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Zeta potential of air bubbles in presence of frothers

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1. Introduction

Solid particles, gas bubbles, and organic droplets in aqueous solutions acquire a surface charge. Solid particles are the most studied and possible origins of the charge include adsorption of ions, preferential dissolution of constituent ions, and ionization of surface species (Heimenz and Rajagopalan, 1997). Our interest is gas bubbles.

The charge on a gas bubble surface may play a role in bubble coalescence and bubble attachment to particles, events encountered in many industrial processes such as mineral flotation, waste and potable water treatment (Fukui and Yuu, 1980; Buckley et al., 1989; Kubota and Jameson, 1993; Kelsall et al., 1996; Yoon and Mao, 1996; Yang, 2000). Most bubble charging studies have considered ionic species, inorganic salts and surfactants (Lu et al., 2005). This communication considers the effect on bubble charge of frother, a non-ionic surfactant used in flotation systems that specifically acts at the bubble surface. Yoon and Yordan (1986) examined some high molecular weight frothers and here we examine some more commonly used ones. An important action of frothers is assisting in the creation of the small bubbles (e.g. 0.5–2.5 mm) required in the flotation process.

2. Background

Measurement of surface charge or zeta potential of gas bubbles faces the difficulty of introducing bubbles into a measurement cell and controlling buoyancy (Yang et al., 2001). The pioneers were McTaggart (1922) and Alty (1926) who developed a spinning tube

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ABSTRACT

The zeta potential of bubbles generated by ultrasonication was determined for a range of frother types. At concentrations close to flotation practice (<20 ppm) the effect of frother was negligible. With increasing concentration (up to 100 ppm) F150 and pentanol decreased charge and MIBC and heptanol increased negative charge but the change remained small. An effect on bubble charge does not appear to contribute to the action of frothers, in particular the reduction in bubble size. The data are briefly discussed in light of models of bubble charging in water and in presence of non-ionic surfactants.

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technique. They found that air bubbles were negatively charged in distilled water.

Sirois and Millar (1973) based a method on the deviation of the rise path of a bubble exposed to a uniform horizontal electric field. A limitation was the electric field led to convection currents inside the relatively large cell employed, restricting measurements to short time intervals (0.3 to 0.4 s). Collins et al. (1978) modified the method by reducing the cell dimensions. Convection was reduced but the bubbles rose too quickly to track visually. Yoon and Yordan (1986) produced smaller bubbles ranging from 40–80 µm but the problem of buoyancy remained (Yang et al., 2001). Usui and Sasaki (1978) used the Dorn effect (i.e., the potential established by a rising swarm of bubbles) to infer the zeta potential.

Some of the contributions in the past 20 years are summarized in Table 1. A variety of techniques were used to generate bubbles but the results in water alone are consistent showing a negative charge over most of the pH range, with an iso-electric-point (iep) between pH 1 and 3.5.

The evidence, therefore, is that bubbles are negatively charged in water alone over most of the pH range. The mechanism involves a combination of orientation of the water molecule dipole at the surface (Paluch, 2000) and structural differences between water in the vicinity of the surface and in the bulk that induces selective adsorption of hydroxyl anions (Currie and Alty, 1929; Karraker and Radke, 2002) or exclusion of cations (Horne and Young, 1972).

Frothers are non-ionic surfactants, commonly alcohols and polyglycols, used in flotation to control (reduce) bubble size and provide some froth stabilization. Both these functions imply an impact on the properties of the air–water interface (bubble surface). And the question posed here is whether bubble charging plays any part. There is little information on the role of non-ionic surfactants on bubble

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Table 1

Zeta potential and formation conditions of air bubbles from the literature

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iep	pH range	Zeta potential mV	Bubble formation and electrolyte conditions	Reference
1.5	1.5 to 11.5	0 to -58	Injecting nitrogen through	Li and
			a glass frit provided at the	Somasundaran
			bottom of a Buchner using	(1991)
			10 ⁻² M NaCl	
>3	3–11	-0.27 to -29.7	Ultrasonication using	Kim et al. (2000)
			10 ⁻² M KCl	
3-3.5	2.4-11.5	5.5 to -51.8	Supplying electric current	Yang et al. (2001)
			to platinum wire using	
			10 ⁻² M NaCl	
2.5	2.5-11	0 to -58	Micropipette used and no	Fan et al. (2004)
			electrolyte was used	
3-3.5	2-12	8 to -39	Ultrasonication using	Cho et al. (2005)
			10 ⁻³ M KCl	()

charge. The orientation of the frother (polar groups to the water side, non-polar groups to the air side) and the tendency to order water molecules (via hydrogen bonding) around the polar group imply an effect (Paluch, 2000; Karraker and Radke, 2002).

