechanism of amines on the quartz surface. Furthermore, the physical model of foam structure evolution was established to explain the migration of bubble, amine reagents, and quartz particles among different interfaces, with the aim of laying a profound background for understanding the effect of amines on bubble performance (including foaming ability and foam stability), so as to promote the efficient utilization of amine reagents.

2. Materials and methods

2.1. Samples and chemicals

The pure quartz minerals (Zhengzhou Yinfeng Laboratory Reagent Co. Ltd.) were ground with a ceramic ball mill and then screened (-0.074mm 100%), immersed in 10 ωt% hydrochloric acid for 24 hours, after that washed with deionized water to neutral. XRF analysis showed that the purity of the sample was high and met the requirement of pure mineral, and the results are shown in Table 1. Table 2 lists the four amine reagents used in this study, all of which are from Aladdin Chemical Reagents Co. Ltd., chemically pure. The pH regulators, NaOH and HCl, are analytical purity (Zhengzhou Yinfeng Laboratory Reagent Co. Ltd.). Deionized water was used throughout the study.

2.2. Methods

2.2.1. Micro-flotation tests

Micro-flotation experiments were performed on XFG hanging tank flotation machine with a 50 cm^3 flotation cell, fixed impeller speed of 2000 RPM. Two grams of samples with 40 cm^3 of deionized water were used in each test. The pulp was first conditioned for 2 min to uniformly disperse the particles. Then, HCl or NaOH was added to adjust the pH to desired values. After that the pulp was conditioned with collectors for 2 min. The flotation was conducted for 3 min. The float and sink were weighed after filtration and drying. The recovery was calculated based on the mass of products. The flotation tests

were performed 3 replicates and the average was reported as a final value. The micro-flotation flow chart is shown in Fig. 1.

Table 1. The XRF results of the pure quartz minerals

Composition	SiO_2	Al_2O_3	CaO	K_2O	P_2O_5	MgO	Na_2O	Fe_2O_3
Content (%)	99.03	0.469	0.103	0.0852	0.0740	0.0726	0.0675	0.0485

Table 2. Amine reagents used in the study

Amine reagents	Chemical formula	Molecular weight/(g·mol^{-1})	CMC values/ mol · dm^3
DHA	$(CH_3(CH_2)_5)_2NH$	185.35	1.5×10^{-3}
DDA	$CH_3(CH_2)_{11}NH_2$	185.35	1.2×10^{-3}
ODA	$CH_3(CH_2)_{17}NH_2$	269.51	1.5×10^{-4}
OLA	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2NH_2$	267.49	1.0×10^{-4}

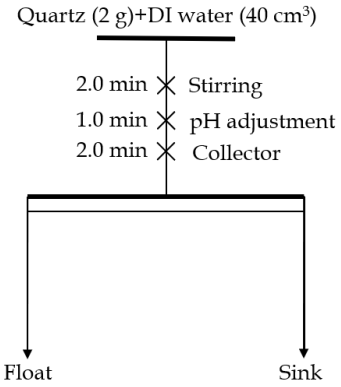


Fig. 1. Flowchart of the micro-flotation tests

2.2.2. Bubble property analysis

JPM2012 foam analyzer was used for the determination of the foaming behavior and stability of bubbles (Shanghai zhongchen digital technic apparatus co., Ltd.) shown in Fig. 2. The dimension of the quartz glass tube is 45 mm inner diameter × 55 mm outer diameter × 280 mm height. Different from traditional self-made measuring equipment, the instrument automatically takes pictures at regular intervals and records the height of the foam through an automatic camera system. There are 5 conductances along the glass tube to measure the conductivity of different heights. The conductivity resolution is 0.01 μs/cm. The foaming ability of the bubble is determined according to the conductivity, and the half-life of the foam is determined according to the change of the foam height. The instrument is connected to the computer to easily observe the shape and height of the foam and calculate relevant parameters at any time. The test procedures are as follows, 25 cm^3 of a certain pH amine solution is added to the quartz glass tube, and then the glass tube is connected to the device, the air pump is automatically filled with air, and the air flow rate is set to 300 cm^3/min, inflating for 50 s. The variations of foam height and morphology are observed until the half-life appeared. The computer automatically calculates the parameters of the foam based on the video image. Each experiment was repeated three times.

Foaming property refers to the amount of the foam produced, in which the foaming property of the solution is characterization by Bikerman coefficient (IB), which is calculated as the ration of the final foam volume to the air flow (Barbian, et al. 2003; Bikerman 1973; Karakashev, et al. 2012),

$$\mathrm{IB} = \frac{V_{Ffoam}}{D_{Fgas}} \tag{1}$$

Foam stability refers to the ability to maintain a foamy state, measured in terms of foam half-life, which is defined as the time it takes for the foam height to decay in half after inflation has ceased (Ip et al., 1999). Each measurement was repeated thrice for reporting the average data.

