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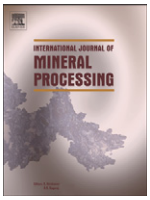

Zeta potential of single and polymer-coated microbubbles using an adapted microelectrophoresis technique

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ABSTRACT

The zeta potential of microbubbles, generated by injecting pressurised air into water and then releasing the pressure, was determined in the absence and presence of different polyacrylamides. Air was dissolved in either water or solutions of cationic, anionic, amphoteric or nonionic polymers at a constant pressure of four atmospheres. The charge of the bubbles at the shear-zeta plane was measured using a modified microelectrophoresis glass cell, held at a stationary level, at varying pH (2.0–12.0). Known practical problems with this technique were solved, and these solutions are described in detail. The anionic, amphoteric and nonionic polymers increased the negative charge of the bubbles, but the isoelectric point (iep) remained constant at about pH 2.0. Conversely, in the presence of the cationic polymer, the bubbles exhibited positive surface charges between pH 2.0 and 8.0 and an iep of pH 8.0. The results revealed the existence of an important interaction mechanism between air bubbles and polymeric macromolecules; neither this mechanism nor its practical implications have been reported in the literature to date, especially in the treatment of wastewater by flocculation followed by dissolved air flotation (DAF).

1. Introduction

The knowledge of bubble charge in aqueous solutions is important in many areas, namely, food processing, mineral processing and water and wastewater treatment. The charge of bubbles determines their interactions with solid particles, oil droplets and with other bubbles. In general, gas bubbles suspended in aqueous solutions acquire a surface charge, where the charge density and sign depend on the solution chemistry. The most likely charging mechanism involves the asymmetric dipoles of water molecules residing at the gas–liquid interface (Engel et al., 1997; Paluch, 2000). Other mechanisms responsible for bubble surface charge may include adsorption of ions, residual surfactants, dissociation of ionic groups, and charge separation (Hunter, 1981, 2001).

The interactions among ions, molecules and organic components and air bubbles have been studied by several authors, focusing on their applications in many processes (Grattoni et al., 2003; Liu et al., 2002; Moosai and Dawe, 2003; Najafi et al., 2007; Phianmongkhol and Varley, 2003; Su et al., 2006; Yang et al., 2001; Yoon and Yordan, 1986).

Measurements of bubble zeta potential in the presence of polymers are relevant to the flotation of ores and to pollutant removal in water and wastewater treatment. The adsorption of polyacrylamides onto air bubbles may influence the kinetics and efficiency of these flotation processes as well as particle flocculation. The study by Han and Dockko (1998) showed that the electrostatic natures of both bubbles and particles are important parameters in particle removal by dissolved air flotation (DAF).

This work studied the surface charge of single air bubbles in water and in the presence of polyacrylamide solutions, commonly used as flocculants in flocculation–flotation processes (Bolto et al., 1996; Kitchener, 1972; Rout et al., 1999; Rubio, 2003). The interactions between air bubbles and polymer flocculants are thought to play key roles in the formation of so-called “aerated flocs”; these aerated flocs are defined as floc/bubbles aggregates that have a very low density, which allows for a very fast solid/liquid separation. This is of great importance in liquid effluent treatment (Carissimi, 2003; Colic et al., 2001; Da Rosa and Rubio, 2005; Rodrigues and Rubio, 2007).

Thus, knowledge of these interactions may enhance the potential for applications of the flocculation–flotation processes in the environmental field (effluent control and water reuse), increasing its treatment capacity and lowering dosages and costs for polymers and other reactants.

Furthermore, knowledge of the interfacial behaviour of macromolecules adsorbed at bubble surfaces may aid in the selection of polymers, for example, in the processes of pollutant/contaminant removal in the production of drinking water and/or effluent treatment and in the selective flocculation of mineral particles.

The zeta potential of gas bubbles has been determined experimentally and many studies have been published reporting bubble charge in

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different electrolytes and/or frother solutions. The results of several of these important contributions are summarised in Table 1.

Table 1 shows that there have been a good number of important studies on the zeta potential of bubbles, most evaluating the effects of electrolyte and/or surfactant solutions but fewer in the presence of polymers. Uniquely, Malley (1995) reported values of the electrophoretic mobilities of bubbles in the presence of polymers, but this author claimed that the results had low precision, showing high relative standard deviations (from 25% to 100%). Yet, this work may be considered a pioneer and may therefore be used as a reference for the existence of changes in bubble charge when polymers are employed.

Although the electrophoresis technique has been widely utilised and may be the most suitable technique to determine bubble zeta potential, the procedure poses many practical problems. The main drawbacks are related to the introduction of gas bubbles into an electrophoresis cell, the rapid rise of large bubbles and the migration of microbubbles toward the electrodes. These problems have not been fully described in the literature and can often lead to erratic measurements, particularly when a smooth, horizontal bubble flow across the cell is required or when bubbles with a wide size distribution are examined.

Table 1
Zeta potential of bubbles at the air/water interface—a summary and a brief description of selected studies.