There is no consensus as to the action of frothers in helping create small bubbles (Machon et al., 1997). One interpretation of frother action is that they retard coalescence; that is the flotation machine produces small bubbles and the frother preserves them (Laskowski, 2003). One component of this action may be electrostatic repulsion, as once considered in the case of salts which likewise form small bubbles (Zieminski and Whittemore, 1971). There are other results that have raised the question of a role of bubble charge. Gélinas et al. (2005) from an interferometry study argued that frother influenced the thickness of the water film on a bubble, which suggests the 'plane of slip' (where zeta potential is located) may vary with frother type and concentration. The observations of Azgomi et al. (2007a) implied that frother type has a significant impact on bubble rise velocity in a swarm, large bubbles in a polyglycol frother solution rising at the same velocity as bubbles about half the size in a pentanol solution. One hypothesis was the frothers, by altering the bubble charge, changed the retardation effect associated with the Dorn potential. Modeling bubble-particle interaction requires understanding the role of surface charge (Collins et al., 1978; Healy, 2006) and frothers are usually present.

Addressing these possible roles of bubble charging was the motivation for this communication. But, regardless, the study fills a gap in the flotation literature.

Based on the work of Azgomi et al. (2007b) and Moyo et al. (2007) the frothers selected were methyl isobutyl carbinol (MIBC), F150

Table 2

Summary of frother properties and suppliers

Frother	Structure	Formula	Molecular weight g/gmol	Supplier	Grade %
n-pentanol	Aliphatic alcohol	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	88.15	Fisher Scientific	99.7
MIBC	Aliphatic alcohol	сн ₃ снсн ₂ снсн ₃ сн ₃ он	102.18	Dow Chemicals	99
n-heptanol	Aliphatic alcohol	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH	116.20	American Chemicals	99
F150	Polyglycol	H(PO) ₇ OH ^a	425	Flottec, USA	99

^a PO= C_3H_6O .



Fig. 1. Zeta potential of air bubbles in deionized water using 10^{-3} M KCl. At least 7 repeats at each indicated pH were made with a standard deviation of ca. 5 mV.

(a polyglycol), *n*-pentanol and *n*-heptanol to give a wide range in frother-related properties. The bubbles were generated using ultrasonication.

3. Experimental

3.1. Materials

Table 2 gives the frother type, structure, supplier and grade. Analytical grade sodium hydroxide, potassium chloride (Sigma Aldrich) and hydrochloric acid (Fisher Scientific) were used for preparing solutions. De-ionized water was used after purging with air to improve the yield of bubbles by ultrasonic energy (Awad, 1996).

3.2. Methods

Solutions were prepared with 10⁻³ M KCl background electrolyte at set pH using a total volume of 100 mL. The sample was placed in an ultrasonic bath ("Tru-Sweep" ultrasonic cleaner Model No. 275DA, Crest Ultrasonics Corp.) for 15 minutes to generate bubbles. Electrophoretic mobility was measured by a laser zetameter ("Zeta Compact", CAD Instrumentation) using an image analysis technique. The bubbles were clearly evident, which is an advantage of this instrument. The instrument outputs the zeta potential applying the Smolukowski equation. Every measurement represents the mean of at least 7 repeats with a standard deviation of ca. 5 mV.

4. Results

Zeta potential of the (air) bubbles in water alone is recorded in Fig. 1. The zeta potential decreased from ± 1.4 to ± 40 mV over the pH range 3.1 to 11.8 with an iep at pH 3.2, values close to the literature (Table 1).

Figs. 2-5 show the effect of the four frothers on the zeta potential as concentration is increased from 10 to 100 ppm. The general trend



Fig. 2. Zeta potential of air bubbles in presence of 10 ppm of the tested frothers.



