

The effect of divalent metal ions on the zeta potential of bubbles

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Abstract Micro-bubbles are used in electro-flotation (EF) and dissolved air flotation (DAF) for particle separation. The efficiency of these flotation processes depends on the collision of bubble and particle and the collision efficiency is affected by certain parameters with respect to the size and zeta potential of bubble and particle. Therefore, it is necessary to monitor not only the zeta potential of the particle, but also that of the bubble. Gas bubbles are reported to be generally negatively charged in water. In this paper, we report a study performed to measure the zeta potential of bubbles in solutions containing divalent metals and find factors which can produce positively charged bubbles. Calcium and magnesium ions were selected as divalent metal ions because natural water normally contains an appreciable quantity of them. It was found that bubbles are negatively charged in CaCl_2 solutions whereas, under certain conditions, they become positively charged in MgCl_2 . Charge reversal of bubbles was observed above 10^{-2} M Mg, especially above pH 9. A probable principle that explained the charge reversal could be a combined mechanism with both specific adsorption of hydroxylated species and formation of hydroxide precipitates. Creating solution conditions that can produce positively charged bubbles in flotation methods might make it possible to remove particles using lesser amounts of coagulant or even none at all.

Keywords Bubbles; charge reversal; divalent metal; electro-flotation; zeta potential

Introduction

Recently, techniques based on micro-bubbles such as those in electro-flotation (EF) and dissolved air flotation (DAF) are being increasingly utilized for the treatment of water and wastewater. The flotation process is known by several different names, including electro-flotation, dissolved air flotation and dispersed air flotation, depending on the method used to generate the bubbles in the system (Burns *et al.*, 1997). The efficiency of these flotation processes depends on certain characteristics of the bubbles, such as the degree of their coalescence, the size, and the zeta potential of bubbles (Li and Somasundaran, 1991). A collision efficiency diagram constructed using trajectory analysis (Han *et al.*, 2001) showed that it is necessary to monitor not only the zeta potential of the particle, but also that of the bubble. Some researchers have carried out experiments to control the zeta potential of bubbles using surfactants (Kubota and Jameson, 1993; Yoon and Yordan, 1986). However, these studies revealed little information about the effect of inorganic electrolytes on the zeta potential of bubbles. Gas bubbles are generally reported to be negatively charged in water and inorganic electrolytes (Li and Somasundaran, 1991). Therefore, this study was performed (1) to measure the zeta potential of bubbles in solutions containing divalent metal ions, and (2) to find out which factors can produce positively charged bubbles.

Materials and methods

Based on the principle of electrophoresis measurement (EPM), the zeta potential of the bubbles was measured with a set of equipment comprising an electrophoresis cell,

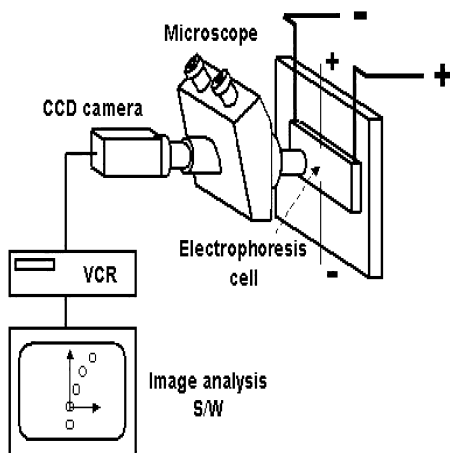
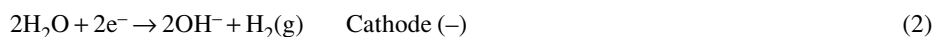


Figure 1 Zeta potential measurement apparatus

microscope, CCD camera and a video image analyser, as shown in Figure 1 (Dockko *et al.*, 1998). The electrophoresis cell, as shown in Figure 2, is made of two slide glasses, with inner dimensions of 50 mm (length) \times 40 mm (width) \times 2 mm (depth). A potential difference was applied across the platinum electrodes on each side of the cell.