Authors	Brief description
Collins et al. (1978)	Zeta potential of very small gas bubbles generated by electrolysis in a microelectrophoresis cell in the presence of cetyltrimethylammonium bromide (CTAB) and sodium sulphate solutions.
Usui et al. (1981)	Measurements of the sedimentation potential (Dorn effect) of argon bubbles generated by fritted-glass-sphere gas diffusers dispersers were used to evaluate the effects of bubble size on their zeta potential in sodium hexadecyl sulphate, butanol, aqueous solutions and distilled water.
Kubota et al. (1983)	Determination of the zeta potential of air bubbles, generated by a DAF method, in surfactant solutions (sodium dodecyl benzene sulphonate, sodium dodecyl sulphate and cetylpyridinium chloride).
Yoon and Yordan (1986)	The zeta potential of microbubbles (microelectrophoresis), generated by a microfoam method, was measured in different concentrations of anionic, cationic and nonionic surfactants in aqueous solutions over a wide pH range.
Li and Somasundaran (1992)	Measurements of bubble electrophoretic mobilities (bubbles generated using a fritted-glass gas disperser) in NaCl and $A1Cl_3$ solutions. Studies of the effect of salt concentrations, aluminium hydroxide species formation and solution pH.
Han and Dockko (1998)	Zeta potential of air microbubbles, formed as in a DAF technique, using a microelectrophoresis cell with video camera. The study investigated the effect of bubble charge on the removal efficiency of solid particles using a coagulant over a wide pH range.
Saulnier et al. (1996, 1998)	The zeta potential of air bubbles, generated by a precision syringe, in solutions of surfactants and monodistributed nonionic/anionic surfactant mixtures was measured using the spinning-tube technique. The aim was to evaluate the surfactant concentrations and adsorption times at the bubble/solution interface.
Yang et al. (2001)	Use of a microelectrophoresis technique coupled to a video camera to measure the zeta potentials of oxygen and hydrogen bubbles generated by electrolysis in different electrolyte solutions (NaCl, $CaCl_2$, and $AlCl_3$).
Phianmongkhol and Varley (2003)	Determination of the zeta potential of air bubbles, generated by a Gilson pipette, in three protein solutions (BSA-bovine serum albumin, β-casein and lysozyme) and their binary mixtures. A microelectrophoresis technique was used to investigate the effects of protein concentration and ionic strength on bubble properties and foam behaviour.
Najafi et al. (2007)	Use of a laser-electrophoresis technique to measure the electrophoretic mobility of oxygen, nitrogen and air bubbles generated by the nucleation of nanobubbles in gas-supersaturated electrolyte solutions.
Elmahdy et al. (2008)	Measurement of the zeta potential of air bubbles generated by ultrasonication using a laser-electrophoresis technique to evaluate the effects of the presence of different frothers at concentrations ranging from 10 to 100 mg/L.

Still, many studies have not mentioned these difficulties, probably because the authors used video cameras, vertical bubble flow inside the cell and surfactant solutions that stabilize the bubble suspensions and also prevent bubble coalescence (Han and Dockko, 1998; Kubota et al., 1983).

In this context, the present work presents several adaptations of the electrophoresis technique for more accurate measurements of the electrophoretic mobility of microbubbles (as generated, for example, in a DAF technique) using a horizontal microbubble flow inside a microelectrophoresis cell without either a digital camera coupled to the micrometer or surfactants in the solutions. Accordingly, the aim of this work was to fully evaluate the effect of polyacrylamide macromolecules on the zeta potential of air bubbles in water while improving the technique and the quality of results. The improved measurements of bubble charge will provide a better understanding of the interactions between bubbles and polymers in flocculation–flotation processes.

2. Experimental

2.1. Materials and reagents

The commercial polymers employed and their main properties are summarized in Table 2. A full characterization involving the structural and charge density of these polyacrylamides was already described by Oliveira et al. (2010). Sodium hydroxide (Vetec®), sodium chloride (Synth®) and hydrochloric acid (Vetec®) were of analytical grade. All solutions were prepared according to the manufacturer's instructions using deionised water. At room temperature, the deionised water had a conductivity of 1.3 μS/cm, a surface tension of 72.8 ± 0.1 mN/m, and an equilibrium pH of 6.1. Acetone, nitric acid (5% v/v) and chromic-sulphuric acid solutions were used for cleaning glass materials.

2.2. Methods

A Rank Brothers microelectrophoresis apparatus, Mark II, was used to determine the electrophoretic mobilities of air microbubbles generated by a dissolved air flotation (DAF) technique. The system was composed of microelectrophoresis equipment with a modified electrophoresis cell, a pair of platinum electrodes, a DAF unit for producing the microbubbles and a glass cylinder to allow the rising and sampling of bubbles in the cell. Fig. 1 shows the experimental setup including a description of the microelectrophoresis technique coupled with the bubble-generation system.

The flat section of the cell had a rectangular cross-section with internal dimensions of approximately 1 mm deep, 10 mm high and 40 mm long. This cell was modified to allow microbubble flow through it by attaching two pieces of glass tubing to the cell (0.5 cm in diameter and 2.0 cm long; Fig. 2) according to Yoon and Yordan (1986).

In addition, the transverse cross-sectional area of this cell was determined by accurate calibrations performed with an optical microscope (Zeiss Stemi SV 11) coupled to a digital camera (Sony

Table 2
Summary of polyacrylamide properties and suppliers.

Polymers	Charge	Average molecular weight, g/gmol	Supplier
A100	anionic	5.9×10^6	Kemira®
C448	cationic	3.7×10^6	Cytec®
AM8170	amphoteric	6.1×10^6	Nalco®
SNF920SH	nonionic	6.0×10^6	Floerger®