KINETICS OF BUBBLE-PARTICLE ADHESION IN FLOTATION

by

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Introduction

1.1.-General

Froth Flotation is a physico-chemical process commonly used for beneficiating a wide variety of ores, coal, oil shale, tar sand, industrial waste and other biological substances. The importance of this process to the economy of the whole industrial world is enormous, approximately 2×10^9 tonnes of crushed rock is treated annually by flotation and the proportion of base-metals won by this process is about 95% (Kitchener, 1984).

The majority of minerals required by the man occur in complex aggregates (ores) of different minerals of which only one or two will be of value and, consequently, it is necessary to physically remove the undesired minerals prior to metallurgical processing. This involves finely grinding the ore in order to liberate the various minerals from each other, and then separating them, almost always by flotation.

The success of the flotation process depends on rendering selected minerals in a pulp hydrophobic and hence floatable while keeping or making, all the other minerals hydrophilic. In the simplest case, this is achieved by adding a surface-active agent called collector which has selectivity for the mineral to be floated. Normally, however, additional reagents are required to accentuate the differences in the surface chemical properties of the minerals. Depressants are added to prevent flotation of unwanted minerals and activators are used to promote the adsorption of collector on a given mineral. Air bubbles blown into the pulp and stabiblized by the addition of a frother, most commomly a nonionic surfactant, collect the hydrophobic particles and carry them to the froth layer at the top of the slurry, where they concentrate and overflow into a launder. The hydrophylic minerals or tailings are recovered from the bottom of the flotation cell.

The basic step in flotation, namely, the capture of mineral particles by bubbles and their collection in the form of a froth, is considered to occur in three main stages. (Derjaguin and Duckin, 1961 ; Laskowski, 1974)

a) Bubble-particle collision with the formation of a thin wetting film.

b) Thinning and rupture of the disjoining film which separates the colliding bubble and particle for the bubble/particle attachment to occur.

c) Formation of a stable bubble-particle aggregate capable of withstanding considerable disruptive forces operating in the cell.

The first of these stages is controlled by the hydrodynamic conditions in the cell and related solution chemistry for the production of bubbles of suitable size while the other two, which deal with the attachment efficiency and contact angle formation, depend mainly on the physico-chemical conditions, particularly the degree of hydrophobicity of the mineral particles. This dynamic concept of flotation introduced by Derjaguin and coworkers have shown that for a particle to be floatable, not only dewetting of the particle surface has to be thermodynamically favorable (contact angle > 0°) but kinetic criteria (induction time < time of contact) are to be satisfied.

The second stage, the thinning and rupture of the wetting film, is regarded as the most important stage in flotation (Derjaguin and Skukakidse, 1961; Rao, 1974; Laskowski, 1974; Finch and Smith, 1979 ; to name a few) because of its rate-determining effects. It is well known that on the approach of a bubble to a mineral particle the intervening film undergoes thinning and, usually, after a definite length of time, it becomes unstable and subsequently ruptures. The lifetime of the disjoining film from the onset of bubble deformation to film rupture is known as the induction time. When this time is greater than the bubble/particle contact time, the particle adhesion would be impossible even if after contact, the contact angle was large. In view of the dynamic considerations involved in the induction time concept, it is considered a better flotation criterion than the contact angle, in fact, flotation chemistry studies conducted using induction time measurements have always shown a good correlation between induction time and flotation response. The contact angle, on the contrary, does not always explain flotation behaviour.

Derjaguin and Duckin (1960), based on the DLVO theory of colloidal stability, developed the disjoining pressure concept to explain the stability of wetting layers. For flotation purposes, the disjoining pressure, P_d, is considered to be the equilibrium pressure set up within the liquid film separating the two interfaces (solid/liquid and liquid/gas) opposing direct contact betweem them (Klassen and Mokrousov, 1963) and it is thought to consist of three main components, each representing a specific type of interaction.

$$P_d = P_{elec} + P_{vdW} + P_{stru} \quad [1.1]$$

where P_{elec} is the contribution due to the electrical forces which arises when the electrical double layer at the liquid/gas interface begins to overlap that present at the mineral surface, P_{vdW} corresponds to London-van der Walls dispersion forces between atoms and P_{stru} includes the forces arising due to the presence of surfactant molecules at the interfaces and to hydration of any hydrophilic group. Depending upon the individual contribution of these components, the disjoining pressure can either prevent or accelerate the adhesion process. Positive disjoining pressure corresponds to stable films while negative disjoining pressure to unstable ones. It can be stated that whether or not a colliding particle sticks to a bubble is primarily a question of the stability of the wetting layer. Typically, thick stable wetting films are characteristic of hydrophilic mineral surfaces, whereas on hydrophobic surfaces, they are very unstable and have a short life.

The measurement of the magnitude and range of influence of the individual contributions of the disjoining pressure have been the subject of a good deal of research in the last two decades. The most prominent contributions come from the work of Kitchener and co-workers

(Read and Kitchener, 1969; Laskowski and Kitchener, 1969; Blake and Kitchener , 1972; Pashley and Kitchener, 1979) who studied the properties and behaviour of disjoining films of various thickness on naked and methylated (hydrophobic) silica surfaces using interferometry and ellipsometry techniques. One of the major finding of these early investigations was the recognition that the electrical contribution to the disjoining pressure, P_{elec}, has long-range influence (>60 nm.) and indeed has a significant bearing in the kinetics of the attachement process. In the present work, the zeta potential of microbubbles stabilized in solution of different types of surfactants will be determined with the purpose of studying the role of the bubble charge in the adhesion process. The results of the research conducted by Kitchener and co-worker have also shown that dispersion and structural forces are important only at smaller thickness (< 20nm) and can only influence the rate of thinning in the absence of significant electrostatic repulsive force. These investigators claim that in flotation the dispersion forces always oppose film thinning and therefore the instability of a disjoining film on hydrophobic solid can only be satisfactorily explained by hydrophobic structural effects.

While most of the early research in froth flotation was concerned with the chemistry and mode of action of the collectors, activators, depressants, and frothers, which are added to render the desired mineral hydrophobic, in recent years, there has been an increasing interest in the physical and chemical aspects of the adhesion process such as the hydrodynamic interaction between bubbles and particles and the thinning and rupture of the disjoining film . Two aspects that, in this regard, have captured the attention of investigators in recent years are, firstly, the determination of the contact time, i.e., the time available while the particle approaches the front of the bubble, then moves sideways and travels around the bubble, and secondly, the determination of the induction time or the time required for the wetting layer to thin and rupture. The discussion of the contact time is outside the scope of this thesis but induction time measurements will be conducted in the present work to study the flotation chemistry of the quartz-dodecyl amine hydrocloride system.

1.2.-Objectives of the proposed work

The purpose of this investigation will be to study the role of some physical and chemical variables in the particle-bubble adhesion process. Particular attention will be paid to study the role of bubble charge.

To achieve this goal, the investigation will be conducted in three different phases. The first phase will be concerned with the measurements of zeta potential of air bubbles produced in solutions of anionic, cationic and nonionic type of surfactants using electrophoresis technique. On the basis of the results, physico-chemical mechanisms responsible for the presence of electrical charge on the bubbles will be proposed.

The second phase will involve measurements of induction time for the quartz/dodecyl amine hydrochloride flotation system under different experimental conditions. To meet this goal, an improved induction time apparatus has been constructed. Micro-flotation tests will also be done to determine the correlation between induction time and floatability.

In the final stage, the role of bubble charge in the attachement process of quartz particles to air bubbles will be examined using induction time and micro-flotation techniques. Air bubbles of known electrical charge will be produced using the results of chapter II.

Since the topics covered in the three stages are to some degree independent of each other, they will be written with self-contained formats. Each chapter will have its own Introduction, Experimental, Results, Discussion and Conclusion sections.

CHAPTER II

Zeta Potential Measurements on Microbubbles Generated Using Various Surfactants

2.1.-General

Air bubbles play a very important role in the froth flotation process. They selectively collect hydrophobic particles from an ore pulp and lift them by virtue of their bouyancy to the surface of the pulp, whereby the mineralized froth is removed.

In conventional froth flotation processes, air bubbles are produced by shearing off larger bubbles into smaller ones between the rotor and the stator of the rotating impeller inside the flotation machine. However, air bubbles are usually unstable in pure water and tend to coalesce with each other. It is, therefore, necessary to stabilize them by means of a surfactant, known as a frother, which adsorbs at the air/water interface and causes the bubbles to behave somewhat as rigid spheres (Harris, 1976).

Inside the flotation cell, bubbles and particles may establish contact as they slip past each other within the agitated pulp. However, only a fraction of the total number of collisions between solid and air phases results in successful bubble-particle adhesion. Under quiescent conditions, the adhesion efficiency depends on two parameters, i.e., the induction time, which is defined as the time required to thin the film between bubble and particle, and the residence time of the particle on the bubble. The latter is determined by the hydrodynamics of the system, while the induction time is primarily a function of chemistry. For example, the addition of a collector will increase the hydrophobicity of the particle, which will help reduce the time required to thin the intervening film. Eigeles and Volova (1969) have indeed shown that the induction time decreases with increasing collector addition.

Another important factor in determining the induction time is the electrical characteristics of the particles and bubbles. If the bubble and particle have the same charge, electrostatic repulsive forces will present an energy barrier for the film thinning. On the other hand, if the gas bubbles and the mineral surface carry opposite charges, the film will rupture instantaneously by electrostatic attractive forces, provided that the particles are sufficiently hydrophobic.

An extensive amount of work has been done to study the behavior of charged mineral particles, while very little work has been done to study the electrical properties of the gas bubbles that are used in various flotation processes. In this regard, the objective of this study has been to measure the zeta potentials of microbubbles stabilized in solutions of ionic and nonionic surfactants under different conditions. It is hoped that this new information will bring about a better understanding of the complex mechanisms involved in the bubble-particle adhesion process.

2.2.-Literature Review

According to McTaggart (1922), Quincke was probably the first to carry out systematic studies on the electrification of liquid/gas interfaces. His major finding was that air bubbles acquire different charges depending on the solution composition, and that air bubbles exhibit negative charges in pure water. Further works on the electrification of gas bubbles were carried out separately by McTaggart (1922), Alty (1924) and Gilman and Bach (1938). The most important conclusions drawn from this earlier research were as follows: Firstly, bubbles acquire negative charges in pure water, supposedly due to negative adsorption of cations. Secondly, in systems comprising electrolytes, the sign of the electrical charge acquired by the bubbles depends on the type and concentration of the electrolyte used. One characteristic of these earlier studies was that the information obtained was rather qualitative, providing information as to whether bubbles generated using a given surfactant or electrolyte is positive or negative.

Derjaguin and Dukhin (1960) have shown that the rate of flotation is critically influenced by the electrical charges carried by both the mineral particles and the bubbles. More recently, Derjaguin and Dukhin (1981) have suggested that when the bubbles and the particles have opposite charges, the flotation is instantaneous. However, even in these recent studies, there is a general lack of experimental data.

The first systematic effort aimed at obtaining information regarding electrical charges on the bubbles in surfactant solutions and their effect on flotation was made by Dibbs et al. (1974). These investigators used a streaming current technique to study the quartz-amine flotation system. Their results indicate that bubbles produced in the presence of dodecylamine hydrochloride give a positive current which increases with increasing amine concentration. They have also shown that the best flotation results are obtained when the quartz particles have charges opposite to those of the bubbles. The same technique has been used by Yoon (1984) for determination of the charges of microbubbles generated using both ionic and non-ionic surfactants.