The gas bubbles formed during electrolysis in the electrophoresis cell are generated by the following redox reactions that occur at the platinum wires:



While a large bubble has too rapid a rising velocity to be measured, bubbles of smaller diameter can be used to keep track of the movement of bubbles in an electrophoresis cell. Hydrogen gas bubbles have a smaller diameter and so were used to measure desired bubble characteristics. In addition, the solubility of hydrogen is much lower than that of oxygen, which means hydrogen gas bubbles keep a relatively constant shape while being observed through the microscope. A major practical problem that can arise when using the EPM to

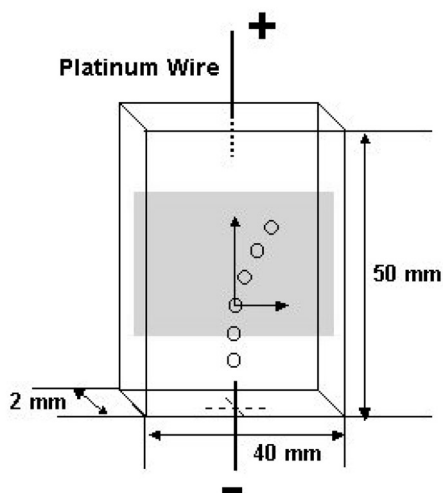


Figure 2 Electrophoresis cell

measure zeta potential is that, because of the electro-osmotic effect in a thin cell, it is important to measure bubbles moving in the stationary layer. To avoid an electro-osmotic effect, the stationary level was derived from Eq. (3) and we measured the velocities of the bubbles at this point (Collins *et al.*, 1978). In this study, the microscope was focused on the stationary level in the cell and only bubbles showing a clear image on the videotape were measured.

$$y = \pm h/\sqrt{3} \quad (3)$$

where y : the position of the stationary layer from the midpoint of the cell, and h : half of the depth of the cell.

The bubbles were photographed/recorded on video with a CCD camera. When electric fields are applied to rising bubbles, bubbles may move in the opposite direction according to their charge. The movement of bubbles was recorded on videotape and the video image analysed by image analysis software. The horizontal velocities of bubbles were obtained by analysis of the videotape with an image analyser. The electrophoretic mobility of the bubbles was derived from this velocity. Then the zeta potential of the bubbles can be calculated from the measured horizontal velocity with the Smoluchowski equation (Eq. (4)).

$$\zeta = \frac{\eta V_e \lambda_o A}{\epsilon_o \epsilon_r I} \quad (4)$$

where ζ = zeta potential (V)

μ = viscosity ($0.89 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$) at 25°C

ϵ_o = the permittivity of a vacuum ($8.854 \times 10^{-12} \text{ kg}^{-1} \text{ m}^{-3} \text{ s}^4 \text{ A}^2$)

ϵ_r = the relative permittivity (or dielectric constant = 78.5)

I = Electric current (A)

λ_o = Electrical conductivity of solution ($\Omega^{-1} \text{ m}^{-1}$)

A = Cross-sectional area of cell (m^2)

V_e = Velocity (m s^{-1})

Calcium and magnesium ions were selected as the divalent metal ions to be used to make the desired solutions because they are ions that occur in significant concentrations in many natural waters. To exclude the effect of the anion, the chloride salt was injected into distilled water. Solution conditions for measuring the zeta potentials of bubbles are shown in Table 1. To examine a relationship between metal ions, including their hydrolysis products, and the zeta potential of bubbles, metal species distribution diagrams were constructed and the zeta potential of hydroxide precipitates was measured.

Results and discussion

Zeta potential of bubbles

Zeta potential – pH curves obtained for solutions at four different CaCl_2 and MgCl_2 concentrations are shown in Figure 3 and 4, respectively.