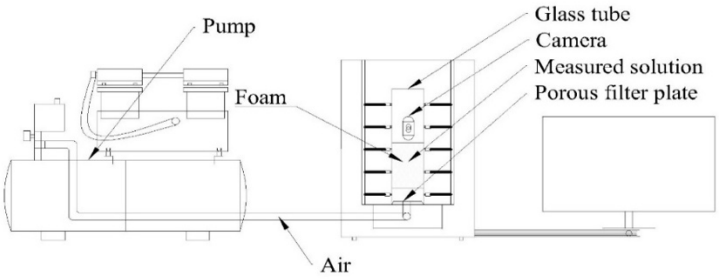


Fig. 2. Equipment of the foam analyzer

2.2.3. Surface tension measurements

The surface tensions of the amine solution were measured using a JK99c Surface Tension Meter (Shanghai zhongchen digital technic apparatus co., ltd) by the plate method. The tension meter was firstly soaked in solutions. In order to avoid the effects of residues, the platinum plate was cleaned successively with alcohol and water, and then flame dried. After that the solution was poured into the measuring container to stabilize for 10 min before the measurement. The room temperature (25°C) was remained constant throughout the entire measurement. After the balance was reached, the values were recorded. Each solution was measured three times to obtain an average value.

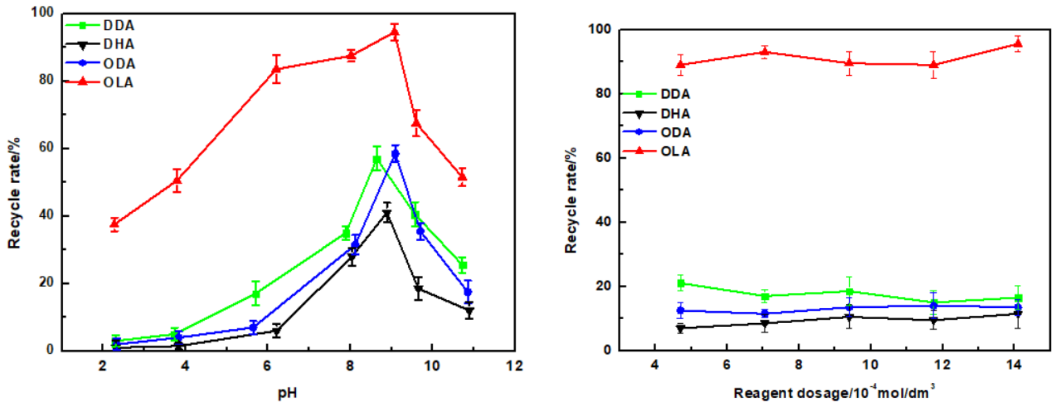
2.2.4. Zeta potential measurements

Zeta potential measurements were carried out by a Zetasizer Nano-ZS90 electrophoresis instrument equipped with a rectangular electrophoresis cell. Quartz samples were ground to −2 μm and the suspension was prepared by adding 2 mg of mineral samples to 4 cm^3 desired solutions. Then, the suspension was sonicated for 3 min to ensure adequate dispersion of the fine mineral particles. After settling for 2 min, the supernatant was taken for the zeta potential measurements.

3. Results and discussion

3.1. Micro-flotation results

The floatability of quartz at different pH values was tested when the concentration of amines was fixed at 1.2×10^{-4} mol/dm^3 (shown in Fig. 3a). The recovery rates of the four kinds of amines follow a similar trend, where recycle rate increases rapidly until pH=9, and then decreases gradually with the increase of pH value. Among them, the recovery rate of OLA was significantly higher than that of the other three amines, reaching 95%. Apart from pH, the effect of amines concentration on quartz at pH=6±0.5 is presented in Fig. 3b. The variation trends in recovery was similar among the four kinds of amines. The recovery rate of the amines remains relatively stable over the entire concentration range. At the same time, the recovery of OLA was obviously greater than the other three amines.



(a) (b)

