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On the nanobubbles interfacial properties and future applications in flotation

S. Calgaroto, K.Q. Wilberg [1], J. Rubio *

Minerals Engineering Department, PPGE3M – Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalves 9500, Prédio 75, Sala 124, Porto Alegre, Brazil[2]

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ABSTRACT

Nanobubbles, generations forms, basic studies and applications constitute a growing research area, included their usage in advanced mineral flotation. Yet, there are investigation needs for sustainable generation procedures, stability and understanding the nanobubbles interfacial properties and structures. Results proved that a reduction in pressure makes the super-saturated liquid suffers cavitation and nanobubbles were generated. Medium pH and solutions tested were adjusted, in the air saturation vessel, before the nanobubbles were formed, and this allowed to control (in situ) the surface charge/zeta potential-size of the forming nanobubbles. Measurements obtained with a ZetaSizer Nano equipment showed zeta potential values, in the presence of 10^{-2} mol L^{-1} NaCl, displaying sigmoidal pH behaviour between pH 2 (+26 mV) and 8.5 (−28 mV); an isoelectric point was attained at pH 4.5 and were positively charged (up to 23 mV) in acidic medium, a phenomenon which has not been previously observed. In alkaline medium, bubbles were highly negative zeta potential (−59 mV) at pH 10. The double layers appear to play a role in the formation of stable nanobubbles providing a repulsive force, which prevents inter-bubble aggregation and coalescence. Accordingly, the sizes of the nanobubbles depended on their charge and increased with pH, reaching a maximum (720 nm) around the isoelectric point (±5 mV). Highly charged and small nanobubbles (approximately 150–180 nm) were obtained in the presence of surfactants (10^{-4} mol L^{-1} of alkyl methyl ether monoamine or sodium dodecyl sulphate); the zeta potential values in these experiments followed a similar trend of other reported values, validating the technique used with the nanobubbles sizes varying with pH from 150 to 400 nm. Thus, charged and uncharged stable nanobubbles can be tailor-made with or without surfactants and it is expected that their use will broaden options in mineral flotation especially if collectors coated nanobubbles (“bubble-collectors”) were employed. A detailed and updated review on factors involving stability, longevity and coalescence of nanobubbles was made. It is believed that future trend will be on sustainable formation and application of nanobubbles at industrial scale contributing to widen applied research in mineral, materials processing and liquid effluent treatment by advanced flotation.

1. Introduction

The electrokinetic zeta potential of air bubbles plays a significant role in bubble-mineral particle interaction, bubble-oil droplet attachment and bubble coalescence affecting several industrial processes, namely mineral flotation, oil sands separation, and water and wastewater treatment. In oil sands, the bitumen-bubble attachment depends on the magnitude of the zeta potential, which thus affects the bitumen recovery and froth quality (Schramm and Smith, 1987; Liu et al., 2000; Schramm et al., 2003; Creux et al., 2009; Hampton and Nguyen, 2010; Fan et al., 2012; Sobhy and Tao, 2013).

Effects of various parameters on the zeta potential of air bubbles in aqueous solution have been studied thoroughly for years, and many authors have found that solution chemistry, medium pH, surfactant type and concentration, bubble size, the experimental technique employed and water temperature all play significant roles (Collins et al., 1977; Usui and Sasaki, 1977; Kubota et al.,

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Abbreviations: SDS, sodium dodecyl sulphate; IEP, isoelectric point; DAF, dissolved air flotation; Psat, saturation pressure; Qsat, flow-rate; EDA3B, alkyl methyl ether monoamine; SDS, sodium dodecyl sulphate; DAH, dodecyltrimethyl ammonium chloride; DTAC, dodecylamine hydrochloride.

* Corresponding author. Tel.: +55 51 33169479; fax: +55 51 33169477.
E-mail address: jrubio@ufrgs.br (J. Rubio).

[1] Visiting Scientist.

[2] www.ufrgs.br/ltm.

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1983; Kubota and Jameson, 1993; Yoon and Yordan, 1986; Li and Somasundaran,1992; Saulnier et al., 1996, 1998; Yang et al., 2001; Takahashi, 2005; Najafi et al., 2007; Elmahdy et al., 2008 and Weihong et al., 2013).

On the other hand, only a few studies have been conducted with stable nanobubbles in water alone, with inert electrolytes or in the presence of surfactants (Takahashi, 2005; Najafi et al., 2007; Weihong et al., 2013).

The most common approach for determining a bubble's surface charge is through electrophoretic mobility measurements from which zeta potential values are calculated (Collins et al., 1977; Kubota et al., 1983; Yoon and Yordan, 1986; Okada et al., 1990; Li and Somasundaran, 1992; Han and Dockko, 1998; Phianmongkhol and Varley, 2003; Najafi et al., 2007; Elmahdy et al., 2008; Oliveira and Rubio, 2011; Fan et al., 2012; Weihong et al., 2013). However, the main source of error in the size of bubbles employed in mineral flotation (0.8–3 mm diameter) stems from the high rising velocities of the bubbles in a gravitational field, which are sometimes much higher than the electrophoresis velocities. Therefore, researchers have attempted to devise techniques to generate smaller bubbles to reduce the rising velocity or to minimise the effects of buoyancy during electrophoretic mobility measurements, which can all lead to inconsistent results. Recently, Uddin et al. (2013) used a novel apparatus to measure electrical charge of bubble swarms (~1 mm mean bubble diameter) and claimed that this approach (bubble sedimentation potential) was in good agreement with the values of the isoelectric point for purified waterreported in the literature.

