



Effect of alcohol frothing agents on the coalescence of bubbles coated with hydrophobized silica particles



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HIGHLIGHTS

- Effect of frothing agents and particles on bubble stability decoupled.
- Frother adsorbed on particles may be carried to the bubble increasing its stability.
- Interfacial oscillation caused by bubble coalescence led to particle detachment.
- Frothers dampened bubble oscillation and effectively reduced particle detachment.

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ABSTRACT

The stability of capillary-pinned bubble pairs covered with hydrophobized particles in aqueous solutions of 1-pentanol or methyl isobutyl carbinol (MIBC) was studied using high-speed cinematography. Glass particles were first rendered hydrophobic by covalently bonding a linear alcohol onto the solid interface to achieve a specific hydrophobicity (i.e. contact angle of 43° measured with the captive bubble on a treated wafer) and effectively avoid the presence of any mobile hydrophobizing surfactant. The resistance to coalescence of the bubbles was measured at different frother concentrations and for various initial bubble interfacial areas covered by particles; with particle coverage not exceeding the contact region between the bubbles.

Frother molecules were shown to delay the coalescence of bubbles whereas particles were not present in a sufficient quantity at the interface of the bubbles to provide steric stability. However, in some cases in the presence of MIBC, the particles were believed to act as means of transportation for the frother molecules to the surface of the bubbles thus forcing the local relaxation of the interface, which improved bubble stability.

The coalescence of two bubbles released energy causing a rapid motion of the interface. This motion was sufficient to expel a fraction of the attached particles from the interface. The addition of frother, and of particles in some cases, increased the dampening of the oscillatory motion generated by bubble coalescence. In general, damped bubble oscillations were associated with a reduced quantity of particles detaching from the bubble. Although particles were observed to dampen the oscillation of the bubble, they were not as effective as the frother molecules in reducing the detachment of particles upon bubble coalescence. This finding is believed to be of relevance for industrial applications such as froth flotation.

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1. Introduction

Bubbles and drops are at the centre of many industrial applications. As such they are the subject of extensive studies. The length-scale of these studies, as defined by Weaire and Hutzler (1999), varies from continuous foams e.g. (de Vries, 1958; Bikerman, 1973; Malysa et al., 1981; Pugh, 2005) to smaller scales investigating molecular effects

e.g. (Sheludko, 1967; Langevin and Sonin, 1994; Wang and Yoon, 2006; Karakashev and Ivanova, 2010). Investigations over smaller length-scales can potentially suffer a lack of accuracy by neglecting multi-bubble effects (Szekrényesy et al., 1992). Such studies are nevertheless essential to establish stability criteria with their associated physical/chemical principles. In most cases, a relatively good correlation can be found between the stability of single films and that of static foams (Angarska et al., 1998).

The observation of interacting bubbles emerging from adjacent capillary tips has been popularised by the work of Lessard and Zieminski (1971). It has been used as a substitute to bubble swarms as

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it provides better control within the experimental system thus giving more insight into parameters affecting bubble stability. For example, this technique and its variants have been effectively used to characterise aqueous inorganic electrolyte solutions (Lessard and Zieminski, 1971; Christenson et al., 2008) as well as aqueous surfactant solutions (Sagert and Quinn, 1978; Drogaris and Weiland, 1983; Yang and Maa, 1984; Gourram-Badri et al., 1997; Kracht and Rebolledo, 2013) and the behaviour of Pickering droplets (Thompson et al., 2012; Morse et al., 2014). Clearly, the method can be adapted to simplify many processes or applications involving bubbles or droplets.

Froth flotation is considered an elaborate industrial process. It contains three phases (i.e. solid, liquid, gas) and relies on the interfacial chemistry of the different phases, which is altered by the addition of various reagents. The stability of the bubbles is thus influenced by the presence of solid particles (Dippenaar, 1982; Johansson and Pugh, 1992; Kaptay, 2006; Morris et al., 2014) and solutes in the liquid continuous phase (Cho and Laskowski, 2002; Nasset et al., 2006; Cappuccitti and Finch, 2008). Reagents used in the stabilisation of the air–water interface are (co-)surfactants, generally referred to as frothers, which are amphiphilic molecules containing a hydrophilic head and a hydrophobic tail. The minimisation of the molecule energy drives their adsorption at the air–water interface thus accommodating both moieties of the frother molecule. In practice, the frother is also seen to interact with the solid–liquid interface, which may change the properties of (i) the air–liquid interface and (ii) the solid–liquid interface.

Fuerstenau and Pradip (1982) have long established that common frothers, including methyl isobutyl carbinol (MIBC), adsorb at the coal–water interface through hydrophobic interaction. Surprisingly, the adsorption of MIBC onto coal particles does not appreciably change the contact angle of the particles (Miller et al., 1983). Although no change in hydrophobicity was detected, it was noted that high concentrations of MIBC caused a significant increase in the induction time (i.e. the contact time between a particle and a bubble required for attachment to take place). The action of the frother seems to be dependent upon the type of frother and the minerals (Gourram-Badri et al., 1997; Ang et al., 2013). The adsorption of frother molecules may cause a significant reduction in the bulk concentration of frother. Such change in concentration may affect the gas dispersion properties and the foam properties (Kuan and Finch, 2010). In all the cases previously presented, the mineral employed was naturally ‘hydrophobic’ according to mineral processing practices (see further discussion in Section 2.2). It should be noted that particles coated with covalently bonded agents were found to adsorb surfactants as well, which may affect the foaming of solutions (Hunter et al., 2009a; Bournival et al., 2014c). In all cases, the relative concentration of frother and particles (i.e. surface area) determines the extent of interaction and the properties of the system.