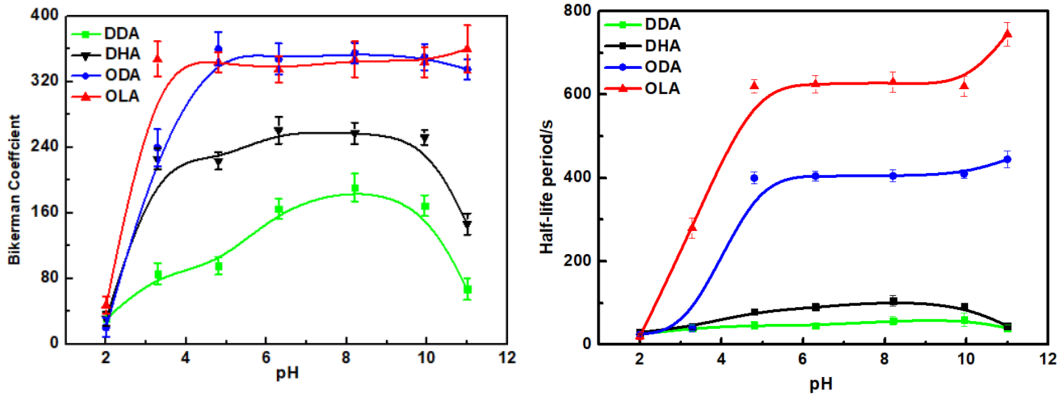
Fig. 3. Micro-flotation results for different conditions, (a) flotation recovery of quartz as a function of pH; (b) flotation recovery of quartz as a function of amine concentrations, pH = 6±0.5

3.2. Foam analysis of four amines

Flotation foam performances play a vital role in the flotation effect. Based on the results of above quartz flotation tests, the foaming and stability of the four amine reagents before and after the interaction with quartz were studied.

3.2.1. Two-phase foam

The effect of pH on the properties of the four amine foams was examined by a foam analyzer (shown in Fig. 4). As observed, the Bikerman coefficient of the four amines increased rapidly under pH=5, then maintains relatively stable at pH=5-9. As the pH continues to increase, the variation trends of the four amines were slightly different, the Bikerman coefficient of DDA and DHA decreases rapidly, and that of ODA decreased slowly, yet the OLA was mildly rised. The order of foaming ability from large to small was: OLA ≈ ODA > DHA > DDA. It can be seen from Fig. 4b that the half-life of OLA and ODA increased with the increase of pH value with a rapid growth trend at pH=2-4, and a plateau appears between pH=5-10, then the half-life period continuous increase. While the pH has a little effect on the half-life of DDA and DHA, and the half-life was relatively higher at pH=6-8, and the half-life of foam was ordered as: OLA > ODA > DHA > DDA.



(a) (b)

Fig. 4. Effect of pH on foam parameters, (a) the foam Bikerman coefficient; (b) the foam half-life of four amines (the dosage of the four amine is 1.2×10^{-4}mol/dm^3)

According to the pH test of the two-phase foam, the foam performances of the four amines were higher at pH=6-10, and then the effect of reagent dosage on the foam properties of the four amines were examined, directly using deionized water without adjusting pH. Results from Fig. 5a showed that the Bikerman coefficients of DDA and DHA increased rapidly up to 6×10^{-4} mol/dm^3 and then slowed down after that concentration. For ODA and OLA, the dosage of amine has little effect on it. Fig. 5b showed the effect of the amount of the agent on the half-life of the four amine foams. As can be seen from the Fig. 5b, with the amount of the amines increased, the half-life of the ODA and OLA increased rapidly first and then decreases gradually. When the dosage is 6×10^{-4} mol/dm^3, the half-life of ODA reached the maximum value of 600 s; when the dosage was 9×10^{-4} mol/dm^3, the half-life of OLA was up to the maximum of 650 s. The amount of the amine agents has little effect on DDA and DHA similar to the trend of Bikerman coefficient. When the dosage was 12×10^{-4} mol/dm^3, the half-life of the two reaches a maximum of 80 s and 70 s, respectively.

The driving force for collector adsorption at liquid/air interfaces might be the hydrophobic effect (Wu, et al. 2016). At liquid/air interfaces the cost in free energy is drastically reduced (Schelero and von Klitzing 2015). The adsorption of collector molecules at liquid/air interfaces and the resulting bubble collapse process were schematically illustrated in Fig. 6 (Monte and Oliveira 2004; Liu, et al. 2016a). (a) The bubbles that have been just formed or merged reach a short equilibrium state. (b) The liquid film is continuously drained, and the hydration layer begins to move. At the initial stage, the bubble was slightly deformed, but the forces on the inner and the outer surface counteract each other, and the surfactants were evenly distributed at the gas-liquid interface; (c) The hydration layer continuously

migrates to the lower layer by gravity and so on, so as to the surfactant was dragged and moved by the hydration layer, resulting in the decrease of the surfactant molecular density of the upper layer and the increase of surface tension. When the force received from the outer surface was not enough to restrain the diffusion of the gas inside the bubbles, the bubbles are deformed greatly. (d) Almost all the surfactant molecules on the membrane move to the bottom, causing the surface tension of the upper part of the bubble to reach the maximum. Consequently, various forces inside the bubble constantly dash the upper liquid film, then the bubbles become severely deformed and eventually cracked.