One important limitation of the streaming current technique, as pointed out by Collins et al. (1978), is that there is a lack of theoretical analysis to obtain more useful information, such as zeta potential, from the streaming current. For this reason, Collins et al. (1978) measured the electrophoretic mobilities of small gas bubbles generated by electrolysis. However, the experimental data presented by these investigators were not extensive.

Usui and Sasaki (1978) used the Dorn potential or the sedimentation potential technique to measure the zeta potentials of bubbles in aqueous solutions of anionic, cationic and nonionic surfactants. The results reported show that in the case of ionic surfactants, the sign of the zeta potential is determined invariably by the charge of the polar group of the surfactant; that is, cationic surfactants produce positively charged bubbles and anionic surfactants produce negatively charged bubbles. It is interesting to note that nonionic surfactants produce negatively charged bubbles and the zeta potential does not change significantly with the surfactant concentration. More recently, Usui et al. (1981) observed, using the same technique, that the zeta potential of a bubble is significantly affected by its size. These investigators did not study the effect of pH, however, which is an important variable in flotation practice.

Other investigators used the electrophoresis technique. Kubota et al. (1983) used a flat cell to measure the zeta potentials of bubbles generated by the dissolved air technique. Presumably, these bubbles were small enough for their mobilities to be measured. These investigators showed that when using anionic surfactants, i.e., dodecylbenzene sulfonate and sodium dodecylsulfate, the negative zeta potential increases with increasing concentration until it reaches a plateau near the critical micelle concentration (CMC). With a cationic surfactant, i.e., cetylpyridinium chloride, the authors observed positive zeta potentials. Fukui and Yuu (1982) also used a flat cell in which small bubbles were generated by electrolysis. In the presence of cetyltrimethylammonium bromide (CTAB) and ethanol, they observed positive zeta potentials, which decrease with increasing electrolyte (sodium sulfate) concentration.

The electrophoresis techniques employed by McShea and Callaghan (1983) involves a spinning cylinder. They showed that bubbles are negatively charged both in distilled water and in the presence of 10^{-4} M KCl at pH 7. Nonionic surfactants produced negatively charged bubbles while cationic and anionic surfactants produced positively and negatively charged bubbles, respectively.

2.3.-Experimental

2.3.1.-Reagents

The surfactants used in this study to stabilize bubbles are listed in Table 2.I. These reagents were used as received, without further purification.

To study the effect of inorganic electrolytes on the zeta potentials of microbubbles, certified ACS grade potassium chloride (Fisher Scientific Company) was used. Reagent grade hydrochloric acid and sodium hydroxide solutions were used for pH control. Double-distilled water, prepared in an all-glass still, was used in all the experiments. Chromic acid was used for cleaning the glassware and the electrophoretic cell. Ultra-pure compressed nitrogen (99.999%), as obtained from AIRCO Industrial Gas Company, was used to produce the microbubbles.

2.3.2.-Equipment and Procedure

In order to be able to measure the electrophoretic mobility of air bubbles in a flat cell, it is necessary to produce very small bubbles so that their buoyancy force is reduced to a minimum. In the present work, microbubbles (40- to 80-micron) were produced in a system similar to that described by Sebba (1971).

A Rank Brothers particle microelectrophoresis apparatus, Mark II, was used to determine the mobilities of the microbubbles. The flat cell was modified as shown in Figure 2.1. The two pieces of glass tubing

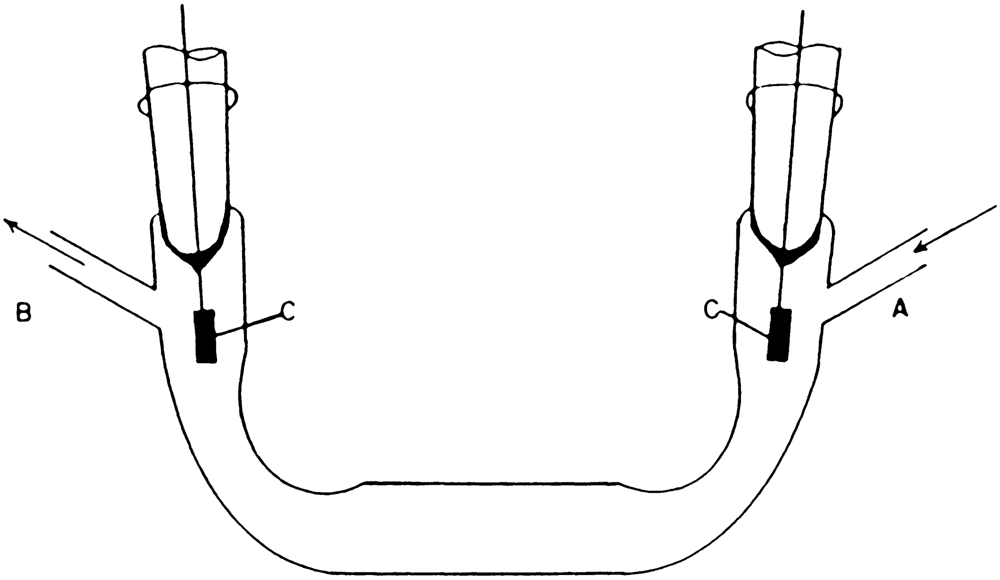
Table 2.1

Description of Surfactants Used in Zeta Potential Experiments

Surfactants	Chemical Formula	M.W.	Status	Purity	Source
Anionic					
Sodium Dodecyl Sulfate	$C_{12}H_{25}OSO_3Na$	288.38	Solid	R.G.	BHD Chemical, Ltd.
Sodium Oleate	$C_{17}H_{33}COONa$	304.0	Solid	R.G.	Fisher Sci. Co.
Cationic					
Dodecylamine Hydrochloride	$CH_3(CH_2)_{11}NH_2HCl$	221.82	Solid	R.G.	Eastman
Cetyl Pyridinium Chloride	$C_{21}H_{38}ClNH_2O$	358.0	Solid	R.G.	Pfaltz and Bauer, Inc.
Nonionic					
Polypropylene Glycol	$H[OCH(CH_3)CH_2]_nOH$	425.0	Liquid	*	Aldrich
Polyoxyethylene Methyl Ether	$CH_3(OCH_2CH_2)_nOH$	350.0	Liquid	*	Aldrich
Polyoxyethylene Dodecyl Ether	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$ (Brij 35)	1199.6	Solid	*	Aldrich
	$C_{12}H_{25}(OCH_2CH_2)_4OH$ (Brij 30)	362.56	Liquid	*	Aldrich

R.G. = Research Grade

* = Not specified



A INLET
B OUTLET
C PLATINUM ELECTRODES

Figure 2.1. Modified flat cell

(1.6 mm ID) attached to the cylindrical parts of the cell were to allow continuous passing of the microbubble suspension through the cell while measuring the depth of the cell and focusing the microscope at the stationary level. When the microscope was focused properly, the flow of the microbubble suspension was stopped and the mobilities were measured immediately. An electrical field was applied to the solution by means of two platinized-platinum electrodes. Ten readings were taken at each stationary level and averaged in a given experiment.

All measurements were carried out at ambient temperature and, after each test, the flat cell was cleaned with chromic acid and double-distilled water prior to the next set of measurements.

2.4.-Results

2.4.1.-Anionic Surfactants

Two anionic surfactants, i.e., sodium dodecyl sulfate and sodium oleate, were used to generate microbubbles, and the zeta potentials were measured under various experimental conditions.

2.4.1.1.- Sodium dodecyl sulphate:

a) Effect of concentration

Figure 2.2 shows the results obtained at pH 10.3 ± 0.2 by varying the concentration of the surfactant from 10^{-5} to 10^{-2} moles/l. As shown, the bubbles were negatively charged throughout the concentration

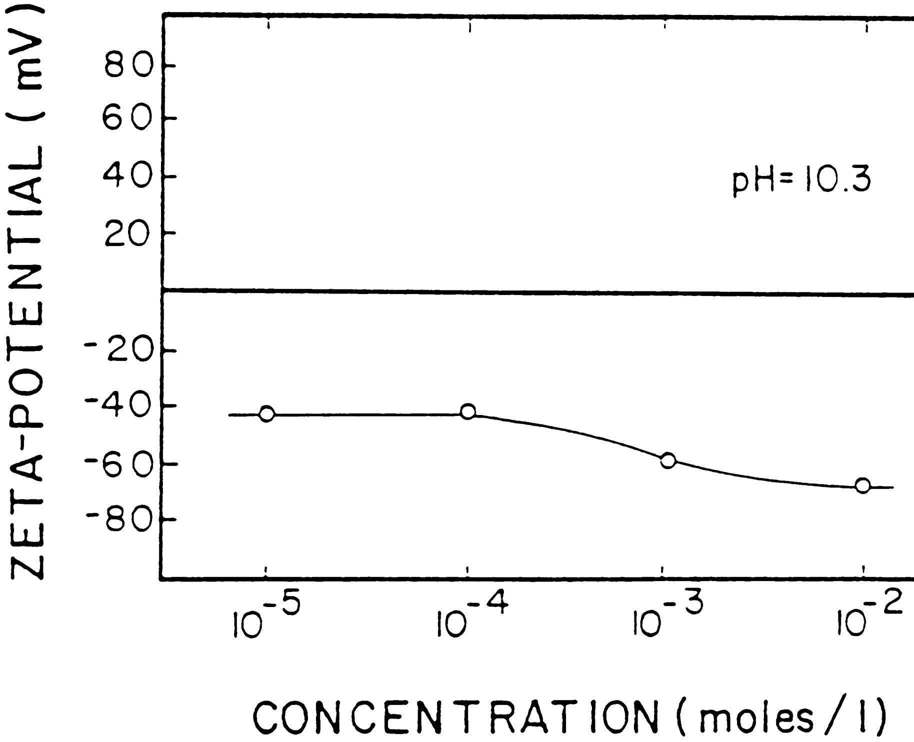


Figure 2.2. Effect of concentration on the zeta potential of microbubbles generated using sodium dodecyl sulfate solution at pH 10.3

range studied. It, thus, shows that the charge of a bubble is determined by the charge of the polar group of the surfactant molecule that is adsorbed on its surface.

The zeta potential becomes more negative with an increase in the surfactant concentration, which is most likely due to the fact that the adsorption density at the air/water interface increases with increasing concentration. These results are in agreement with the work of other researchers. McShea and Callaghan (1983) and Kubota et al. (1983) showed that in the presence of sodium dodecylsulfate (SDS), the bubble charge becomes more negative with increasing concentration. The latter investigators also used the electrophoresis technique.

b) **Effect of pH**

Figure 2.3 shows the results of the zeta potential measurements conducted on the microbubbles stabilized by SDS as a function of pH. Three different sets of experiments were carried out using 10^{-4}, 10^{-3} and 10^{-2} moles/1 SDS solution. In all three cases, the zeta potentials remain negative throughout the pH range studied. It is also shown that the zeta potential becomes more negative as the concentration of the anionic surfactant increases.

Note that the zeta potential tends to become less negative as the pH approaches 3, which may be attributed to the adsorption of neutral hydrolysis products on the surfaces of the bubbles. At pH values above 5, where the surfactant is completely ionized, the zeta potentials remain more or less constant at a given concentration.

