

# Reversal of Bubble Charge in Multivalent Inorganic Salt Solutions —Effect of Aluminum

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The charge of bubbles in aqueous solution is important in determining their interactions with particles, droplets, and other bubbles. While bubbles are known to be negatively charged in such media as water and sodium chloride solutions, they are found here to exhibit unusual positive surface charge characteristics in solutions of trivalent aluminum cations. Analysis of the results indicates that the reversal of bubble charge can be attributed to specific adsorption of  $\text{Al}^{+3}$  and its hydroxo complexes at the gas-liquid interface in the low pH range and to precipitation of aluminum hydroxide in the intermediate pH range.

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## INTRODUCTION

Gas bubbles in aqueous solutions are of great interest to researchers in many fields, such as food processing, mineral beneficiation, and waste water treatment (1-4). The effectiveness of the bubbles is controlled by such properties as the size and the rate of coalescence, which in turn depends, among other things, on the surface charge of the bubble. It is known that in pure water and in solutions of simple inorganic electrolytes the gas bubbles are negatively charged, whereas in the presence of surfactants the charge of the bubbles is governed by the charge of the head group (5-15). Although the electrokinetic behavior of gas bubbles in aqueous solutions has been studied for over 100 years, only recently was it found by the authors that the presence of  $\text{MgCl}_2$  in the solution causes a reversal of the bubble charge due to the specific adsorption of the cationic metal ions and metal hydroxo complexes, and the formation of the metal hydroxide precipitate at the gas-liquid interface (16). The objective of this work was to study the effect of trivalent aluminum ion on the

zeta potential of the bubble. The effect of the concentration of aluminum hydroxo species as well as the solution pH on the electrokinetic behavior of bubbles is reported.

## MATERIALS AND METHODS

ACS certified grade inorganic salts, NaCl and  $\text{AlCl}_3$ , and pH modifying reagents, hydrochloric acid and sodium hydroxide, were purchased from Fisher Scientific Co., and were used without further purification. All salt solutions were prepared using triply distilled water and stored in volumetric flasks. For each of the tests, 200  $\text{cm}^3$  of the stock solution was transferred to a 250- $\text{cm}^3$  centrifuge bottle for pH adjustment and was allowed to stand undisturbed for 24 h. The solution was then centrifuged for 40 min at 9000 rpm (8300 g) in a Sorvall RC-5B refrigerated superspeed centrifuge maintained at room temperature to remove metal hydroxide precipitate, if any. The supernatant was decanted and used for zeta potential measurements.

An experimental setup was designed to monitor the electrokinetic behavior of bubbles; a detailed description of the experimental setup and procedure is given in an earlier paper

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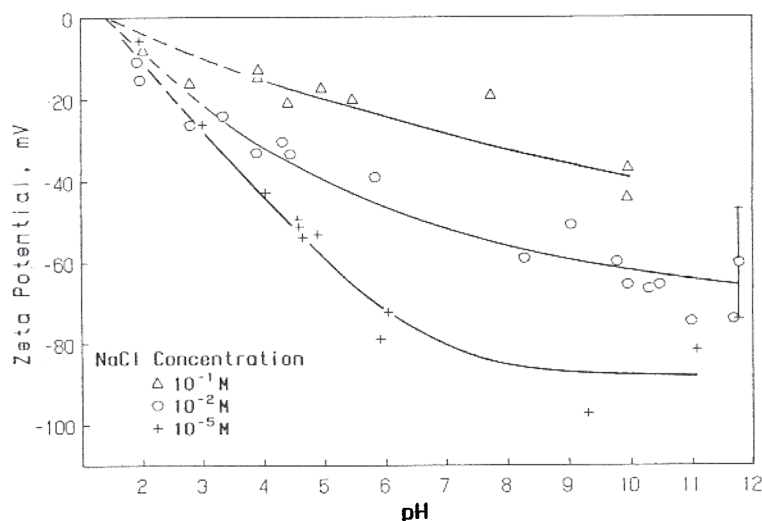


FIG. 1. Zeta potential of bubbles as a function of pH in NaCl salt solutions.

(16). The size of the bubbles measured was estimated to be  $\sim 5 \mu\text{m}$  or smaller. Although some larger bubbles were also present in the system, their rising speed was too fast to be measured. The solution was also examined without bubbles for the presence of particles, if any.