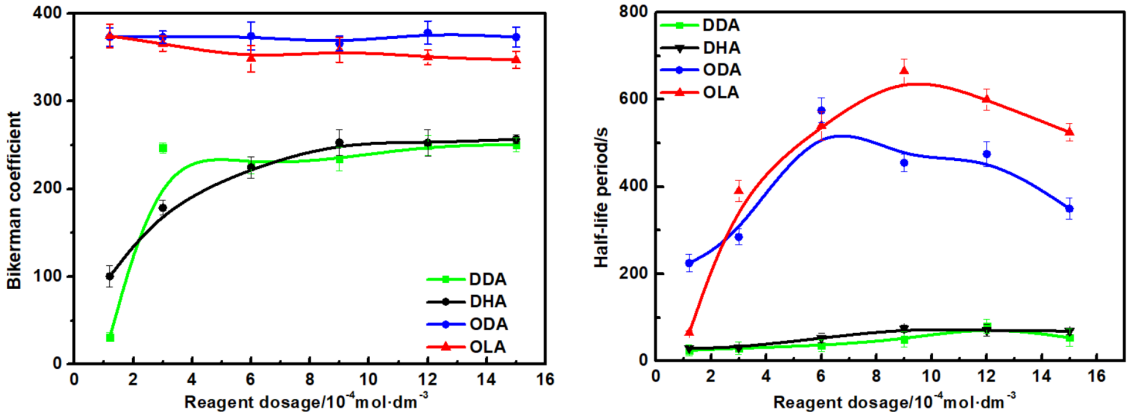


Fig. 5. Effect of amine dosage on foam parameters, (a) the foam Bikerman coefficient; (b) the foam half-life of four amines

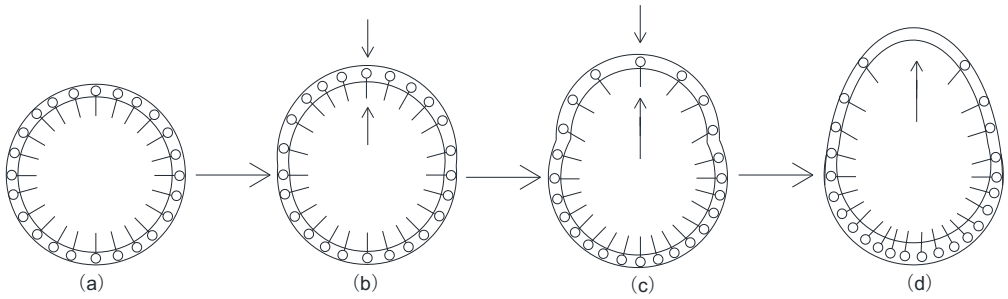


Fig. 6. The evolution process of bubble burst

According to the above two-phase foam research, it is inferred that the formation and the further change process of liquid film between two similar bubbles occur as in Fig. 7. (a) The two bubbles get closer to each other, forming a thick layer by hydration; (b) the bubbles were squeezed to each other, then forming a platform with a radius of R; (c) under the combined action of attraction and separation pressure in plateau region (Ip, Wang and Toguri 1999; Wang, et al. 2003), the liquid film drains and the bubbles were further deformed; (d) With the flow of the hydration layer, the bubbles merge with each other into polygons; (e) The bubbles after the merger reach a short balanced, infinitely closed to the circle; (f) The liquid film of circular bubbles moved downward due to various forces such as gravity. (g) The foam was broken, the surface of the film forms ripples or the thickness is changed, and the liquid film was in a metastable state.

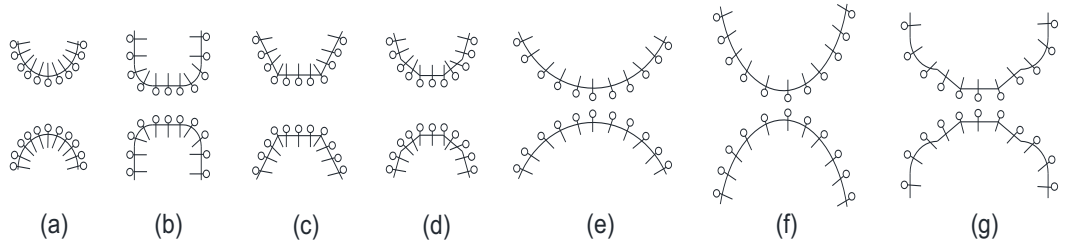


Fig. 7. The variation process of the liquid film of two bubbles

3.2.2. Three-phase foam

Considering the experimental results of the two-phase foam, it is determined that the pH is 6 and the concentration of the amine is 1.2×10^{-4} mol/dm^3. The effect of different particle size of quartz (-109~75 μm, -75 ~38 μm, -38 μm), solid powder concentration on the foaming and stability of three-phase foam was investigated (Fig. 8) by adding quartz to four amine solutions (DDA, DHA, ODA, OLA). It can be seen from Fig. 8a that the concentration of quartz solids has little effect on the Bikerman coefficient of the four amines. However, with the decrease of quartz particle size, the Bikerman coefficient of DDA and DHA increased. For ODA and OLA, solid particles still have little effect on the Bikerman coefficient of the bubble. It was apparent that in the four amine solutions, the finer the particle size of the quartz solid particles, the half life of the foam was longer, and the foam was more stable (Fig. 8b), At the same time, when the concentration of the quartz particles 8-10%, the half life of the foam was longer, the order is: ODA > OLA > DHA > DDA.