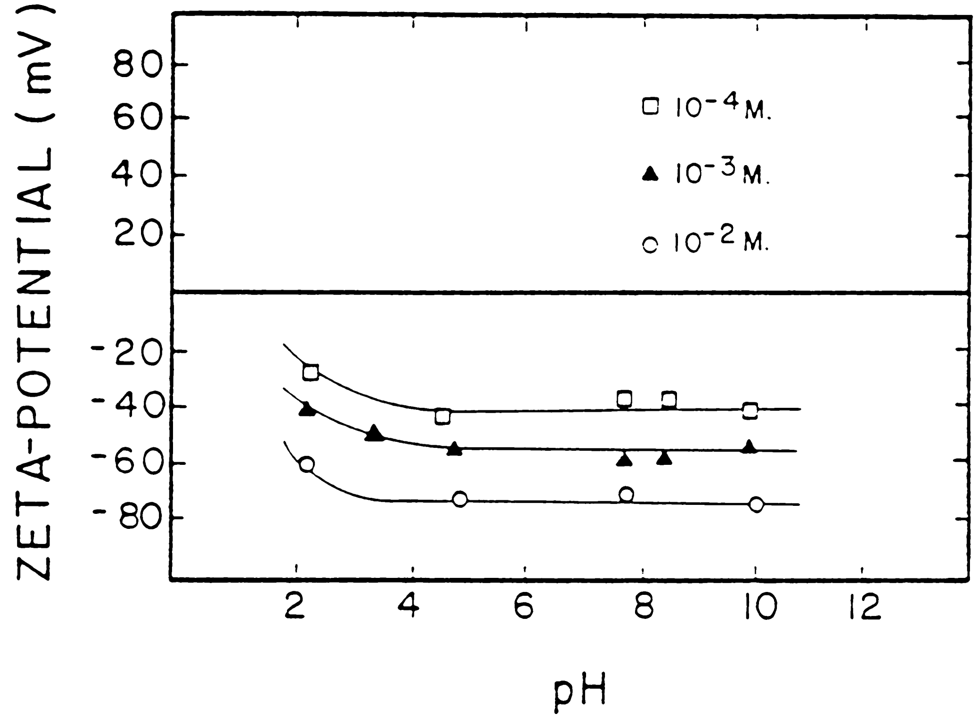


Figure 2.3. Effect of pH on the zeta potential of microbubbles generated using different concentrations of sodium dodecyl sulfate solution.

c) Effect of electrolyte addition

It has been well established that the zeta potentials of charged particles are reduced in the presence of indifferent electrolytes due to double-layer compression. In order to see if the same is observed with bubbles, the zeta potentials of microbubbles were measured in the presence of KCl as a function of its concentration. The bubbles were stabilized by 1×10^{-5} moles/l of SDS at pH 10.6. The results given in Figure 2.4 show that the zeta potential does decrease with increasing electrolyte concentration, suggesting that the electrical double-layer around a bubble behaves similarly to that around a particle. Collins et al. (1978) and Fukui and Yuu (1982) also observed a decrease in the zeta potential of bubbles with increasing electrolyte (Na_2SO_4) concentration. These investigators used cetyltrimethylammonium bromide (CTAB) and ethanol to produce the bubbles.

2.4.1.2.-Sodium oleate:

a) Effect of pH and surfactant concentration

Figure 2.5 shows the results obtained with the bubbles generated in the presence of 10^{-5} and 10^{-4} moles/l sodium oleate solutions. The bubbles exhibit negative zeta potentials which become more negative at higher concentrations. As is the case with SDS, the charge of the bubbles is shown to be determined by the charge of the polar group.

Compared to those generated using SDS (Figure 3), the bubbles

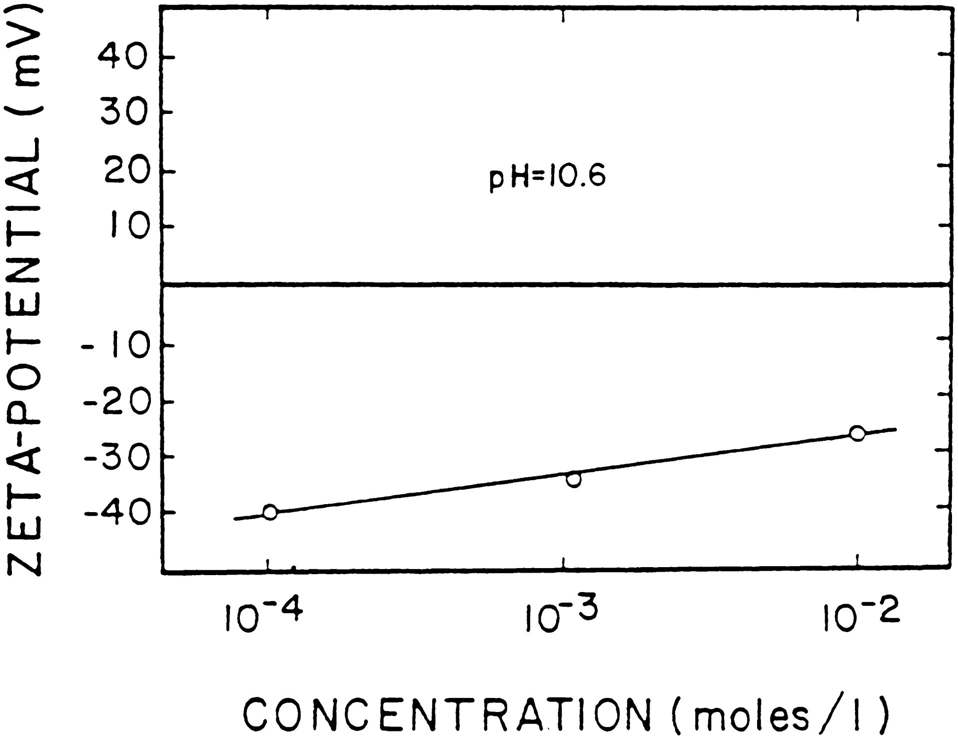


Figure 2.4. Effect of KCl concentration on the zeta potential of microbubbles generated using 1×10^{-5} mole/l sodium dodecyl sylfate solution at pH 10.6.

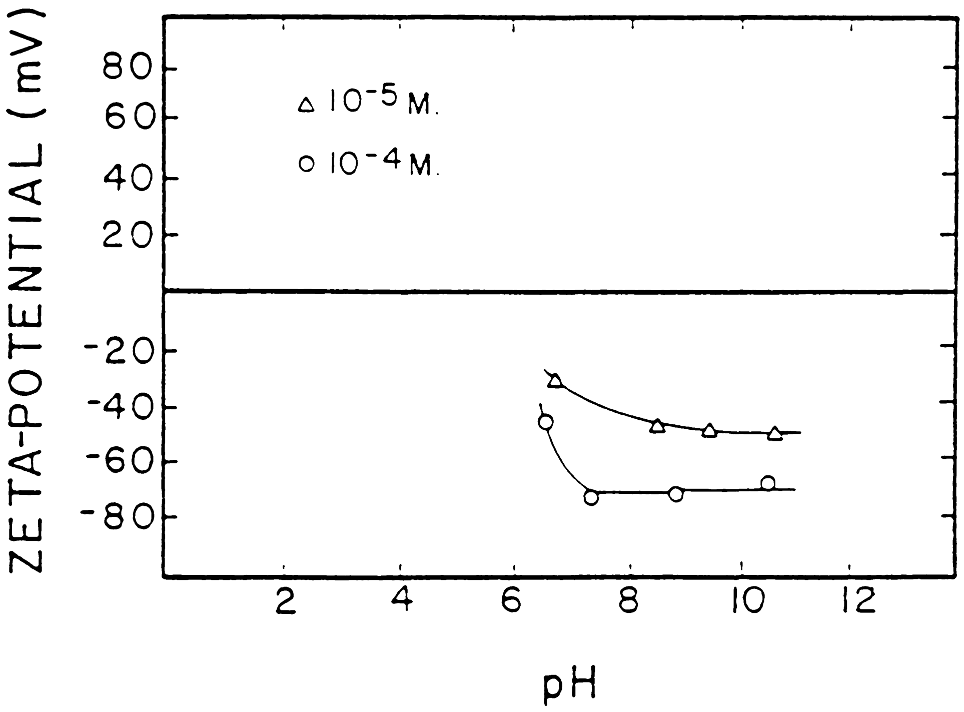


Figure 2.5. Effect of pH on the zeta potential of microbubbles generated using different concentrations of sodium oleate solution.

generated in the presence of oleate show a more significant pH dependence. When the pH was kept in the alkaline region, the zeta potentials of the bubbles remained relatively constant. However, as the pH was reduced to about 6.4, the zeta potential was considerably less negative. This may be explained by the acid formation, which becomes significant when the pH approaches 6. The pK_a values of sodium oleate have been reported to be 5 (Fuerstenau, 1982).

2.4.2.-Cationic Surfactants

2.4.2.1.-Dodecylamine hydrochloride:

a) Effect of concentration

Figure 2.6 shows the results of the zeta potential measurements conducted on the microbubbles generated using dodecylamminium hydrochloride (DAH). The surfactant concentrations were varied while keeping the pH constant at 7.1. As shown, the bubbles are positively charged at this pH and the zeta potential increases with increasing concentration. The results show again that the charge of the bubbles is determined by the charge of the polar group of the surfactant. Other investigators (Dibbs et al., 1974; Usui and Sasaki, 1978; Collins et al., 1978; Kubota et al., 1983; McShea and Callaghan, 1983) have also showed that bubbles are positively charged in the presence of cationic surfactants.

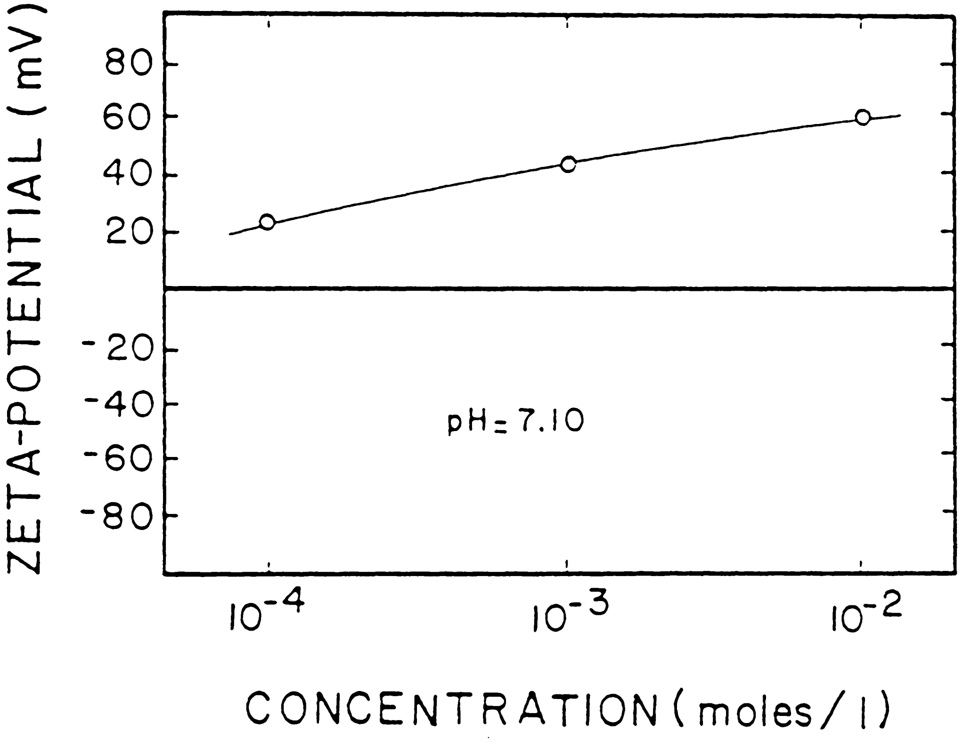


Figure 2.6. Effect of concentration on the zeta potential of microbubbles generated using dodecyl amine hydrchloride at pH 7.1.

b) **Effect of pH**

Figure 2.7 shows the effect of pH on the zeta potentials of microbubbles generated using DAH solutions of different concentrations. It shows that in the acidic range, the zeta potentials are positive in sign and the magnitude remains relatively constant. However, as the pH is increased from 6 to 10, the zeta potential becomes less positive, reaching the isoelectric points (i.e.p.) in the range of pH 10-10.5. Above this pH range, the zeta potential reverses its sign and becomes more negative with further increase in pH.

