

Electrokinetic Potential of Microbubbles Generated in Aqueous Solutions of Weak Electrolyte Type Surfactants

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The electrokinetic potentials of microbubbles generated in aqueous solutions of weak electrolyte type flotation collectors, primary amines, and fatty acids have been measured by means of a microelectrophoretic technique. It has been found that while the ζ potential of a bubble in a solution of a strong electrolyte type surfactant is entirely determined by the type of surfactant, being negative in the presence of an anionic surfactant and positive in the presence of a cationic surfactant, the ζ potential of a bubble in the presence of a weak electrolyte surfactant may be, depending on pH, either positive or negative. The isoelectric points of the bubbles have been found to correlate very well with those of the colloidal precipitate present in the solution when the solubility limit of a free amine, or acid, is exceeded. This indicates that the negative sign of the ζ potential of bubbles produced in alkaline aqueous solutions of dodecylamine and the positive sign of the ζ potential of bubbles produced in acidic solutions of fatty acids can be explained by armoring of the bubbles by a partially hydrophobic precipitate.

Introduction

The effect of the electrical charge of mineral particles on particle-to-bubble attachment in flotation has been known for quite some time.¹ Derjaguin and Shukakidse² found that the flotation of stibnite sharply decreased as the ζ potential of the particles was increased beyond a critical value. Jaycock and Ottewill³ demonstrated that the flotation rate of silver iodide particles in the presence of cationic surfactant was highest when the ζ potential values of AgI were close to zero.

Since the interaction between a particle and a bubble during the attachment depends on both the electrical charge of the solid/liquid and liquid/gas interfaces, it is obvious that the electrical charge of the bubble in this process may be as important as that of the particle.

Dibbs, Sirois, and Bredin⁴ attempted to measure bubble electrical charge from the streaming potential of gas bubbles in the presence of dodecylamine and to correlate it with the ζ potential and floatability of quartz particles. Collins, Motarjemi, and Jameson⁵ used a rectangular quartz cell and measured electrophoretic mobilities of fine gas bubbles generated by electrolysis. In the flotation studies that followed, they confirmed experimentally that the flotation rate constant depended strongly on the particle and bubble electrical charges.⁶

In the case of ionic surfactants, Usui and Sasaki⁷ revealed that the sign of the ζ potential coincided with the charge of the polar group of the surfactant; i.e., it was positive in solutions of cationic surfactants and negative in solutions of anionic surfactants. It is of interest to note that Usui and Sasaki⁷ measured the Dorn potential of gas bubbles; this has long been a controversial subject. Dukhin⁸ and Derjaguin and Dukhin⁹ claim that the diffusion processes can be significant for the external field of droplets or bubbles. In the equations which they derived for the Dorn potential, the first term represents the contribution to the potential of the moving bubble arising from the ζ potential, while the other terms arise from the diffusional electric effects and adsorption. For solid particles, the derived equations reduce to Smoluchowski's equation only when the diffusion coefficients of the ions of concern

are identical. For bubbles, some other conditions must also be fulfilled. Dukhin⁸ claims that only at low concentration of a reagent of moderately low surface activity does measurement of the Dorn effect at $Pe \gg 1$ and $Re < 1$ permit determination of the ζ potential from the simple form of Smoluchowski's equation.

Large ζ potential values in Usui and Sasaki's⁷ publication were attributed by Hunter¹⁰ to the use of the Dorn effect technique and the classical Smoluchowski equation without any additional corrections. Kubota et al.¹¹ working with microbubbles obtained smaller ζ potential values for the same surfactants. In the light of these observations, the ζ potentials calculated by Usui et al.¹² from the Dorn effect for bubbles of various sizes seem to be even more questionable.

In order to explain the effect brought about by the surfactants, the charge of bubbles in aqueous solutions of simple inorganic salt solutions must be first understood. Alty¹³ used an experimental cell similar to that described by McTaggart.^{14,15} The measurements revealed that the

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bubbles had an electrical charge even in distilled water and that the charge did not depend on the nature of the gas. Ekserova and Zakhareva¹⁶ studied the stability of microscopic equilibrium films and calculated the surface potential from DLVO theory. Their experiments showed that the isoelectric point was situated at pH 4.85 for the water/gas interface. The experiments, carried out at constant ionic strength (10^{-4} mol-dm⁻³) gave iep = 4.5. Since at this pH the adsorption of H⁺ and OH⁻ ions at the water/gas interface is apparently identical, they concluded that OH⁻ ions are mostly responsible for the charge on gas bubbles in aqueous solutions.