The objective of this study is to determine the roles of frothers and particles on the stabilisation of air bubble pairs produced on capillaries. In flotation, particles are made hydrophobic by using another class of surfactant: a collector. Residual amounts of collector may affect the bubble interface and stability. To specifically isolate the effect of the frother, the particles were made hydrophobic by an esterification process thus eliminating the need for a collector. An analysis of the process taking place after the coalescence of the bubbles is also included. Such analysis is used to decouple the roles of the frother molecules and the particles in preventing the detachment of particles due to bubble coalescence. This system provides a better control of the individual effects of particle hydrophobicity and frother addition than a system using a collector, where free molecules may adsorb on the bubble surface. However, it should be understood that, as the collector, the adsorption specificity of frothers is not perfect, and some frother may be found at the solid–liquid interface.

2. Experimental procedure

2.1. Materials

Soda-lime glass beads were purchased from Potters Industries Pty Ltd (Melbourne, Australia). The particles had a density of 2.5 g cm^{-3} as given by the manufacturer. The volume–surface equivalent particle diameter (d_{32}), determined with a Mastersizer 2000 (Malvern), was found to be $64.0 \text{ }\mu\text{m}$ while the 90% passing size ($d_{0.9}$) was $92.5 \text{ }\mu\text{m}$.

An ammonia solution (28%) and hydrogen peroxide (30%) (Ajax Finechem) were used for cleaning the particles. Following the cleaning of the particles, the hydrophobization of the particle surfaces was carried out using 1-butanol (Chem-Supply, LR grade), acetone (Chem-Supply, $\geq 99.8\%$), and ethanol (Chem-Supply, $\geq 99.8\%$).

The effect of weakly surface active frother-type alcohols was studied. 1-pentanol (Sigma-Aldrich, $\geq 99\%$) and 4-methyl-2-pentanol (Aldrich, $\geq 98\%$), also known as methyl isobutyl carbinol (MIBC), were used for that purpose. MIBC is extensively found in the mineral processing industry in the process of froth flotation and 1-pentanol is a typical linear weakly surface active alcohol of lower molecular weight. Both frothers have been extensively characterised under static conditions (Wang and Yoon, 2008; Bournival et al., 2014b) as well as under dynamic conditions (Cho and Laskowski, 2002; Cappuccitti and Finch, 2008; Bournival et al., 2014d). In some experiments, potassium chloride (KCl) (Ajax Finechem Pty Ltd, AR grade) was used as a background electrolyte.

All glassware was cleaned using an alkaline solution. This cleaning method involved soaking the glassware for 5–15 min in a solution made of 120 g of sodium hydroxide (NaOH) (Sigma-Aldrich, $\geq 97.0\%$) dissolved in 120 g of water and diluted with 1 L of ethanol. The glassware was then thoroughly rinsed with water. The water used throughout was dispensed from a Milli-Q Pure water system and had a resistivity of $18.2 \text{ m}\Omega \text{ m}^{-1}$.

Other laboratory equipment in contact with the solutions (e.g. stainless steel capillaries, magnetic stirrer bar, etc.) was sonicated in ethanol and in water.

2.2. Cleaning of particles and surface modification

The particles were cleaned following the procedure of Hunter (2008). A 16.5 v/v% aqueous ammonia solution was heated to $80 \text{ }^\circ\text{C}$. The particles were then placed into the solution and 14.3 v/v% hydrogen peroxide was added. The particles were left in the mixture, maintained at $80 \text{ }^\circ\text{C}$, for 5 min. This procedure was used to remove any organic surface films by an oxidative breakdown of the contaminants (Kern, 1990). The particles were then washed and resuspended in fresh water several times, until the pH returned to that of Milli-Q water. The particles were dried in an oven at $60 \text{ }^\circ\text{C}$ and stored in a desiccator.

The hydrophobization of silica particles can be carried out by adsorption of a surfactant. However, such strongly surface-active molecules will also adsorb at the air–water interface. To avoid any such reduction in surface tension of the bubbles through surfactant adsorption, the particles were covalently hydrophobized by esterification. The coating produced through esterification, which is considered to form a uniform monolayer (Biggs and Grieser, 1994), can be made using alkyl alcohols with the extent of hydrophobicity dictated by the length of the alkyl chain (Kimura et al., 1998). The initial alkoxylation reaction starts with the physisorption of the alcohol molecule to the silanol group. This reaction is followed by the chemisorption of the alcohol molecule to yield a covalently bound alkane coating through a condensation reaction. Alcohol-esterified silica surfaces have been found to be resistant to hydrolysis (Ossenkamp et al., 2001; Hunter, 2008).

The alcohol used to hydrophobize the particles was 1-butanol. This alcohol produced particles of intermediate hydrophobicity, as

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