This behavior seems to be in agreement with the findings of Dibbs et al. (1974) obtained using the streaming current technique. These investigators explained this charge reversal in terms of the changing hydrolysis of amminium ions to neutral amine at high pH.

2.4.2.2.-Cetyl pyridinium chloride

a) **Effect of pH and surfactant concentration**

Contrary to the results obtained with DAH, the zeta potentials of microbubbles produced in the presence of CpCl remain relatively constant with pH, as shown in Figure 2.8. This result is not surprising because pyridinium ions do not undergo hydrolysis to become neutral species at alkaline pH. It is also shown that the zeta potential becomes more positive with increasing surfactant concentration, which can be explained with increasing packing density of the surfactant on the

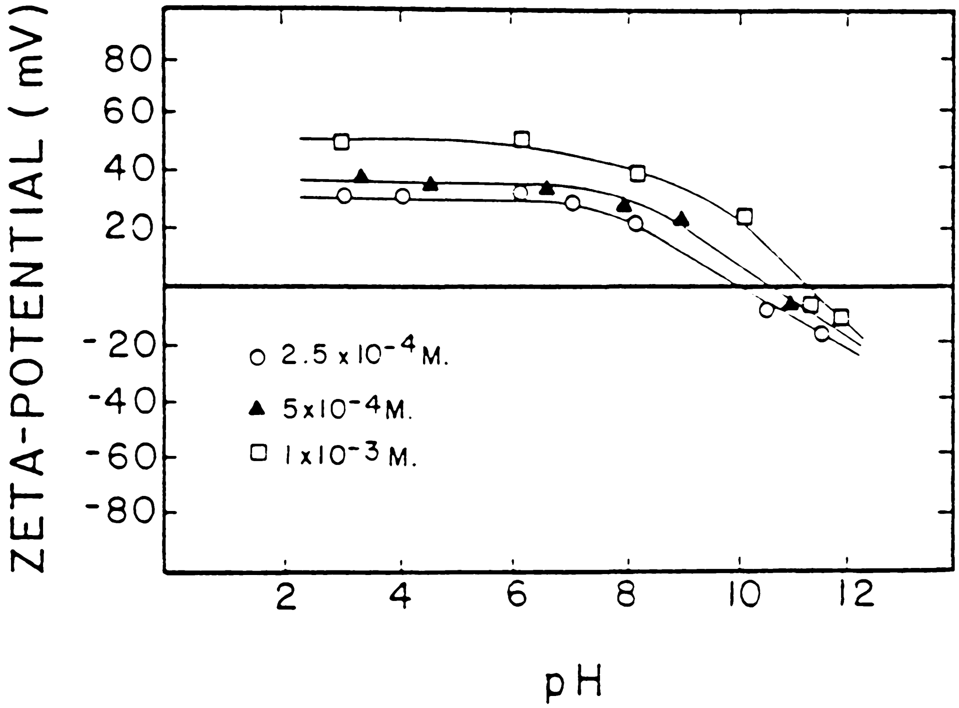


Figure 2.7. Effect of pH on the zeta potential of microbubbles generated using different concentrations of dodecylamine hydrochloride solution.

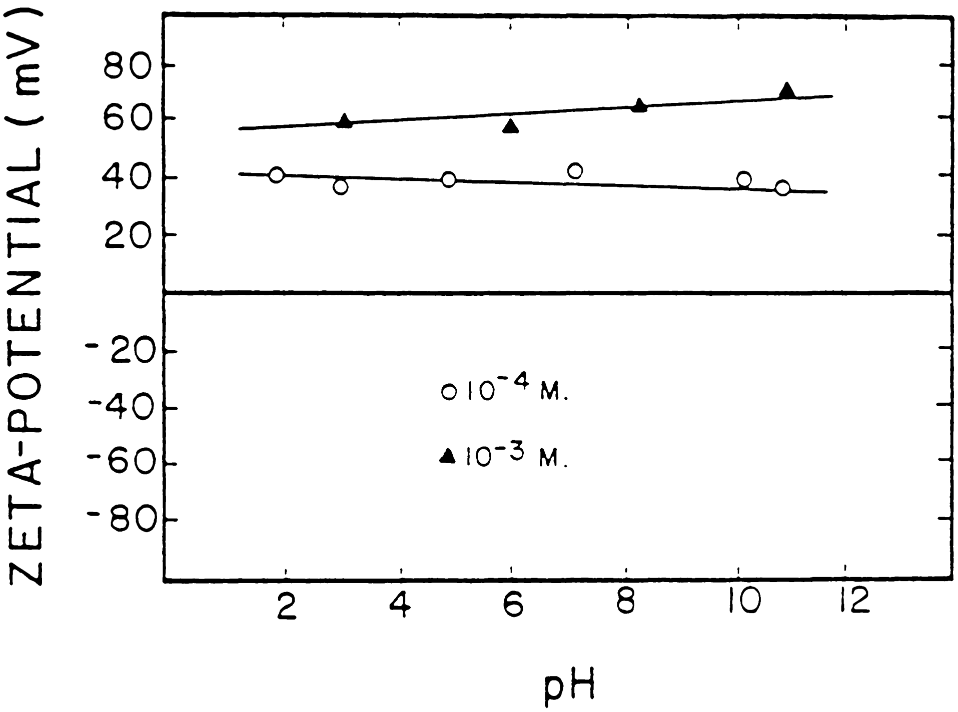


Figure 2.8. Effect of pH on the zeta potential of microbubbles generated using different concentrations of cetyl pyridinium chloride solution.

bubble surface. Kubota et al. (1983) also observed a positive charge on bubbles stabilized by CpCl.

2.4.3.-Nonionic Surfactants

Microbubbles generated using nonionic surfactants have been used for the flotation of micronized coal particles (Yoon, 1982; Yoon et al., 1984). Attempts to use microbubbles generated using ionic surfactants for flotation failed; in general, poor selectivity was observed as compared to using microbubbles generated using nonionic surfactants. The nonionic surfactants used for flotation tests included: polypropylene glycol (PPG) (average MW = 425), polyoxyethylene dodecyl ether with varying numbers of ethylene oxide groups, and polyoxyethylene methyl ether.

2.4.3.1.-Polypropylene glycol

Figure 2.9 represents the results of the zeta potential measurements conducted on the microbubbles stabilized by PPG 425 as a function of surfactant concentration at several different pH values. At a given pH, the zeta potential remained nearly constant over the PPG concentration range studied. It is interesting to note that, contrary to the results previously obtained for ionic surfactants, the zeta potential seems to be independent of the PPG concentration. This suggests that the increase in surfactant adsorption at the gas-solution

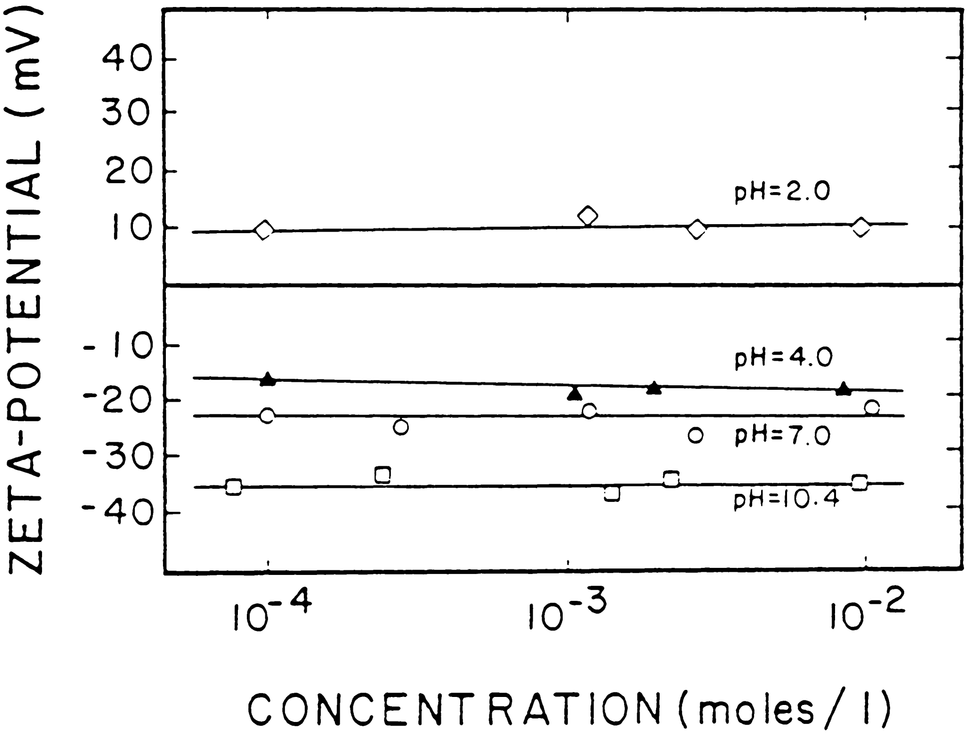


Figure 2.9. Effect of concentration on the zeta potential of microbubbles generated using polypropylene glycol solutions of different pH.

interface does not increase the net charge.

The same data given in Figure 2.9 are plotted as a function of pH in Figure 2.10. The error bars indicate the spread of data points due to concentration change. The microbubbles become increasingly negative with increasing pH. However, at pH about 3.3, the zeta potential is reversed to become positive at lower pH. These results may suggest that the frother molecules have an affinity toward H^+ ions, probably due to the presence of ethylene oxide groups.

2.4.3.2.-Polyoxyethylene methyl ether

a) Effect of surfactant concentration

Figure 2.11 shows the results obtained with polyoxyethylene methyl ether (average MW = 350) as a function of concentration at five different pH values. As has been the case with PPG-425, the zeta potential does not change significantly with the surfactant concentration in neutral and acidic solutions. However, at pH 8.2 and 10.2, the negative zeta potential increases with increasing concentration, which might be attributed to the micelle formation. It is well known that polyoxyethylene alkyl ethers can form micelles while polyoxypropylene alkyl ethers cannot (Leja, 1982; Schick, 1967), which explains the zeta potential increase observed with the former surfactant but not with the latter.

Figure 2.12 shows the results of the zeta potential measurements conducted as a function of pH on the microbubbles produced using 6×10^{-4}

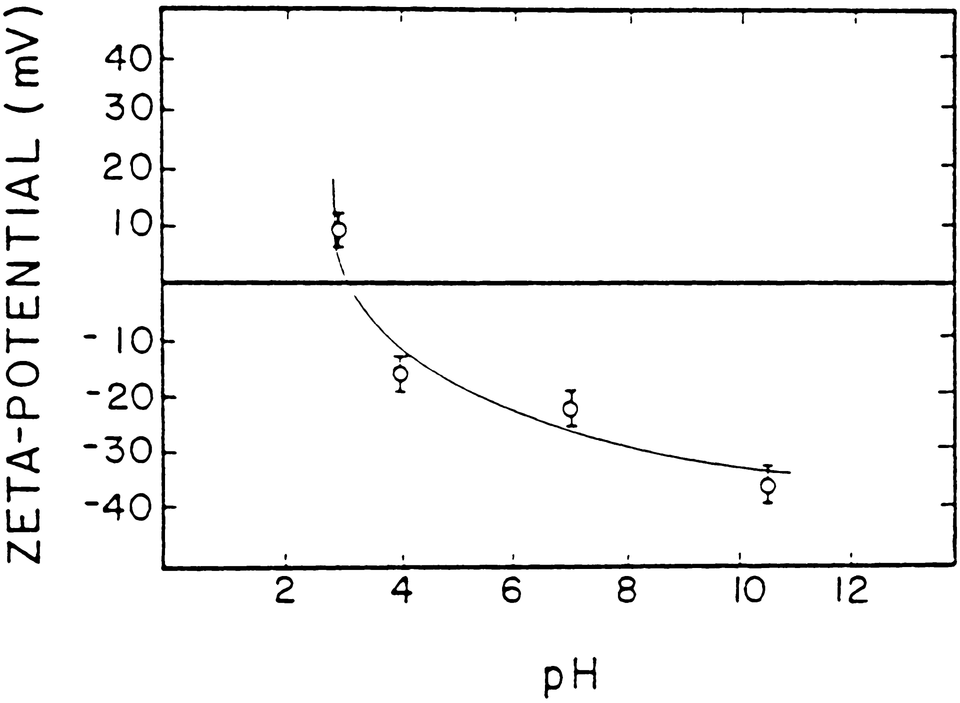


Figure 2.10. Effect of pH on the zeta potential of microbubbles generated using different concentrations of polypropylene glycol solution.