McShea and Callaghan¹⁷ confirmed that bubbles were negatively charged in slightly acidic aqueous solutions and in potassium chloride solutions.

Some researchers observed that the bubbles in an aqueous solution of dodecylamine (cationic surfactant) acquired negative charge.^{4,18} This effect is further studied in this paper in the presence of weak electrolyte type surfactants. Laskowski and co-workers¹⁹⁻²¹ have recently reported that the colloidal precipitate which appeared in the aqueous solution of primary alkylamines under alkaline conditions when the amine solubility was exceeded (2×10^{-5} mol-dm⁻³ for dodecylamine) had all the typical properties of a colloidal system with a clear iep (around pH 11 for dodecylamine). They found that in such a solution of cationic surfactant, negatively charged colloidal species may appear (above pH 11 for dodecylamine). The same phenomenon was observed for fatty acids.²² The precipitate which was observed in acidic solution when the solubility of a free fatty acid was exceeded (1.3×10^{-5} mol-dm⁻³ for lauric acid) also exhibited a clear isoelectric point (around pH 3.5 for lauric acid). Positively charged species may then also appear in the aqueous solutions of anionic surfactants (in the pH range below 3.5 for lauric acid). The presence of such a precipitate was revealed to have a very strong effect on the ζ potential of mineral particles,^{20,21} and it is obvious that it may also affect the electrical charge of bubbles. Since the weak electrolyte type surfactants, such as primary aliphatic amines and fatty acids, are typical flotation collectors, the aim of this project is to further study the effect that such colloidal species may have on the electrical charge of bubbles generated in solutions of such surfactants.

Experimental Section

Reagents. Research grade dodecylamine hydrochloride and lauric acid were obtained from Eastman, and research grade sodium oleate, sodium dodecyl sulfate, and sodium dodecane sulfonate were obtained from Fisher Scientific Co.

Equipment and Procedure. In the present work, microelectrophoretic mobilities were measured by using a vertical, flat-type cell described in detail by Yoon and Yordan.¹⁸ A Rank Brothers Mark II microelectrophoretic apparatus was used to determine the electrophoretic mobility of microbubbles. The mobility was then converted to ζ potential by using Smoluchowski's equation.

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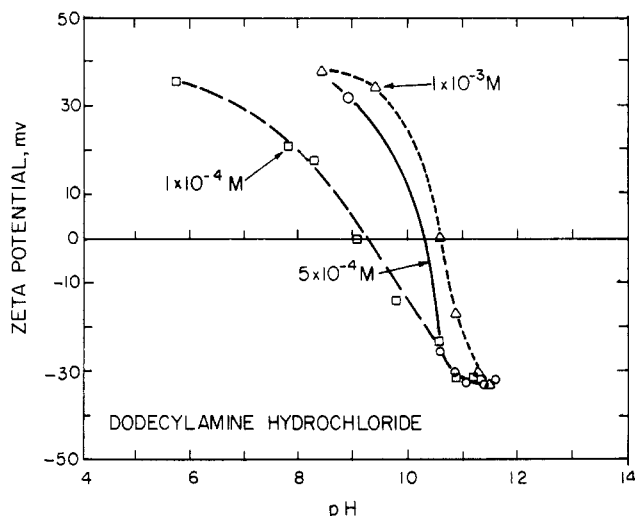


Figure 1. Effect of pH on the ζ potential of microbubbles generated in dodecylamine hydrochloride aqueous solutions.