Table 1 Solution conditions for measuring ζ -potential of bubble

	Ca	Mg
Metal concentration	10^{-5} , 10^{-4} , 10^{-3} and 10^{-2}	
pH	3–12 (at increments of 1)	
Background electrolyte	NaCl 0.01 M	NaCl 0.01 M

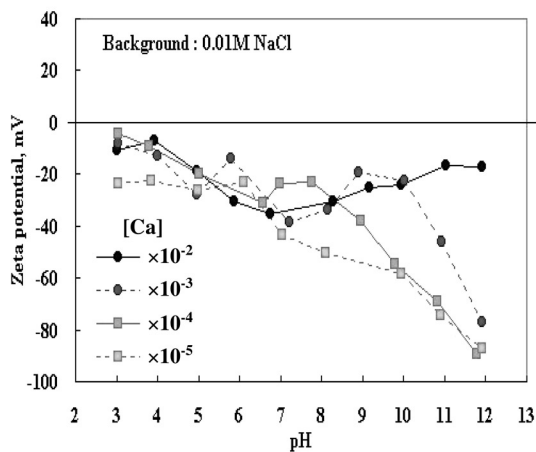


Figure 3 Zeta potential of bubbles in CaCl_2

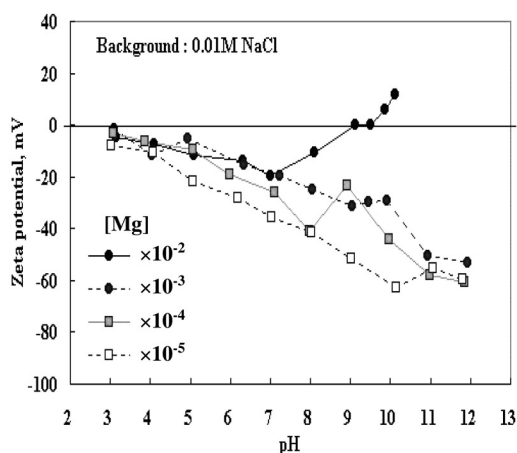


Figure 4 Zeta potential of bubbles in MgCl_2

Figure 3 shows that the bubbles are negatively charged over the entire calcium concentration and pH ranges studied. The magnitude of the zeta potential decreased with an increase in calcium concentration and a decrease in the pH value. However, the zeta potential of bubbles in 10^{-2} M CaCl_2 solution did not continue to reduce as the pH in the solution became alkaline (above pH = 7), but increased. Figure 4 shows that the magnitude of the zeta potential also decreased with an increase in magnesium concentration and a decrease in pH value. However, the zeta potential of bubbles became positive in 10^{-2} M MgCl_2 , especially in the alkaline pH region. In this case, an isoelectric point exists at pH 9.

Factors causing the charge reversal

To explain the role of metal ions and their hydrolysis products on the observed bubble charges, metal species distribution diagrams were constructed and the zeta potentials of metal hydroxide precipitates were measured using a Zetaphoremeter II, made by Sephy, France. The species distribution diagrams of calcium and magnesium are shown in Figures 5 and 6, respectively.

It can be seen from Figure 5 that, although the exact pH at which $\text{Ca}(\text{OH})_{2(s)}$ starts precipitating in the bulk solution does vary with the total calcium concentration, Ca^{2+} and $\text{Ca}(\text{OH})_{2(s)}$ are always the predominant species in the lower and higher pH regions,