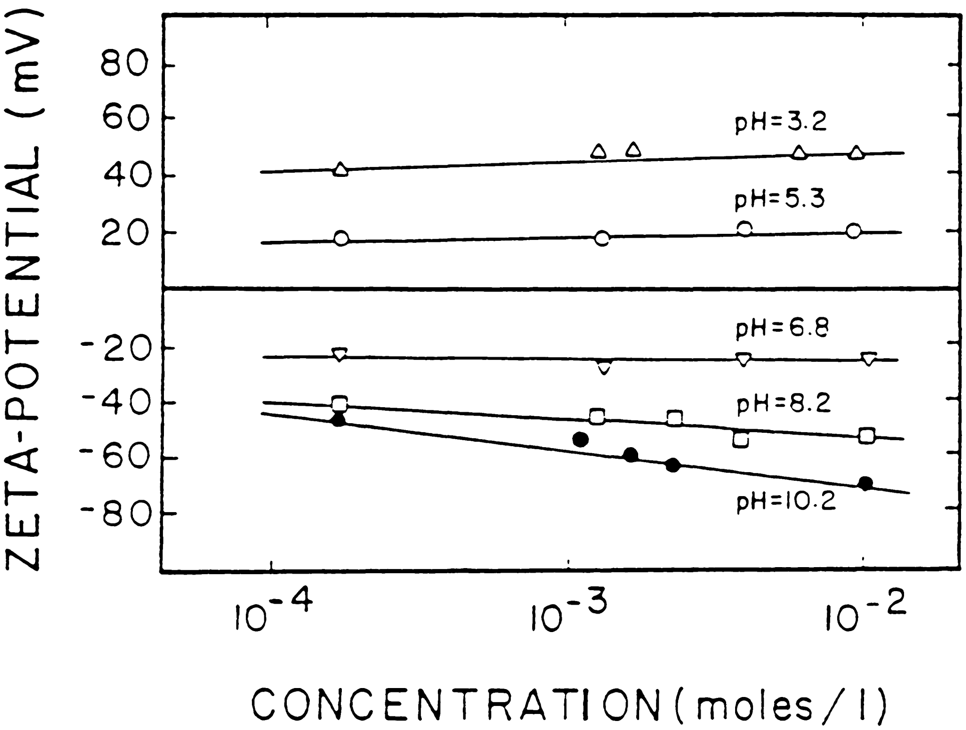


Figure 2.11. Effect of concentration on the zeta potential of microbubbles generated using polyoxyethylene methyl ether solutions of different pH.

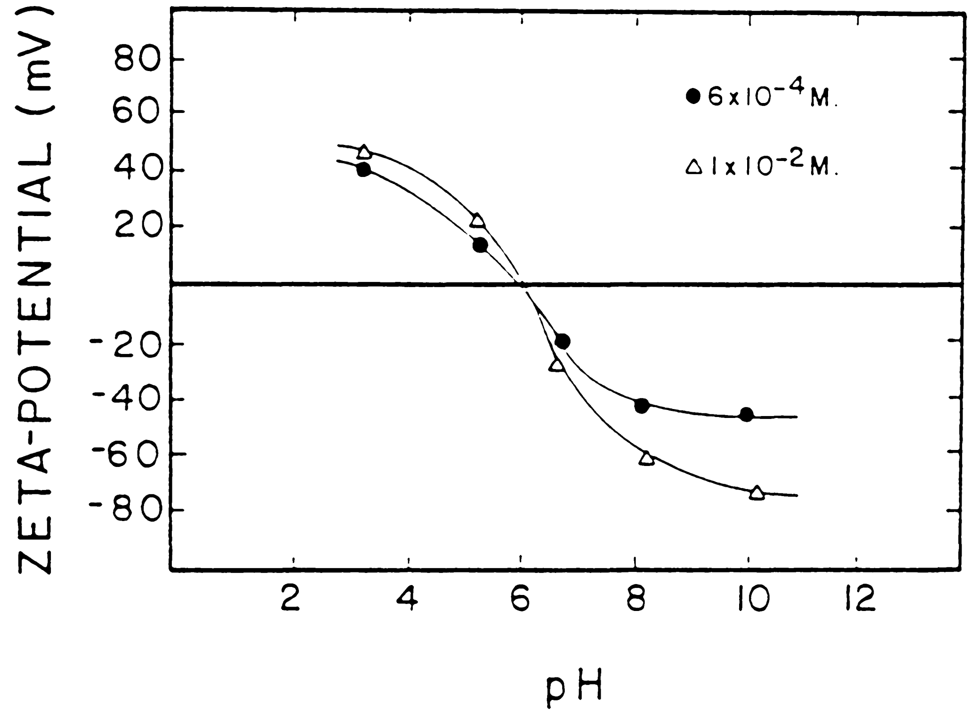


Figure 2.12. Effect of pH on the zeta potential of microbubbles generated using different concentrations of polyoxyethylene methyl ether solution.

and $1x10^{-2}$ moles/l polyoxyethylene methyl ether solutions. As shown, the microbubbles have an i.e.p. at pH 5.9; the bubbles are negatively charged above this pH and positively charged below it. This value is significantly higher than the i.e.p. of the bubbles stabilized by PPG-425 (Figure 2.10). In flotation practice, one can, thus, control the bubble charge by choosing different nonionic surfactants.

2.4.3.3.-Polyoxyethylene dodecyl ether:

a) Effect of surfactant concentration

Figure 2.13 compares the zeta potentials of microbubbles produced with polyoxyethylene dodecyl ether with different ethylene oxide (EO) groups. One has 4 EO groups and the other has 23 EO groups, but its effect is not very pronounced. As shown, in both cases the zeta potentials were negative at pH 7.25, with the magnitude being relatively constant at -40 mv over the concentration range studied. This value is close to that reported by Usui and Sasaki (1978) using the same type of surfactant with an average of 6.5 EO groups per molecule.

It is rather surprising to note that the zeta potential of the microbubbles does not increase with increasing surfactant concentration although this type of surfactant is known to form micelles (Schick, 1967). Usui and Sasaki (1978) have also reported the same trend. In view of the results obtained with polyoxyethylene methyl ether (Figure 11), however, the zeta potential may increase with surfactant concentration (Figure 11) at a higher pH.

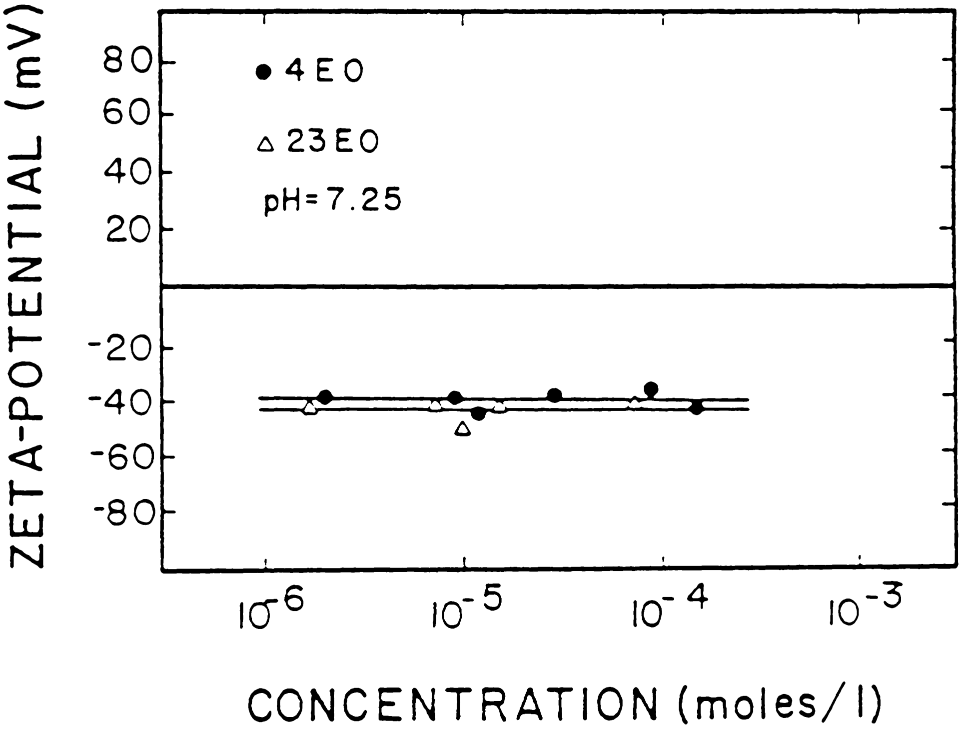


Figure 2.13. Effect of concentration on the zeta potential of microbubbles generated using polyoxyethylene dodecyl ethers with different numbers of EO groups.

Figure 2.14 shows the zeta potential of the microbubbles produced in 1×10^{-5} moles/l polyoxyethylene dodecyl ether solutions as a function of pH. It can be seen that the bubbles are negatively charged throughout the pH range investigated. However, the zeta potential becomes less negative as the pH approaches appromately 2. Note also that the bubbles produced with polyethylene dodecyl ether with 23 EO groups tend to be less negative than those produced with 4 EO groups in an acidic pH range, which may suggest that EO groups attract protons.

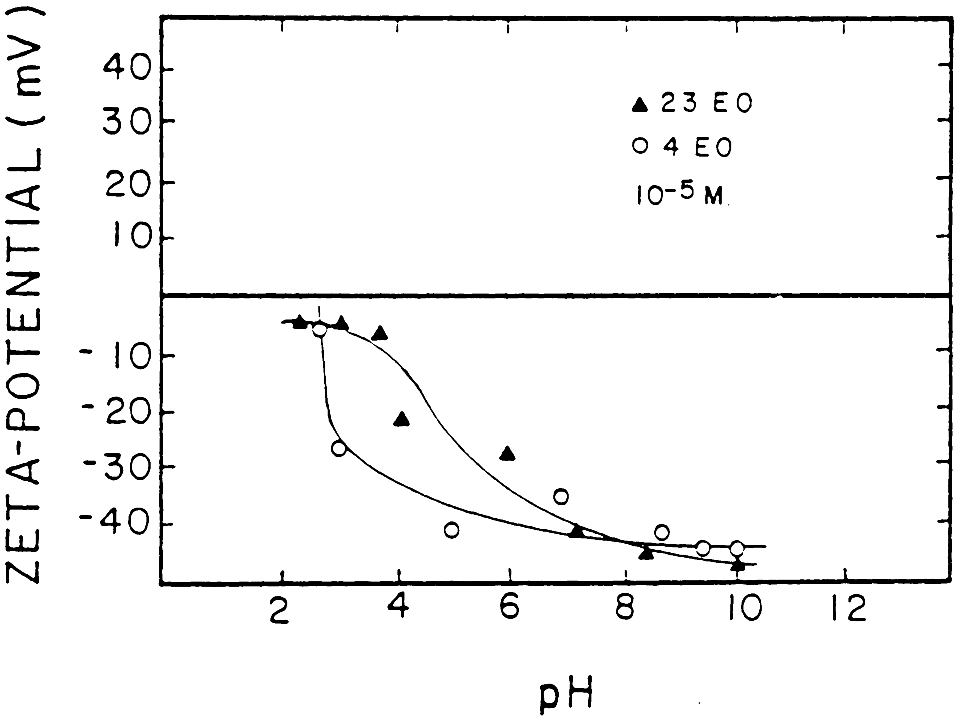


Figure 2.14 Effect of pH on the zeta potential of microbubbles generated using polyoxyethylenes with 4 and 23 ethylene oxide groups.