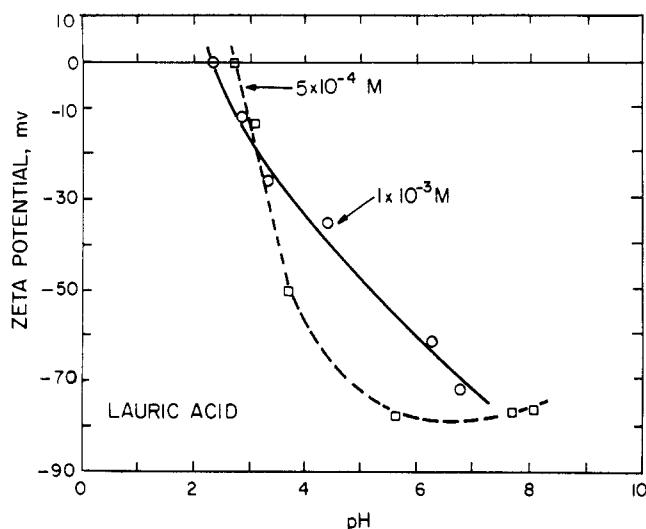


Figure 2. Effect of pH on the ζ potential of microbubbles generated in lauric acid aqueous solutions.

The fatty acid stock solutions were prepared at pH 9-10, and then the pH was adjusted to a desired value. For the amine, the stock solutions were slightly acidic and were manipulated to the desired alkaline range.

All measurements were carried out at ambient temperature, starting with very dilute solutions. After each series of tests, the flat cell was cleaned with chromic acid and double-distilled water prior to the next set of measurements.

Results

As Figure 1 shows, the ζ potential of bubbles generated in dodecylamine hydrochloride solutions can be, depending on pH, either positive or negative. The isoelectric point of bubbles moves toward higher pH values with an increase in the amine concentration and is situated somewhere between pH 9 and 10.5.

Figure 2 demonstrates that the bubbles generated in lauric acid aqueous solutions are negatively charged over a broad pH range, but the ζ potential values quickly approach the isoelectric point around pH 2.5-3.

The isoelectric point of bubbles was easily measured in sodium oleate aqueous solutions and was found to be situated around pH 3.5 (Figure 3).

The experiments carried out with strong electrolyte type surfactants, sodium dodecanesulfonate and sodium dodecyl sulfate, confirmed that the ζ potential of bubbles in

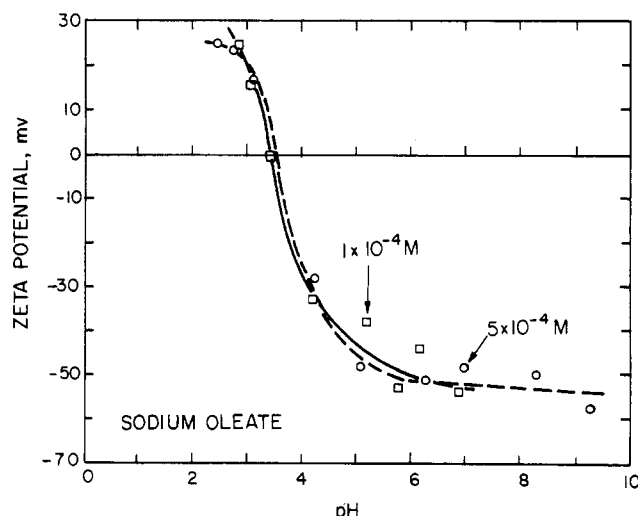


Figure 3. Effect of pH on the ζ potential of microbubbles generated in sodium oleate aqueous solutions.

aqueous solutions of such surfactants was negative over the whole pH range.

Discussion

Firstly, it is to be noted that for all the tested surfactants that are weak electrolytes, the bubbles were found to be, depending on pH, either negatively or positively charged. This is remarkably different from the case of strong electrolyte surfactants, for which Usui and Sasaki,⁷ Kubota et al.¹¹, and Yoon and Yordan¹⁸ showed that the sign of the ζ potential of the bubbles coincided with the charge of ionized surfactant: positive in solutions of cationic surfactants and negative in solutions of anionic surfactants.

The ζ potential vs pH curves for bubbles in the dodecylamine solutions (Figure 1), and the same for dodecylamine precipitate,¹⁹ are very similar. This suggests that the dodecylamine precipitate that is hydrophobic coats the bubbles and renders the ζ potential of the bubbles close to that of the precipitate itself.