Another alternative approach has been to reduce bubbles size either physically or with the use of surfactants (Kubota et al., 1983; Cho and Laskowski, 2002; Grau et al., 2005; Li and Somasundaran, 1992; Kukizaki and Goto, 2006; Najafi et al., 2007; Fan and Tao, 2008; Fan et al., 2010a,b,c; Zimmerman et al., 2011; Fan et al., 2012).

Many authors claim that the gas bubbles in aqueous media always develop negative charges on their surfaces, which suggests that cations (protons) are more likely hydrated and therefore have a tendency to stay in the bulk aqueous medium, whereas the smaller, less hydrated and more polarised anions tend to adsorb on the bubbles' surfaces. However, this specific adsorption has not been fully explained, and its existence has not been universally accepted (Hampton and Nguyen, 2010; Paluch, 2000; Karraker and Radke, 2002; Takahashi, 2005).

Many authors have measured the charge of bubbles in the presence of surfactants, frothers and/or organic solvents (Usui and Sasaki, 1977; Collins et al., 1977; Kubota et al., 1983; Yoon and Yordan, 1986; Saulnier et al., 1996, 1998; Yang et al., 2001; Takahashi, 2005; Najafi et al., 2007; Elmahdy et al., 2008; Weihong et al., 2013). However, all these reagents, especially the surfactants, not only affect the intensity of the zeta potential but also determine the nature of bubble surface charges and bubble sizes; these effects constitute a major disadvantage when one wishes to measure a bubble's charge (Li and Somasundaran, 1992; Usui and Sasaki, 1977).

The generation, properties and applications of nanobubbles have been discussed at length over the last two decades. The experimental evidence of their formation is incontestable, yet a sound theoretical background of their behaviour is still lacking (Hampton and Nguyen, 2010; Ohgaki et al. 2010; Takahashi, 2005). According to Hampton and Nguyen (2010), several mechanisms have been proposed for the hydrophobic force, but in many cases, the force may be due to the presence of nanobubbles at the liquid-hydrophobic solid interface, a fact of great importance in mineral flotation of fine and coarse particles. These authors, among others, review some features of nanobubble stability and formation theories.

Moreover, nanobubble interfacial properties, their kinetic growth to microscopic sizes and their applications in many areas, including ore flotation, are interesting areas to explore. It is believed by a number of authors (Hampton and Nguyen, 2010; Attard et al., 2002; Attard, 2003; Schubert, 2005) that dissolved gases accumulate preferentially at the hydrophobic solid–water interface, and this fact has been revealed by AFM – atomic force microscopy (Attard, 2003; Hampton and Nguyen, 2010). The latter reported that these bubbles may co-exist as nanobubbles, nanopancakes and nanobubble–nanopancake composites and influence the attraction between hydrophobic surfaces in water, bubble–particle attachment and hydrophobic coagulation between particles.

Schubert (2005) reported that the long-range attractive interaction forces between hydrophobic surfaces in aqueous systems are caused by the capillary forces of gas bridges which form at the coalescence of nanobubbles adhering on the surfaces. More, this coalescence would be selective onto hydrophobised particles and that jointly with coarser bubbles would initiate the jump into the three-phase contact at the attachment events in flotation.

Recently, a number of studies confirmed these findings in applications in mineral flotation; main claimed advantages of the presence of nanobubbles are:

1. The presence of nanobubbles increased the contact angles and subsequently enhances the probability of flotation (coal, phosphates), mainly the bubbles–particles attachment and stability (Fan et al., 2012; Sobhy, 2013; Sobhy and Tao, 2013a,b).
2. Nanobubbles enhance particles flotation recoveries of coal particles at lower collector and frother dosages and at high kinetic flotation rate (Sobhy, 2013; Sobhy and Tao, 2013a,b).

The formation and separation (by splitting off from microbubbles) of a fraction of nanobubbles during depressurisation of saturated air in water (as in DAF-dissolved air flotation) have been neglected, although they seem to be critical factors for applications such as pollutants removal and mineral flotation of fine and coarse particles (Rodrigues and Rubio, 2007; Zimmerman et al., 2011).

The current work presents the results of some interfacial phenomena of nanobubbles at the water/air interface in the presence and in the absence of surfactants. The reduction in pressure of super-saturated water with air caused rapid formation of microbubbles (~30–100 μm), and a fraction of nanobubbles (varying from 130 to 720 nm) were separated and thoroughly studied. Contrary to other reported studies, medium pH was found to determine both zeta potential and hence the bubble size.

2. Experimental

2.1. Materials

Bubbles were generated (Fig. 1) by depressurising air–saturated water solutions at a high flow velocity through a needle valve into an empty glass column (50 cm high; 2 cm inner diameter). Saturation of air in water was achieved in a steel vessel containing an internal glass container with a height of 15 cm, an inner diameter of 12 cm and a wall thickness of 1 cm. The container had a height of 14 cm, an inner diameter of 10 cm, a wall thickness of 0.5 cm and a real capacity of 0.7 L (Fig. 1).

The depressurisation-cavitation stage employed had a 2 mm internal diameter needle valve (Globo 012-Santi®, made of steel); the sampling flux of 150 mL was bypassed from the column by clamping the rubber tubing (Fig. 1).

A Kruss® 8451 tensiometer was utilised for the water/air surface tension measurements, and a ZetaSizer Nano ZS (red badge)-