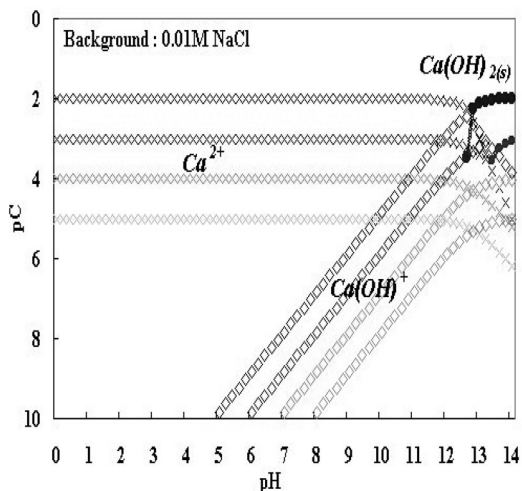


Figure 5 Calcium species distribution

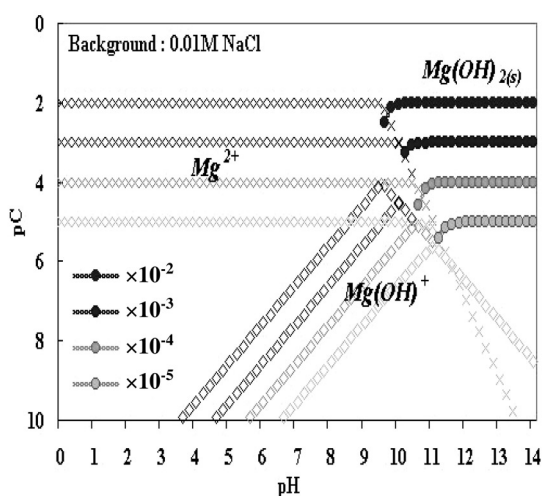


Figure 6 Magnesium species distribution

respectively. The zeta potential of bubbles in 10^{-2} M CaCl_2 solution did not reduce continuously as the pH of the solution turned alkaline (Figure 3). As illustrated in Figure 5, it is affected by Ca(OH)^+ which becomes more important in the alkaline pH region.

Figure 6 illustrates that, although the exact pH at which $\text{Mg(OH)}_{2(s)}$ starts precipitating in the bulk solution does vary with the total magnesium concentration, Mg^{2+} and $\text{Mg(OH)}_{2(s)}$ are always the predominant species in the lower and higher pH regions respectively. When the species present in the solution are taken into consideration, a correlation between the charge reversal of bubbles shown in Figure 4 and the presence of magnesium hydroxide precipitates becomes apparent, especially in the alkaline pH region.

The zeta potential of $\text{Mg(OH)}_{2(s)}$ was investigated, with the results as shown in Figure 7. The solid $\text{Mg(OH)}_{2(s)}$ assumed a positive charge in the alkaline pH region at a concentration of 0.01 M MgCl_2 . The magnitude of zeta potential decreased with increase of pH. Therefore, the positively charged bubbles in 10^{-2} M MgCl_2 solution in Figure 4 can be attributed to the presence of positively charged $\text{Mg(OH)}_{2(s)}$. Though this magnesium hydroxide precipitate also produced a positive zeta potential at 10^{-3} M magnesium concentration, it could not at this lower concentration alter the sign of the zeta potential of the