The thermodynamic equilibrium diagram for dodecylamine aqueous solutions¹⁹⁻²¹ is presented in Figure 4 with experimental points indicating the isoelectric points of the precipitate^{19,20} and the isoelectric points of the bubbles generated in such solutions (from Figure 1). It is interesting to observe that, at a concentration of 10^{-4} mol·dm⁻³, the isoelectric point for bubbles is situated around pH 9.1. Thermodynamic data and the diagram suggest that this point is outside the precipitation range. Thus, this interesting observation seems to indicate that while the diagram is based on bulk thermodynamic data, the precipitation at the liquid-gas interface probably begins at pH values lower than those for the bulk phenomenon.

With regard to this observation, it is interesting to recall Leja's²³ recent review of the precipitation phenomena in the aqueous surfactant flotation systems. For the conditions of precipitation, a deviation from linearity as given by the logarithm of solubility has been experimentally observed for many systems, and different explanations have been found. Heller and Peters²⁴⁻²⁶ established that for not very stable colloidal systems the presence of the liquid/gas interface may dramatically increase the rate of coagulation. Diop and Heller even found that bubbling

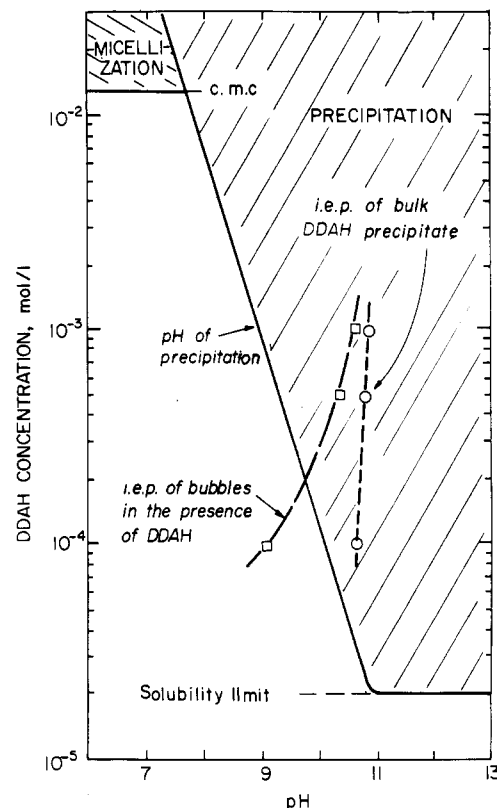


Figure 4. Thermodynamic equilibrium diagram for the aqueous solution of dodecylamine with the points showing the i.e.p. of bulk DDAH precipitate²⁰ and the i.e.p. of bubbles in the presence of DDAH (from Figure 1).

nitrogen for 3 h through an otherwise stable TiO₂ + CuO system led to the coagulation of 90% of the TiO₂ with 85% of the CuO remaining in the suspension.

The approach described in this paper, and further tests on the ζ potential of bubbles along this line of reasoning, may bring important details for both the flotation-related research and the surface coagulation concept. There is, however, a limit in such tests. At too low surfactant concentrations, the fine bubble systems are not stable enough for electrophoretic measurements.

The curves in Figure 4 also show that with an increase in concentration of dodecylamine bubble shielding becomes complete, and the isoelectric points of the bubbles and of the precipitate coincide closely. It is likely that the drop observed in the flotation of quartz with dodecylamine around pH 12 is caused by the high negative values of the ζ potential of the bubbles as shown in this paper.

The classification of ionic surfactant into weak and strong electrolytes was recently shown²¹ to be essential in the understanding of the flotation mechanism. The results of this work further corroborate such conclusions.

Conclusions

The ζ potentials of the bubbles generated in the presence of weak electrolyte type surfactants were found to be, depending on pH, either positive or negative.

The isoelectric points of the bubbles generated in dodecylamine hydrochloride solutions at concentrations ranging from 10^{-4} to 10^{-3} mol·dm⁻³ were found to be in the range from pH 9.1 to 10.6, respectively.

The isoelectric points of the bubbles generated in lauric acid solutions were found to be situated around pH 2.5 (5×10^{-4} and 10^{-3} mol·dm⁻³ concentrations) and around pH

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3.5 for sodium oleate at concentrations ranging from 10^{-4} to 5×10^{-4} mol·dm $^{-3}$.