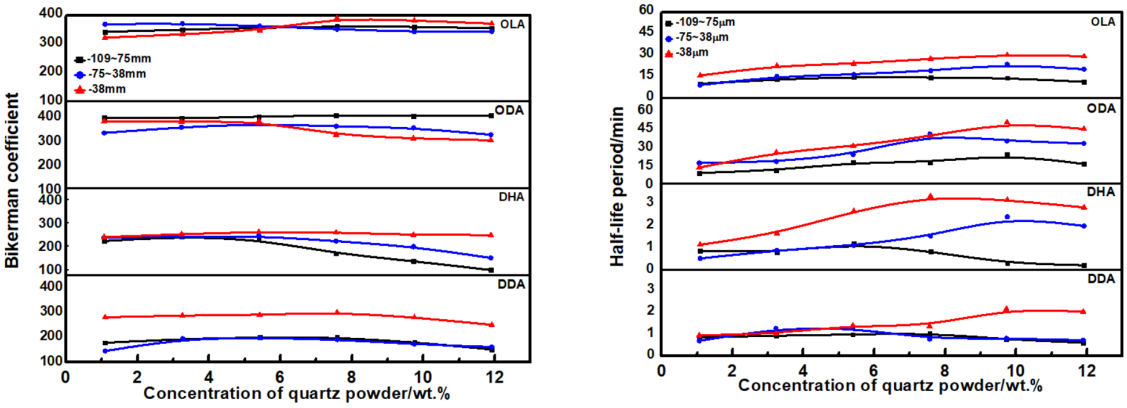


Fig. 8. Effect of quartz powder concentration on foam, (a) Bikerman coefficient; (b) half-life period.

According to the foaming behavior of the three-phase foam, the evolution of the bubbles in the three-phase foam system was deduced (Fig. 9). (a) Inflate in the solution system, producing a large number of regular circular bubbles, and the bubbles were gradually floated by buoyancy. At the same time, the quartz particles were also buoyed. (b) During the floating process, the quartz particles adhere to the bubble while the amine molecules also accumulate on the liquid film of bubble. The bubble volume increases with the liquid film becoming thinner, the bubbles were squeezed each other, and deform toward the most stable hexagon (Wan, et al. 2003). (c) Due to electrostatic attraction, quartz and ammonium ions attract each other and gradually gather together. And the liquid film is continuously drained (Karakashev and Ivanova 2010), causing the gradual rise of the liquid level, the migration of the hydration layer between bubbles and the deformation of bubbles. (d) Since the buoyancy was insufficient to counteract the gravity, the quartz and ammonium ions were gradually deposited. At the same time, with the liquid film drainage, the bubbles continue to merge, from hexagon to polygon. (e) The bubbles after the merger reach a short relative equilibrium state. At this time, the bubbles were infinitely close to the circle. And there were a lot of quartz particles and ammonium ions concentrated on it.