#### RESULTS AND DISCUSSIONS

As indicated in the earlier paper (16), bubbles are negatively charged in NaCl solutions over the pH range examined, and the magnitude of the zeta potential decreases with an increase in salt concentration (Fig. 1). Although no isoelectric point was detected in the pH range studied, the curves at different salt concentrations converge upon extrapolation to a pH value of  $\sim 1.5$ , suggesting that neither  $\text{Na}^+$  nor  $\text{Cl}^-$  ions specifically adsorb at the gas-liquid interface.

In contrast,  $\text{AlCl}_3$  produced some unusual effects. As can be seen in Fig. 2, a reduction in the magnitude of the zeta potential of bubbles is observed in the presence of  $5 \times 10^{-6} \text{ mol/dm}^3 \text{ AlCl}_3$  below the pH of the first zeta potential reversal (ZR1), and above this pH, bubbles become positively charged until about

pH 7.6, where the second zeta potential reversal (ZR2) occurs. An increase in the  $\text{AlCl}_3$  concentration makes the bubbles more positively charged below pH 9, with a maximum of about +40 mV at about pH 7.

The above results clearly show the marked effect of the aluminum ions on the electrokinetic behavior of the bubbles. In order to identify the species involved in producing the above effect, the species distribution diagrams (Fig. 3) were constructed from a knowledge of the free energy of formation of possible species (17). When the species present in the solution are taken into consideration, a correlation between the zeta potential reversals and the presence of the metal hydroxide species becomes apparent (Fig. 4). In zone 1, where  $\text{Al}^{+3}$  is the predominant species, bubbles remain negatively charged at low  $\text{AlCl}_3$  concentration. As the  $\text{AlCl}_3$  concentration is increased, the zeta potential of the bubble becomes less negative and eventually turns positive above a certain concentration which, according to the experimental data, occurs between  $1 \times 10^{-4}$  and  $1 \times 10^{-5} \text{ mol/dm}^3 \text{ AlCl}_3$ . The charge reversal in this zone is attributed to the adsorption of  $\text{Al}^{+3}$  ions at the gas-liquid interface, since the only other cationic species

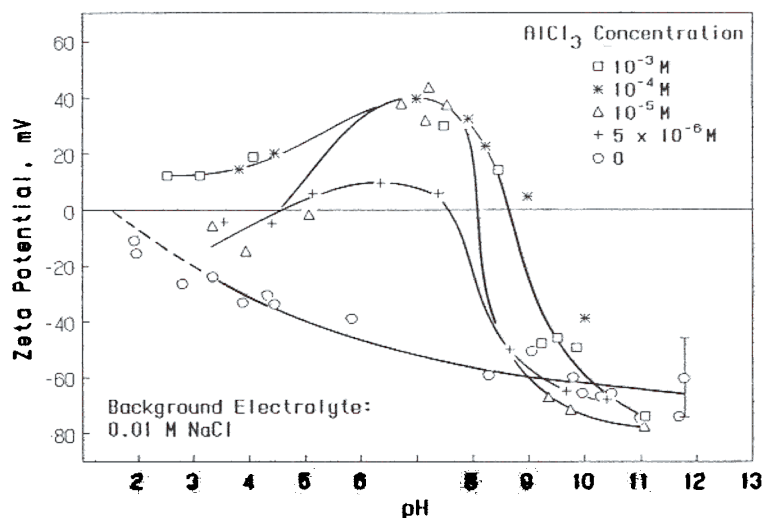


FIG. 2. Zeta potential of bubbles as a function of pH in the presence of  $\text{AlCl}_3$ .

present,  $\text{Na}^+$ , does not adsorb specifically at the interface.