The measured isoelectric points of the bubbles were consistently very close to the isoelectric points of the free amine or free acid precipitate, which appear in alkaline solutions for amine and in acid solutions for fatty acids.

This indicates the electric charge of bubbles in such systems results from the armoring of bubbles by the partially hydrophobic surfactant precipitate.

Registry No. Dodecylamine hydrochloride, 929-73-7; lauric acid, 143-07-7; sodium oleate, 143-19-1; sodium dodecyl sulfate, 151-21-3; sodium dodecanesulfonate, 2386-53-0.

Electrified Droplet Fission and the Rayleigh Limit

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The stability of charged evaporating droplets and the characteristics of their rupture have been investigated by trapping a single microdroplet in the superposed ac and dc electrical fields of an electrodynamic balance. By use of the method of optical resonance spectroscopy to measure the size precisely (to better than 1 part in 10^4) before and after an explosion and using suspension voltage measurements to determine the charge, droplet fission was examined in ionized and unionized gaseous media. Droplet explosions were observed to occur at lower charge densities than predicted by the classical Rayleigh theory. For several organic liquids studied in unionized air, the droplet exploded approximately 20% below the predicted limit of surface charge. The observed mass loss varied from about 1.0% to 2.3%, while the charge loss ranged from 10% to 18%. This is the first reported precise measurement of such small mass loss. In a C^{14} -contaminated balance chamber (partially ionized gas atmosphere), the explosion was also premature, but the mass loss and charge loss varied greatly. An analysis of the surface charge variations associated with thermal fluctuations was performed to determine if such fluctuations might cause the droplet to explode before the Rayleigh limit was reached, but it appears that the external electrical fields complicate the fission process and have a greater effect on the instability than either possible surface contamination or thermal fluctuations in charge.

Introduction

Electrified droplets are encountered in the atmosphere, are involved in metallic powder production, ink-jet printing, microspray lubrication, emulsification, spray painting, and crop spraying, and occur in a variety of industrial processes. Bailey¹ recently reviewed the theory and practice of electrostatic spraying. The characteristics of the fission of electrified droplets are of interest in these applications and in fuel droplet breakup.

An evaporating, electrically charged drop becomes unstable when the repulsive electrostatic force overcomes the attractive surface tension force. The drop then ruptures, sending out one or more daughter droplets and leaving behind a stable residual drop. Lord Rayleigh² first derived the criterion of instability for a conducting droplet of radius a and charge q , obtaining

$$q^2 = 64\pi^2\epsilon_0\gamma a^3 \quad (1)$$

where ϵ_0 is the permittivity of free space and γ is the surface tension of the droplet.

Several experimental studies have attempted to verify this prediction. Hendricks³ in 1962 produced charged oil drops and accelerated them through a large potential to measure size and charge. In nearly all cases the charge on a droplet was near or below the Rayleigh limit. Observations of exploding single droplets were made by Doyle, Moffett, and Vonnegut⁴ using a Millikan-type apparatus.

They reported that the Rayleigh limit was confirmed for droplets of radius 30–100 μ m; however, their method of size determination was crude and resulted in deviations as high as 20–25%. They further reported that at breakup the parent drop ejected a cloud of very small droplets which carried away about 30% of its charge but relatively little mass.

Abbas and Latham⁵ also used a Millikan condenser together with aerodynamic drag measurements to obtain the size before and after breakup. They reported confirmation of the Rayleigh limit with about $\pm 15\%$ scatter. The charge loss was found to be about 25% and the mass loss 20–30%. This relatively large mass loss conflicts with the results of Doyle et al.

Ataman and Hanson⁶ and Schweizer and Hanson⁷ experimented with single charged droplets in a quadrupole trap of Straubel's⁸ design. This quadrupole trap or electrodynamic balance used superposed ac and dc fields to maintain the droplet at the center of the ac ring electrode. The ac field is used to center the droplet, and the dc field is used to balance the gravitational field. A vertical force balance on the droplet gives

$$qC_0V_{dc}/z_0 = m_Dg \quad (2)$$

C_0 is a geometrical constant of the balance ($C_0 = 1$ for a Millikan cell with flat electrodes of infinite extent), V_{dc} is the dc voltage required to suspend the droplet, z_0 is the

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