2.5.-Discussion

The results presented in the foregoing section show that a simple microelectrophoresis technique developed in the present work offers a convenient method of determining the zeta potentials of air bubbles. It has been shown that different surfactants produce different charges on the bubbles. In general, cationic surfactants produce positively charged bubbles, while anionic surfactants produce negatively charged bubbles. Nonionic surfactants, on the other hand, produce negatively charged bubbles in the alkaline pH range and positively charged bubbles in the acidic pH range. The pH also plays an important role in the charging mechanism of bubbles produced with ionic surfactants.

Since the earliest investigations on bubble charge measurements, it has been known that air bubbles produced in pure water are negatively charged (Currie and Alty, 1930; Gilman and Bach, 1938). The charging mechanism proposed by Currie and Alty presumes an orientation of water dipoles at the interface. The orientation of the dipoles is such that negative ions, i.e., OH^-, are attracted to the interface. However, no thermodynamic reasoning is given for the preferred orientation.

When a surfactant is present in the system, the nature of the surfactant molecules adsorbed at the air/water interface will determine the bubble charge. Thus, it is not surprising to see that the bubbles are negatively charged when anionic surfactants are used to generate the bubbles, and positively charged when cationic surfactants are used. It appears, however, that some surfactants are undergoing hydrolysis, in which case the hydrolysis products should determine the bubble charge. Since the hydrolysis of surfactants is pH-dependent, the bubble charge must also be pH-dependent.

2.5.1.-Effect of Anionic Surfactants

It has been shown in Figure 2.3 that bubbles generated using sodium dodecyl sulfate are negatively charged throughout most of the pH range studied. However, the zeta potential tends to become less negative below approximately pH 3, which may be attributed to the acid formation. According to Leja (1982), alkylsulfates are hydrolyzed to produce alcohol and bisulfate at pH values below 3. Since alcohol is nonionic, the bubble charge should become less negative below this pH, as has been observed in the present work. It is possible, however, that the adsorption takes place as alkylsulfuric acid.

Hydrolysis also plays an important role in the bubble charging mechanism in the presence of sodium oleate. As shown in Figure 2.5, the zeta potential is negative throughout the pH investigated, but it becomes less negative as the pH becomes lower than the value of pK_a (=4.9) of the surfactant. Figure 2.15 represents the distribution diagram for the species present in the sodium oleate-water system. The thermodynamic data used for the construction of this diagram are from Ralston (1948). As shown, the concentrations of the negatively charged species, i.e., $RCOO^-$ and $(RCOO)_2^-$, are reduced below pH 7.9, and the neutral species such as RCOOH(aq) and RCOOH(l) become predominant below this pH. This may provide an explanation for the decrease in the

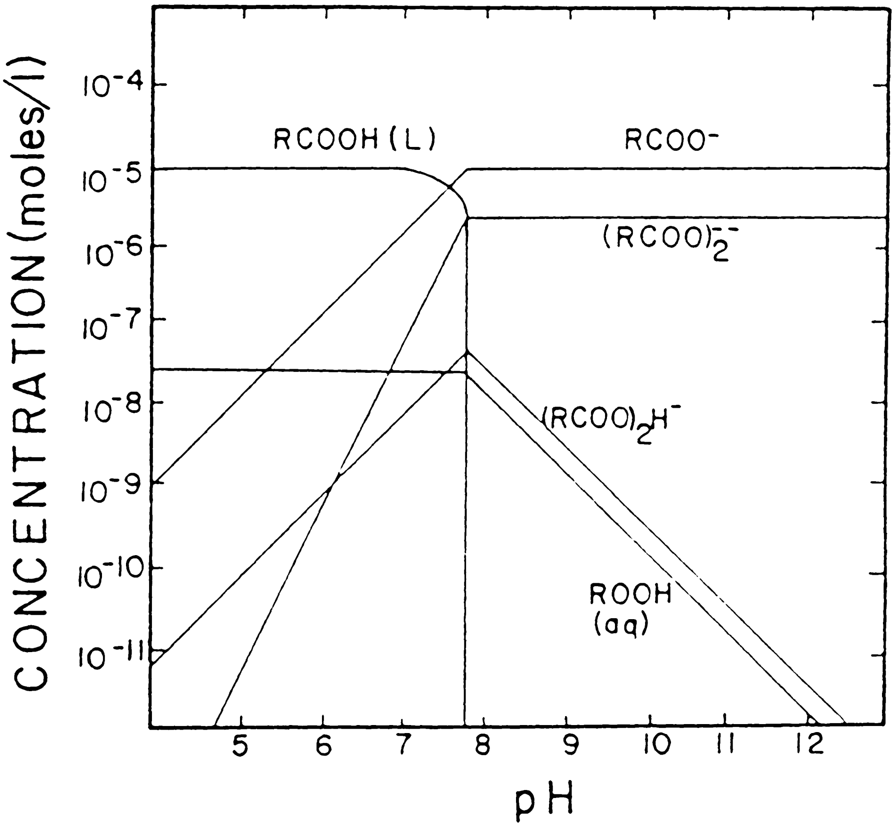


Figure 2.15. Species distribution diagram for the sodium oleate-water system.

negative zeta potential. Note, here, that the most stable oleate species in the acidic pH solutions is in liquid form, i.e., the surfactant precipitates out as RCOOH(l). For this reason, the bubbles become unstable in acidic pH, and the measurements of bubble charge become difficult, as shown in Figure 2.5.

Usui and Sasaki (1978) and Kubota et al. (1983) showed that in the presence of sodium dodecyl sulfate, the bubble charge becomes more negative with increasing concentration up to the critical micelle concentration (CMC), which has been reported to be 8.1×10^{-3} moles/l (Rehfeld, 1967). A similar result has been obtained in the present work, as shown in Figure 2.2; the zeta potential decreases from -40 mv at 10^{-5} moles/l to -70 mV at 10^{-2} moles/l. As the surfactant concentration increases, the adsorption density (Γ) of the surfactant at the bubble surface will increase according to the Gibbs adsorption equation,

$$\Gamma = - \frac{1}{RT} \frac{d\gamma}{d \ln a} \qquad [2.1]$$

in which a is the activity of the surfactant, γ is the surface tension and R and T are the usual constants. The increased packing density of the anionic surfactant at the bubble surface will increase the negative zeta potential until the CMC is reached. At concentrations higher than the CMC, however, Γ will not increase since γ is constant and, therefore, the bubble charge will remain constant.

It appears that the classical double-layer theories can be applied to the charged air bubbles. As shown in Figure 2.4, the zeta potential of bubbles is reduced in magnitude with increasing salt (KCl) concentration due to double- layer compression.

2.5.2.-Effect of Cationic Surfactants

In the present work, two cationic surfactants have been used to study their effects on bubble charge. When using cetyl pyridinium chloride, which is difficult to hydrolize like any other quarternary amminium salt, the zeta potential is positive and remains essentially constant throughout the pH range investigated when the surfactant concentration is relatively low (10^{-4} moles/l), as shown in Figure 2.8. When the surfactant concentration is increased to 10^{-3} moles/l, however, there is a slight tendency for the zeta potential to increase with increasing pH. This small increase might be attributed to the possible increase in the surface activity due to the counterbalancing of the positive charge of the surfactant molecules by the hydroxyl ions. It is well-known that the surface activity of ionic surfactants increases due to the presence of counter ions.

The other cationic surfactant, i.e., dodecyl amminium hydrochloride, is readily hydrolized at alkaline pH and behaves quite differently in the bubble charging mechanism. As has been shown in Figure 2.7, the positive zeta potential is reduced as the pH approaches that of precipitation, and becomes slightly negative at higher pH. These results can be explained by means of Figure 2.16 showing the

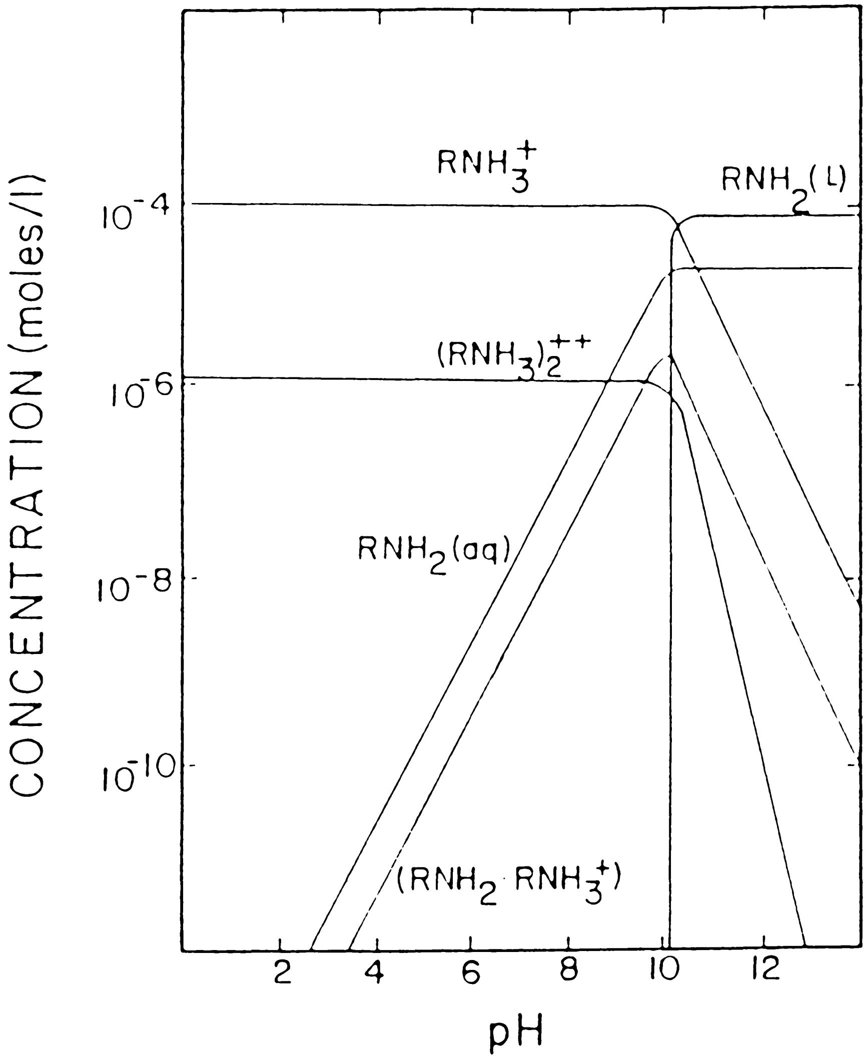


Figure 2.16. Species distribution diagram for the dodecylamminium hydrochloride-water system.

distribution of the hydrolysis products as a function of pH at 1×10^{-4} moles/l. The thermodynamic data used for constructing this diagram are from Ananthpadmanabhan et al. (1980). As shown, the concentrations of charged species such as RNH_3^+, $(RNH_3)_2^{2+}$ and $RNH_2 \cdot RNH_3^+$ decrease above pH 10.2, while the neutral species, i.e., RNH_2, becomes predominant above this pH. Apparently, the adsorption of neutral molecules at the air/water interface gives rise to a slight negative charge, as will be further discussed in the next section.