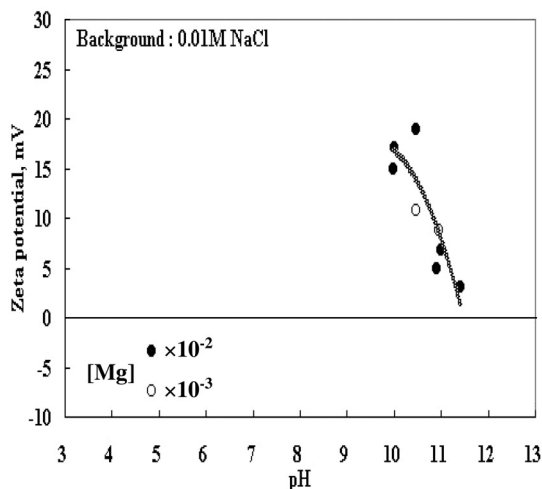


Figure 7 Zeta potential of $\text{Mg}(\text{OH})_{2(s)}$

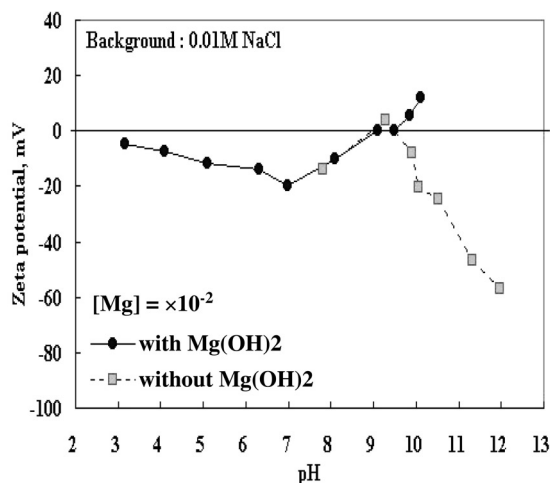


Figure 8 Zeta potential at 10^{-2} M MgCl_2

bubble. The conclusion is that metal hydroxide precipitates, at sufficiently high concentrations, can interact to reverse the zeta potential of bubbles.

As previously stated, charge reversal of bubbles can be explained as having something to do with the presence of positively charged magnesium hydroxide precipitates. To comprehend the mechanism of charge reversal by hydroxide precipitates, it is essential to compare the two conditions: with and without precipitate. Before scrutiny of the effect of magnesium, magnesium hydroxide precipitates were removed by passage through a $0.45 \mu\text{m}$ membrane filter. The difference in the zeta potential profile with and without $\text{Mg}(\text{OH})_{2(s)}$ is shown in Figure 8, where it is shown that the zeta potential of the bubbles decreased to negative values when $\text{Mg}(\text{OH})_{2(s)}$ was absent. Therefore, positive $\text{Mg}(\text{OH})_{2(s)}$ is a critical factor controlling the sign of zeta potential, as already mentioned. Li and Somasundaran (1991) have also reported a possible mechanism concerned with charge reversal of bubbles under conditions where there was an absence of metal hydroxide precipitates in their flotation column.

However, there are also several minor species, $\text{Mg}(\text{OH})^+$ and Mg^{2+} , present in solution in addition to $\text{Mg}(\text{OH})_{2(s)}$, as shown in Figure 6. Considering that the zeta potential of the bubble still maintains a positive value without $\text{Mg}(\text{OH})_{2(s)}$, it is likely that the hydroxylated

species also play a role in the production of a positively charged bubble. Therefore, a probable principle that can explain the procedure of charge reversal is a combined mechanism, with both specific adsorption of hydroxylated species and formation of hydroxide precipitates.

Conclusion

This study was performed to investigate the zeta potential of bubbles and to find factors that can produce positively charged bubbles in solution containing calcium and magnesium metal ions.

The electrokinetic behaviour of bubbles that are generated by electrolysis was measured using electrophoresis measurements (EPM). In the case of calcium, the zeta potential of bubbles was negatively charged over the entire pH range. With magnesium, on the other hand, positively charged bubbles were observed at concentrations of above 10^{-2} M Mg, especially above pH 9. The zeta potential of the bubbles increased both with higher magnesium concentration and at acid pH.

These profiles of zeta potential with magnesium were basically similar to those with calcium. To find out the factors that produce positively charged bubbles in 10^{-2} M MgCl_2 solution, a magnesium species distribution diagram was constructed and the zeta potentials of magnesium hydroxide precipitates were measured. As a result, the positively charged bubbles in 10^{-2} M magnesium solution can be attributed to the presence of positively charged $\text{Mg}(\text{OH})_{2(s)}$. By the same token, the reason why there was no evidence of the charge reversal of bubbles in any of the concentrations of CaCl_2 solution is that calcium hydroxide precipitates are not produced below pH 12.6. Considering that the zeta potential of the bubble still maintains a positive value without $\text{Mg}(\text{OH})_{2(s)}$, it seems that hydroxylated species other than the hydroxide also play a role in producing a positively charged bubble.

Consequently, the zeta potential of bubbles is a function of the type and concentration of metal ion and the pH of the solution. A principle that can be used to explain the process of charge reversal would be a combined mechanism, with both specific adsorption of hydroxylated species and formation of a hydroxide precipitate. It may be possible, therefore, to create solution conditions under which bubbles with positive charges can be formed. This leads to the possibility of removing particles from water by flotation methods where there is a reduced requirement, perhaps even no requirement at all, for use of a coagulant.

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