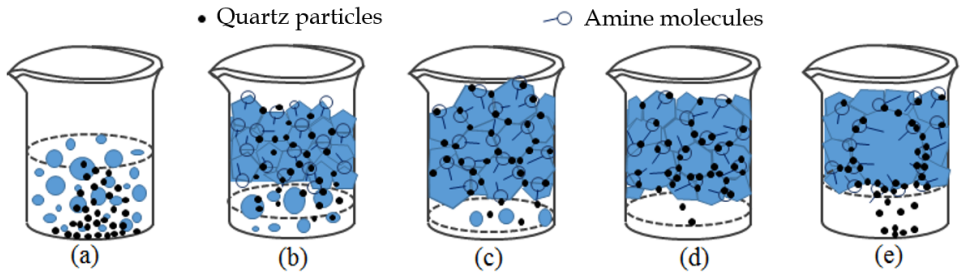


Fig. 9. The evolution of three-phase foam from formation to destruction

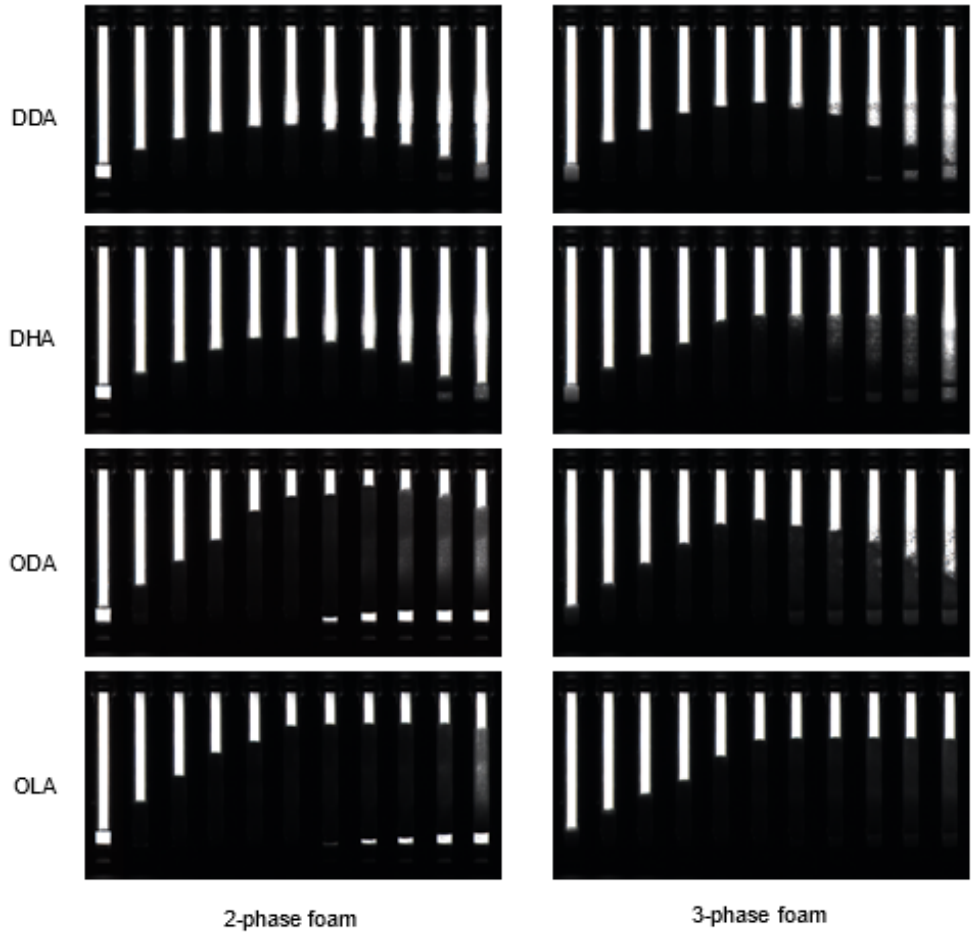


Fig. 10. Variation trend of foam height of four amines over time

3.3. Results analysis

3.3.1. Height variation of four amines

Fig. 10 showed the foam height trends of four amines at various stages (initial stage, foaming stage, peak stage, defoaming stage). The black shadow part indicates the foam. Overall, the foam height of DDA and DHA were significantly lower than that of ODA and OLA, and the foam height of the two-phase foam was lower than that of the three-phase foam. From DDA to DHA, ODA, and OLA, respectively, the adhesion of the foam increases in turn. Obviously, both the two-phase and three-phase foam of DDA do not adhere to the inner wall of the glass. The three-phase foam of DHA are partially adhered, while both the two-phase and the three-phase foam of ODA were adhered to the glass wall, and the defoaming process was slow. The two-phase and three-phase foam of OLA adheres more seriously on the inner wall of the glass, and the deforming was also quite difficult.

3.3.2. Carbon chain structure of the four amines

It was evident from the change in the height of the foam (Fig. 10) that the chain length and the chemical bond types of four amines have a great influence on the performances of the foam. For DDA, DHA, ODA and OLA, the longer chain will promote enhancement of the adsorption onto mineral surface, since the chain-chain hydrophobic interaction will be sufficiently strong to anchor more surfactant molecules onto mineral surface, leading to the hemimicelle formation, even at low concentration (Leite Nunes, et al. 2019). Thus, the foam half-life of OLA, and ODA is significantly stronger than DDA and DHA. Simultaneously, with the increase of the carbon chain length, the hydrophobicity increases, thus directional arrangement is forming on the surface of the hydration layer to reduce the surface tension of the solution. Therefore, the fatty amines with a larger molecular weight have better foaming

performance in a certain range. Thus, the foam diffusion capacity of ODA and OLA is significantly stronger than DDA and DHA.

For unsaturated fatty amines, double bonds have a greater effect on melting point and critical micelle concentration (CMC). When the number of carbon atoms is the same, the unsaturated fatty amine has a lower melting point and a higher critical micelle concentration, that is why the diffusion ability of ODA foam is stronger than that of the OLA under the same conditions. For DDA and DHA, the isomers have better foaming ability than other structures, and thus the performance of DHA foam is slightly better than that of DDA.