The same phenomenon is also observed in zone 2, except that the salt concentration needed to reverse the bubble charge ( $< 5 \times 10^{-6} \text{ mol/dm}^3$ ) in this region is much lower than that in zone 1. The dominant species in this region are  $\text{Al}(\text{OH})_{3(s)}$ ,  $\text{Al}(\text{OH})_{3(aq)}$ , and  $\text{Al}(\text{OH})_2^+$  and/or  $\text{Al}(\text{OH})_{3(aq)}$  or precipitation of  $\text{Al}(\text{OH})_{3(s)}$ . Since  $\text{Al}(\text{OH})_{3(s)}$  precipitates are positively charged in zone 2 (Fig. 5), should

adsorption of these colloidal particles on the negatively charged bubble surface occur, the charge of the bubbles could indeed be reversed. However, since the precipitate was removed by centrifugation prior to the zeta potential measurements, the reversal of the bubble charge must be due to the adsorption of  $\text{Al}(\text{OH})_2^+$  and/or  $\text{Al}(\text{OH})_{3(aq)}$  or precipitation of  $\text{Al}(\text{OH})_{3(s)}$  at the interface. If adsorption of oppositely charged species at the gas-liquid

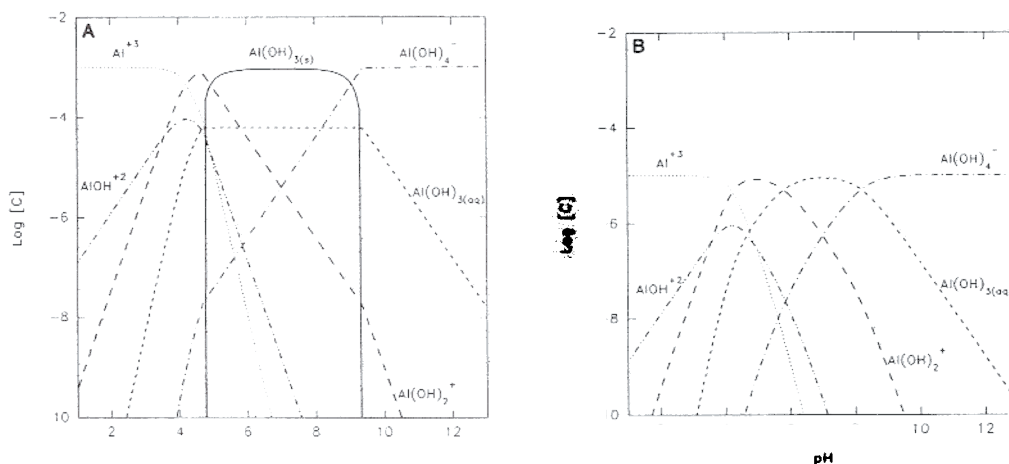


FIG. 3. Aluminum species distribution diagrams as a function of pH at various  $\text{AlCl}_3$  concentrations. Total aluminum concentration is  $1 \times 10^{-3} \text{ mol/dm}^3$  (A) and  $1 \times 10^{-5} \text{ mol/dm}^3$  (B)

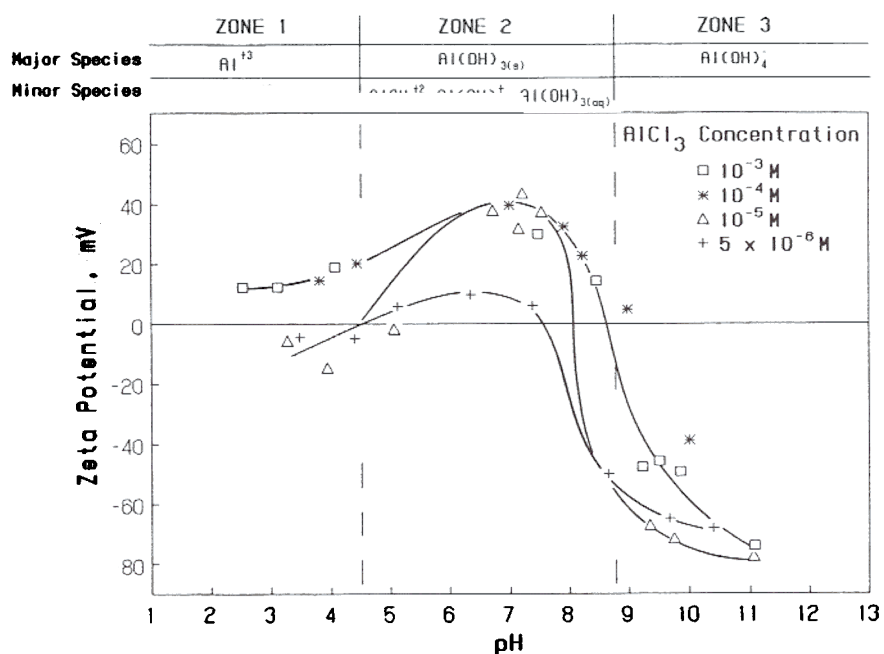


FIG. 4. Correlation between species distribution and zeta potential of bubbles in the presence of  $\text{AlCl}_3$ .