Fig. 3. Zeta potential of air bubbles in presence of 20 ppm of the tested frothers.

remains as in water alone. At low concentrations (10, 20 ppm) the frothers have a negligible effect on the value. The frothers do display diverging trends with increasing concentration: at 30 and 100 ppm for MIBC and heptanol zeta potential became more negative relative to water but for pentanol and F150, the zeta potential became less negative.

Fig. 6 compares the zeta potential in 30 ppm pentanol with 2 ppm F150, the concentrations reported by Azgomi et al. (2007a) as apparently giving the same swarm velocity despite significantly different bubble size. Relative to water, with F150 the charge is more negative and with pentanol less negative at these particular concentrations.

5. Discussion

The frothers selected range from weak (pentanol) to strong (F150) in terms of the concentration required to reduce bubble size and provide froth stability. To compare the frothers we used the common practice of referring to the bulk concentration, in this case in ppm as a 'practical' measure (plus, the exact chemistry of commercial frothers is not always known). Fig. 6 introduces another way to compare, on the basis of similar action (in this case generating the same swarm velocity).

The immediate observation is that the presence of frothers has not altered the general trend in zeta potential with pH exhibited by water alone. The iep remained ca. pH 3 and did not vary significantly with frother type and concentration. Certainly at concentrations typical in flotation systems (usually less than ca. 20 ppm (Gélinas and Finch, 2007)), the results suggest that frother does not influence the zeta potential relative to water alone. The results of Yoon and Yordan (1986) are similar: there was little effect of type and concentration except in one case (polyoxyethylene methyl ether) which increased the iep to ca. pH 6, attributed to a high O to C ratio.

The observations that first motivated the study, therefore, do not appear to be related to an impact of frother on surface charge. If an electrostatic component was at play in retarding coalescence it would imply an increase in the negative charge on adding frother over that of



Fig. 4. Zeta potential of air bubbles in presence of 30 ppm of the tested frothers.



Fig. 5. Zeta potential of air bubbles in presence of 100 ppm of the tested frothers.

water alone but this is not the case. As with salts, an electrostatic model in the bubble formation process is not supported (Craig et al., 1993). An effect of frother on the location of the plane of slip, based on the interpretations of the thickness of a water layer around a bubble (Gélinas et al., 2005), implies that increasing frother concentration would shift the plane outward and the absolute zeta potential would decrease. Although the impact is probably small (Karraker and Radke, 2002), this is not consistently the situation here. An effect on the charge appears insufficient to support any role of the Dorn effect in controlling bubble swarm velocity. While the two frothers in question, F150 and pentanol at the relevant concentrations do show an opposite effect on charge (Fig. 6), arguably consistent with the observations on swarm velocity (the lowered charge in the presence of pentanol compared to F150 indicating a smaller Dorn potential and thus less retardation of the swarm), the magnitude of the difference does not seem large enough to support the hypothesis. In terms of modelling particle-bubble interaction there would seem no reason to modify the electrostatic interaction term for an effect of frother.

While the ambition was not to probe frother uptake mechanisms an observation based on the work of Karraker and Radke (2002) is offered. They proposed a two-site adsorption model of the bubble surface, sites where non-ionic surfactant can adsorb and hydroxide ions cannot, and other sites where surfactant and hydroxide ions compete. At low concentration the surfactant can adsorb without altering the uptake of hydroxide ion and thus charge does not vary. If there is competition exclusion of hydroxide ions and associated ordering of water around the surfactant polar group is expected to decrease the charge. Karraker and Radke concluded that air bubble surface charge is not affected by the structure of non-ionic surfactants and it decreases with increasing surfactant concentration. The present results do not support this. The effects are small but they are reproducible and while for F150 and pentanol the zeta potential did decrease with increasing concentration this was not the case for MIBC



Fig. 6. Comparison of zeta potential at concentrations of pentanol and F150 found by Azgomi et al. (2007a) to give same gas holdup but with significantly different bubble size (see text).

and heptanol which suggests that frother structure may have an effect on the surface charge.

6. Conclusion

At typical flotation dosages (<20 ppm) frothers do not significantly influence the bubble charge. Bubble charging, therefore, does not appear to be a factor in the action of frothers, for example in promoting the production of small bubbles.

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