3.3.3. Surface properties of four amines

Surface tension, which is often represented by the mean surface tension at the pulp surface, is one of the vital factors for mineral flotation (Kirjavainen, et al. 2003; Zhang, et al. 2019). It could be modified to achieve maximum flotation efficiency (Chu, et al. 2002). For further exploration of the effects of the four amines on the flotation and foaming behavior, the relationship between the surface tension and reagent dosage of the four amines was investigated by surface tension measurements (Fig. 11). The surface tension of pure water is 75 mN/m, it can be observed that the surface tension of the four amines was markedly reduced by a small amount of amine and that the tension values remained relatively stable after the concentration exceeded 6×10^{-4} mol/dm^3 for the DDA, ODA and OLA and 9×10^{-4} mol/ dm^3 for the DHA. The downtrend of the surface tension of the four amines was as follows: OLA > ODA > DDA > DHA. The results of Chu et al. explain this phenomenon well (Nguyen, et al. 2003), when the foaming agent is added the solution, the foaming agent molecules are concentrated on the surface of the solution to form a dense surface film, which causing the surface strength of the liquid film is increased, the drainage of the adjacent liquid film is blocked, and the rupture time of liquid membrane is delayed, thereby increasing the stability of the foam (Barbian, et al. 2005). However, when the concentration of the foaming agent is increased to a certain extent, the liquid content of the formed foam is reduced, and the increase of "rigidity" may account for the foam unstable (Kramer, et al. 2012).

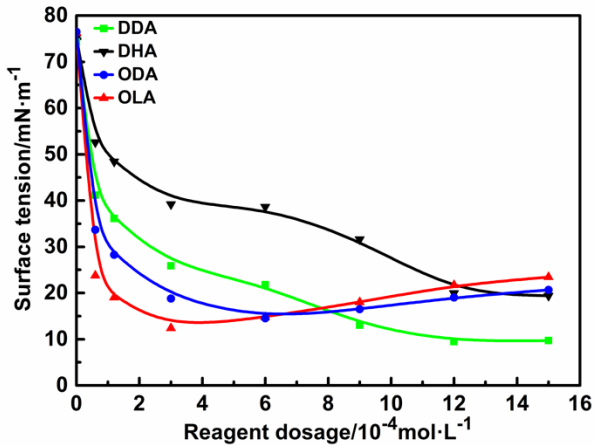


Fig. 11. Surface tension of four amines as a function of reagent dosage

3.3.4. Zeta potential of four amines

The amine collector is a kind of the cationic surfactant. Due to surface adsorption, surface active ions are enriched on the surface to form a layer with positive charges, and the counter ions are distributed in the liquid film to form a surface double layer. When the liquid film becomes thinned to a certain extent, the electrical repulsive action on both surfaces becomes noticeable, preventing the liquid film from becoming thinning further, and this phenomenon is less affected when the liquid film is thicker (Mu 2005). Zeta potential measurement has been widely used as an efficient method to interpret the trend of modification performance caused by the presence of reagents (Jiang, et al. 2018; Xu, et al. 2013). In order to study this effect, the electrokinetic phenomenon of the mineral suspension was explored. The zeta potential on quartz mineral surface in the four amines solution as a function of suspension pH is shown in Fig. 12 at the amine concentration of 6.0×10^{-4} mol/dm^3. From Fig. 12, it was clear that the

isoelectric point (IEP) of quartz is approximately 2.3 above which the zeta potential becomes more and more negative with the increasing of pH owing to the ionization of the hydroxyl groups on the quartz surface, and cationic amine surfactant will absorb on the surface of negatively charged quartz when it was placed in solution (Novich and Ring 1985). The results obtained here were much consistent with those reported in literatures (Kou, Tao and Xu 2010). In the presence of amine reagents, the zeta potential was higher than that in water under the same pH conditions. This can be explained by the adsorption of NH^{4+}, which neutralizes the negative charges of quartz surface and shifts the zeta potential toward the positive direction. The difference in the adsorption increments of four amines can be interpreted by the length of the carbon chain and the group, and the order in the movement amplitude was OLA > ODA > DDA > DHA. This is also the reason OLA's three-phase foam adheres most seriously to the glass wall.

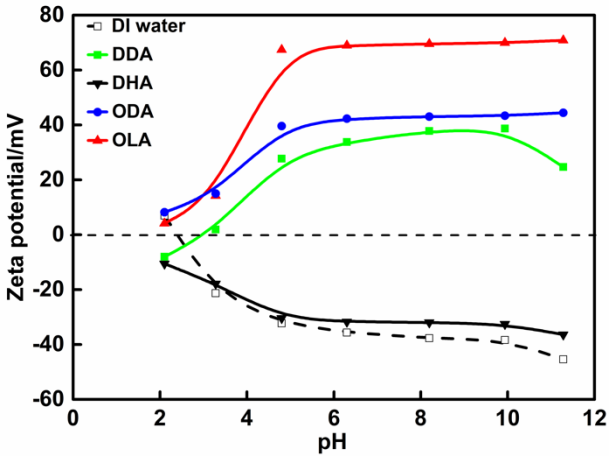


Fig. 12. Zeta potential of the quartz in the presence of four amines as a function of pH