2.5.3.-Effect of Nonionic Surfactants

The nonionic surfactants used in the present work include polypropylene glycol (PPG) (with an average molecular weight of 425), polyoxyethylene methyl ether, and polyoxyethylene dodecyl ether with different numbers of ethylene oxide groups. The charging mechanism of air bubbles in the presence of these surfactants appears to be quite different from those of the ionic surfactants. In the latter case, it has been shown that the charge of the polar group determines the charge of the bubbles and that the hydrolysis of the polar group is playing an important role. The nonionic surfactants do not have charged groups as such, yet their presence on the bubble surface is shown to have a profound effect. The same difficulty is encountered in explaining the charging mechanisms of air bubbles produced in pure water and of pure hydrocarbon droplets suspended in water since there are no apparent chemically-active elements or groups at the interface that can attract the charged species such as H^+ and OH^- ions.

A possible charging mechanism at the interface that has no apparent H^+ or OH^- acceptors may be proposed here on the basis of the difference in the hydration energies of H^+ and OH^- ions. According to the 'best' thermodynamic data listed by Conway (1978), the enthalpy of hydration (H_s^o) of H^+ and OH^- are -1104 and -446.8 kJ/mole. Due to this difference in hydration energy, there will be an unequal distribution of H^+ and OH^- ions at an interface that has no specific affinity toward either one of these ions. In the vicinity of such 'inert' interfaces as air/water and hydrocarbon/water, the more strongly hydrated H^+ ions will have a greater tendency to remain in the bulk aqueous phase than the less strongly hydrated OH^- ions. This results in negative adsorption of protons at the interface, which in turn creates a net negative charge at the surface. The proposed mechanism suggests that the charge arises due to the intrinsic property of water and not to the nature of the interface as long as the second phase, e.g., hydrocarbon and air, does not have a significant acid-base property. Saturated hydrocarbons are not known to have such a property (Fowkes, 1983), and, of course, neither does air.

Although the proposed mechanism suggests that the air bubbles and hydrocarbon oils are negatively charged, the charge density must vary with pH. At a low pH, some of the H^+ ions can move back to the interface due to the increased chemical potential and, likewise, at a higher pH, more of the OH^- ions will be found at the interface. McShea and Callaghan (1983), indeed, showed this to be the case; using the spinning cylinder technique, they showed that the zeta potential of air bubbles produced in pure water is -74.2 ± 60.0 mv at pH 7, -22.5 ± 7.7 mv at pH 6 and -0.6 ± 0.1 mv at pH 4. Wen and Sun (1981) reported that the zeta potentials of the hydrocarbon oil-in-water emulsions are pH-dependent; the i.e.p. values of octane and dodecane are found to be pH 2.5 and that of hexane is pH 2.

Many investigators (Alty, 1926; Gilman and Bach, 1938; Dibbs et al., 1974; McShea and Callaghan, 1983) have studied the effects of inorganic electrolytes on the bubble charge, and showed that the bubbles are negatively charged regardless of the types of electrolytes used. The most likely reason for the negative charge is that, in general, cations have significantly larger hydration energies than anions (Noyes, 1962, 1964; Conway, 1978).

It has been shown in the present work that the bubbles generated in the presence of nonionic surfactants are negatively charged in neutral and alkaline pH solutions, and become positively charged at acidic pH values. The charging mechanism may be considered to be similar to that of the hydrocarbons discussed above. However, the mechanism must also be influenced by the presence of a more polar element, such as oxygen, in the molecular structure. It is conceivable that as the oxygen-to-carbon ratio is increased, the molecule becomes more basic, and the i.e.p. will shift toward the alkaline pH. The fact that the bubbles generated with polyoxyethylene methyl ether show a higher i.e.p. (pH 6) than those generated with polypropylene glycol (pH 3.5) may be explained by the difference in the oxygen-to-carbon ratio. By the same token, one can also explain the results in Figure 14 which show that the zeta potential becomes more negative when the number of ethylene oxide groups is reduced from 23 to 4 in the polyoxyethylene dodecyl ether molecule. The mechanism proposed here may also apply to the charging mechanism of polymers, latexes, rubbers and plastics.

2.6.-Summary and Conclusion

1. A simple modification of the flat-type electrophoresis cell has made it possible to determine the electrophoretic mobilities of microbubbles from which zeta potentials can be calculated.
2. In general, bubbles produced using cationic surfactants exhibit positive zeta potentials while those produced using anionic surfactants exhibit negative zeta potentials. It has been found, however, that the magnitudes of the zeta potentials are reduced when the pH approaches the value of pK_a or the pH of precipitation.
3. Bubbles generated using nonionic surfactants exhibit negative zeta potentials at neutral and alkaline pH values and positive zeta potentials in acidic solutions. It appears that the i.e.p. is determined by the acid-base properties of the surfactant molecule; when using surfactants containing ethylene oxide groups, the longer the ethylene oxide chain, the higher the i.e.p.

4. The fact that H^+ ions have a higher hydration energy than OH^- ions provides an explanation for the negative charges observed at the air/water and hydrocarbon/water interfaces in the absence of any surfactant. Likewise, the fact that cations generally have higher hydration energies than anions can provide an explanation for the negative charges of air bubbles produced in the presence of various inorganic electrolytes.

5. The bubble charge increases with increasing concentration in the presence of ionic surfactants, but not in the presence of nonionic surfactants. However, in the presence of polyoxyethylene methyl ether, the negative zeta potential increases with increasing concentration only at alkaline pH values.

CHAPTER III

Induction Time Measurements For The Quartz-Amine Flotation System.

3.1.- General

The attachment of mineral particles to air bubbles is the most fundamental requirement for successful flotation. This process involves the thinning and rupture of the wetting film between colliding bubbles and particles. The minimum time required for the film to drain to a critical thickness and rupture spontaneously to form a stable bubble-particle aggregate is defined as the induction time. It is a function of the chemistry and hydrodynamics of the system, and provides kinetic information. In this regard, induction time is considered to be a better criterion for flotation than the contact angle (Eigeles and Volova, 1960; Laskowski, 1974), which is a purely thermodynamic quantity.

It can be envisioned that bubble-particle adhesion can occur when the particle-bubble contact time is longer than the induction time. On the basis of this concept, Dobby and Finch (1985) derived an expression for the effect of particle and bubble size on the flotation rate. Similarly, Giedel (1983) has derived an equation for the probability of adhesion.

3.2.-<u>Literature Review</u>

Sven-Nilson (1934) was the first to recognize the importance of induction time in the kinetics of flotation (Leja, 1981). A few investigators (Eigeles, 1950; Glembotsky; 1953; Evans and Ewers, 1953) reported different techniques of determining induction time, but it was not until Eigeles and Volova (1960) carried out a systematic investigation that the full value of the induction time was recognized.

Some of the important findings of Eigeles and Volova's work include the following: i) regardless of the mineral/collector system investigated, the induction time decreases with increasing collector concentration; ii) the induction time increases linearly with increasing particle size; and iii) the induction time decreases exponentially with increasing temperature, from which the activation energy for the bubble-particle adhesion process can be estimated. More recently, Laskowski and Iskra (1970) showed that for methylated quartz, the induction time decreases with increasing salt (KCl) concentration due to double layer compression. Schulze (1984) showed that in the quartz-dodecylamine system, the induction time decreases with increasing pH, reaching a minimum at pH 6.5 and a small maximum at pH 8 before decreasing further.

In the present work, induction time measurement has been carried out for the quartz-dodecylamine system. This system was chosen because equilibrium contact angle and surface tension studies fail to describe the dynamic flotation behavior (Smith, 1963; Finch and Smith, 1973) and the surface chemistry of both the mineral and the collector is well documented.

3.3 Materials and Procedure

3.3.1.-Mineral Samples

Pure rock crystals of quartz from Hot Springs, Arkansas, were obtained from Ward's Natural Science Establishment, Incorporated. For induction time measurements and flotation tests, the mineral was wet-ground in a steel mortar, dried and screened. The -65+100 mesh fraction was treated in hot hydrochloric acid for 3 hours to remove iron contamination and rinsed repeatedly with double-distilled water until there were no further changes in pH. The sample prepared as such was stored in conductivity water in a Pyrex bottle.

3.3.2 Reagents

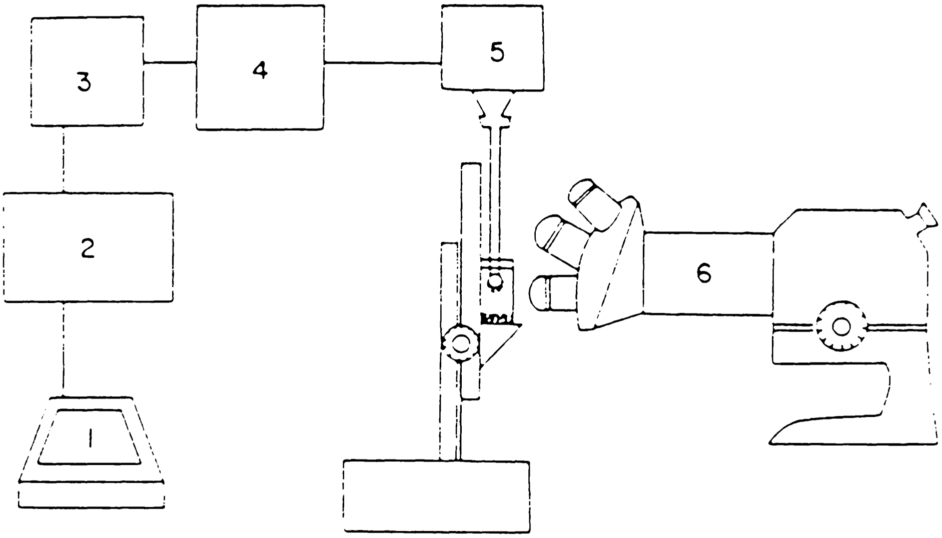
Research grade dodecylamminium hydrochloride (DAH), obtained from Eastman Kodak Company, was used as the collector without further purification. Certified ACS grade potassium chloride from Fisher Scientific Company was used to study the effect of inorganic electrolyte. Reagent grade hydrochloric acid and sodium hydroxide solutions were used for pH control. Double-distilled water, prepared in an all-glass still, was used in all the experiments. Ultra-pure nitrogen (99.999%) from AIRCO Industrial Gas Company was used to produce bubbles for microflotation tests. Chromic acid was used for cleaning glassware, the microflotation cell and the induction time apparatus.

3.3.3 Equipment

An induction time apparatus has been constructed in the present work which has a sensitivity limit of 100-150 microseconds. The basic unit is similar to the one used by Eigeles and Volova (1960) and Trahar (1983), but it operates with a microcomputer and has a greater sensitivity. A schematic representation of the induction time apparatus is shown in Figure 3.1. The microflotation tests were made using a Partridge and Smith (1971) type cell. Bubbles were produced by sparging ultra-pure nitrogen gas through a medium-porosity glass frit at the bottom of the cell. The gas flow rate was monitored using a flowmeter. A gentle agitation was provided by means of a teflon-coated magnetic stirring bar.