interface is the only mechanism responsible for the charge reversal, the amount of monovalent  $\text{Al}(\text{OH})_2^+$  required to reverse the bubble charge in zone 2 is likely to be much higher than that of the trivalent  $\text{Al}^{+3}$  which causes the charge reversal in zone 1. However, it can

be seen from Fig. 3 that the  $\text{Al}(\text{OH})_2^+$  concentration in zone 2 is in most cases below that of the  $\text{Al}^{+3}$  in zone 1.

In the absence of bubbles, bulk concentrations of  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_{3(aq)}$  will be at their equilibrium values. If the surface activ-

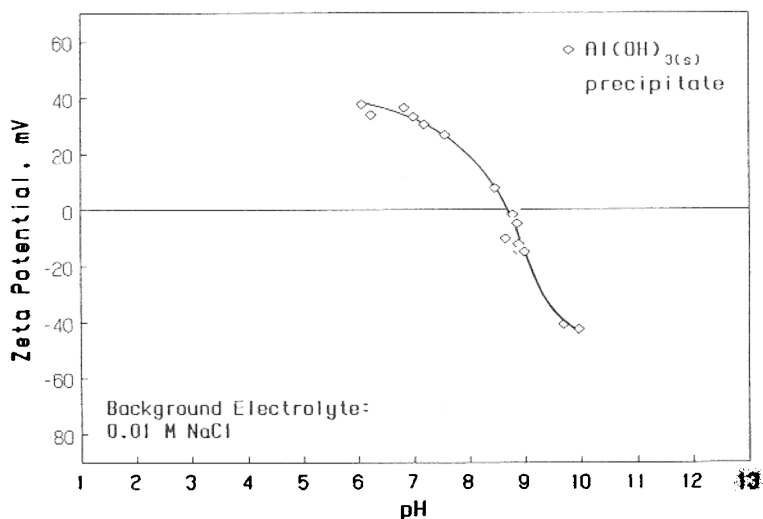


FIG. 5. Zeta potential of freshly precipitated  $\text{Al}(\text{OH})_{3(s)}$  as a function of pH.

ities of  $\text{Al(OH)}_2^+$  and  $\text{Al(OH)}_{3(\text{aq})}$  are sufficiently high, concentrations of these species will be higher at the gas-liquid interface and exceed their equilibrium values. When the concentration at the interface is high enough to exceed the solubility limit of  $\text{Al(OH)}_{3(\text{s})}$ , it will precipitate preferentially at the interface. Since  $\text{Al(OH)}_{3(\text{s})}$  is positively charged below pH 8.8 (Fig. 5), the charge of the bubble will be the sum of the original negative sites and the sites covered with positively charged  $\text{Al(OH)}_{3(\text{s})}$ . The bubble will acquire a net positive charge only when the extent of coverage of the bubble surface by the surface precipitate exceeds a certain value. Once the bubble surface is completely covered by the precipitate, the electrokinetic behavior of the bubbles will be the same as that of the  $\text{Al(OH)}_{3(\text{s})}$  precipitate. This explanation is supported by the observation that an increase in  $\text{AlCl}_3$  concentration shifts the ZR2 toward the isoelectric point of the  $\text{Al(OH)}_{3(\text{s})}$  precipitate.

In zone 3, bubbles remain negatively charged in the concentration range studied. Since  $\text{Al(OH)}_4^-$  is the predominant species in this region, its adsorption at the gas-liquid interface is unlikely. Therefore, the bubble charge should be independent of the added aluminum salt concentration in this zone, as observed experimentally (Fig. 2).

#### SUMMARY

This study has clearly shown that bubbles can be positively charged in electrolyte solutions of multivalent salts depending on the concentration of the dissolved species, which in turn will depend on the salt concentration and solution pH. It is also clear that with a

prior knowledge of the species distribution, bubbles can be made to acquire the desired sign and magnitude of surface charge by adding the required amounts of appropriate salts.

#### ACKNOWLEDGMENTS

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