3.3.5. Charge mechanism of four amine on the quartz surface

For the quartz crystal, the bonding force of the Si-O bond is equal in all directions, so the dissociation surface will not be formed. But the Si-O bond will also be fractured when it is broken, so that a large polarity is produced to cause adsorption of H+ or OH- in the solution, thereby forming Si-OH structure on the surface of the quartz, and then ionization in water to make the quartz surface charge negative. The charge mechanism of quartz surface is shown in Fig. 13.

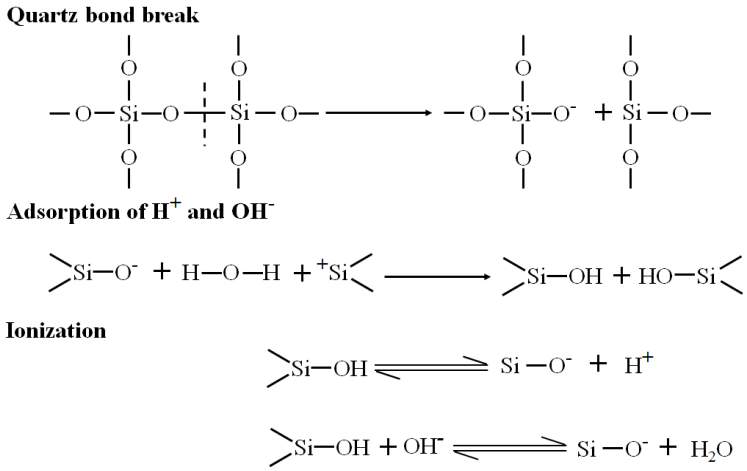


Fig. 13. Charging mechanism of quartz surface

The amine has the following chemical equilibrium in the aqueous solution (Liu, et al. 2015a),

- Dissolution equilibrium, $RNH(CH_2)_3NH_{2(l)} = RNH(CH_2)_3NH_{2(aq)}$
- Ionization equilibrium, $RNH(CH_2)_3NH_3^+ = RNH(CH_2)_3NH_3 + H^+$

- Dimerization equilibrium, $2\mathrm{RNH(CH_2)_3NH_3^+} = \mathrm{RNH(CH_2)_3NH_3^+}$

Consequently, when the amine agents acts on the surface of quartz, they interact with quartz mainly through three kinds of bonding forces, $H(RNH_3^+) - O(SiO_2)$, $H(RNH_2) - (SiO_2)$, $H(RNH_2) - H(Si - OH^-)$ which are formed under acidic, neutral, and alkaline conditions, respectively (Gao, et al. 2015). Therefore, when the collector is adsorbed on quartz, there is a competitive adsorption of various ions. Therefore, the three-phase foam is much more stable than the two-phase foam. On the other hand, in the range of pH 4-9, the amine in the solution mainly exists in the form of RNH^{3+} and RNH_2. Meanwhile, the IEP of quartz (SiO_2) is 2.3, so the surface of the quartz is negatively charged, therefore, the amine reagents are mainly the electrostatic attraction in the quartz surface. At this time, the adsorption capacity of amine cation on the surface of the quartz is better. This also gives a good explanation for the trend of the relevant pH curve.

4. Conclusions

In this study, the bubble foaming property and stability of DDA, DHA, ODA, and OLA in the absence and presence of quartz solid were experimentally explored, the conclusion is as follows,

(1) For the two-phase foam, the effect of pH on the foam properties of four amine collectors was stronger than that of the amine dosage, in the range of pH=6-10, the flotation recovery of four amines was higher, and the foaming and stability of the foam are better. With the increase of the amine dosage, the flotation behavior and foam properties of four amines change slightly, and the ODA and OLA can reach better indexes at lower concentrations.

(2) The three-phase foam was generally more stable than two-phase foam, and bubble properties were followed the order: OLA > ODA > DHA > DDA. This phenomenon can be explained by structure of alkyl amine. Meanwhile, the addition of amine collectors can significantly reduce the surface tension of the solution, accordingly blocking the drainage and delaying the rupture time of the liquid film. Due to the electrostatic adsorption, RNH^{4+} will enrich on the surface of quartz particles, while the counter ions will distribute in the liquid film to form a surface electric double layer, which can prevent the liquid film from being further thinned by electrical repulsion, thus improving the stability of the three-phase foam.

(3) The adhesion of DDA foam was significantly lower than that of the other three amines, which was the reason that DDA was the most widely used. Because excessive foam and viscosity will cause the foam difficult to disperse, worsening the flotation effect.

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