3.3.4.- Procedure

For the induction time measurements, two grams of quartz particles were contacted in a beaker containing 100 ml of DAH solution. After pH adjustment, the mineral suspension was agitated for 15 minutes before it was transferred to a rectangular optical glass cell to form a bed of particles. The cell, containing approximately 20 ml of the collector solution, was then placed on the moving stage of the microscope for measurement. Inside the cell, an air bubble 2 mm in diameter was formed at the tip of the glass tubing using a microsyringe, and left to stand for one minute to reach equilibrium before making contact with the



1.- CRT
2.- COMPUTER
3.- INTERFACE
4 - ELECTRONIC PULSE AMPLIFIER
5.- ELECTROMECHANICAL ACTUATOR
6.- MICROSCOPE

Figure 3.1. Schematic diagram of the induction time apparatus

particle bed. The contact time was pre-set by the microcomputer. Ten measurements were taken at a given contact time on different spots of the bed. Typically, no particles were attached when the pre-set contact time was very short. The contact time was then increased and another ten measurements were made. In this manner, a contact time at which at least five of the ten contacts actually picked up a minimum of one particle was determined. This critical time was taken in the present work to be the induction time. Most of the tests were carried out at ambient temperature, except for those studying the effect of temperature. After each test, the sample was removed from the cell and used for microflotation tests.

In each microflotation test, approximately 1 gram of sample was used with approximately 75 ml of DAH solution. The recovery after one minute of flotation time at the 45 ml/minute STP gas flow rate was taken as a convenient measure of floatability. No frother was used in the flotation experiments.

3.4.- Results

3.4.1.- Effect of pH

Figure 3.2 shows the results of the induction time measurements for the quartz-DAH system as a function of pH. Two different sets of experiments were carried out using $1x10^{-6}$ and $1x10^{-5}$ moles/l DAH solutions. In both cases, the induction time is shown to decrease steadily with increasing pH, indicating that the wetting film becomes more unstable as the pH of the solution increases. This can be attributed to the fact that the adsorption density of the amminium ions on the mineral surface increases with increasing pH (deBruyn, 1955). The induction time is shown to reach a minimum at approximately pH 10.5 and then begins to increase sharply with further increase in pH. The sharp increase in induction time is due to the fact that the collector ions precipitate out as neutral amine, as shown in the distribution diagram of the collector species (Figure 2.16). The thermodynamic data for constructing the distribution diagram are from Ananthpadmanabhan, et. al (1980).

The minimum induction time at pH 10.5 can be attributed to the adsorption of the iono-molecular species, as has been proposed by Somasundaran (1976). Figure 2.16 shows that the concentration of the iono-molecular species ($RNH_2 \cdot RNH_3^+$) reaches a maximum at pH 10.5. It is likely that this species, having twice as large a molecular weight as amminium ions, will have a larger free energy of adsorption and, hence, a greater affinity for the mineral surface. Schulze (1984) reports

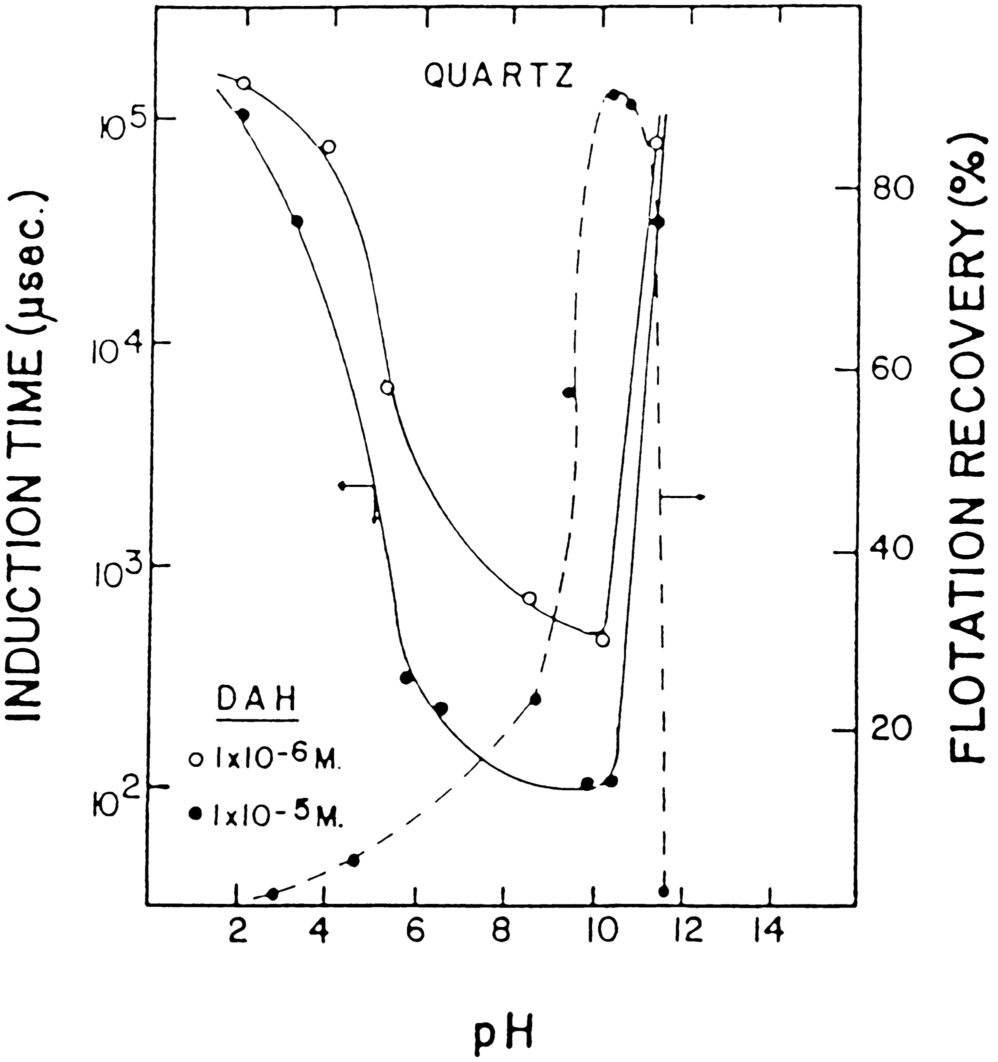


Figure 3.2. Effect of pH on the induction time and flotation recovery of quartz particles using different concentration of dodecylamime hydroclorice (DAH)

similar results, as shown in Figure 3.2; however, his data do not show a sharp increase in induction time above the precipitation pH, and the values are of much higher magnitudes.

Figure 3.2 also shows the microflotation results obtained with 1×10^{-5} moles/l DAH solution. As shown, the flotation recovery reaches a maximum in the pH range of 10-10.5, which corresponds to the pH of the minimum induction time. Induction time, thus, appears to be an excellent criterion for flotation.

3.4.2.- Effect of DAH Concentration

Figure 3.3 shows the results of induction time measurements for the quartz/DAH system conducted as a function of concentration at pH 6.6. Also shown in this figure for comparison are the flotation results. The induction time is shown to decrease with increasing collector concentration, while the flotation recovery increases concommittantly. This finding can be attributed to increasing adsorption density at the mineral surface with increasing collector concentration (deBruyn, 1955), which renders the quartz particles increasingly hydrophobic and destabilizes the wetting film. Eigeles and Volova (1960) observed a similar trend with various mineral/collector systems.

Note that the induction time increases drastically when the collector concentration approaches 10^{-2} moles/l. A similar flotation response has been reported by Somasundaran and Lee (1981). Considering that the CMC of DAH is 1.3×10^{-2} moles/l (Phillips, 1955), adsorption of micelles may be considered responsible for the increase in induction

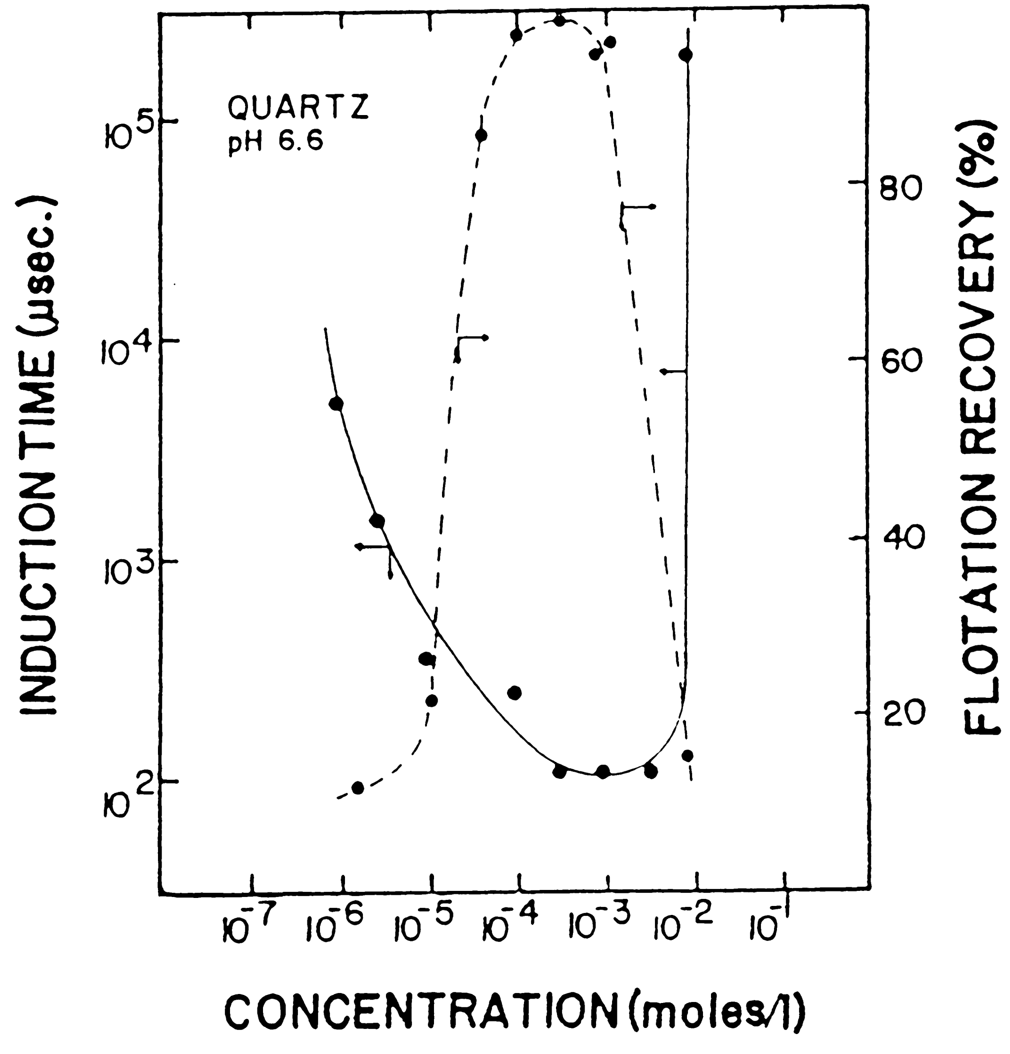


Figure3.3. Effect of DAH concentration on the induction time and flotation recovery of quartz particles at pH 6.6

time and the corresponding drop in flotation recovery. It is possible, however, that at such a high concentration, the formation of a bimolecular layer of adsorbed collector species is possible, although the net effect on flotation would be the same.

3.4.3.- **Effect of Electrolyte**

It has been well documented in literature that flotation can be improved in the presence of indifferent electrolytes (Derjaguin and Schukadise, 1961; Chander and Fuerstenau, 1972; Collins and Jameson, 1976). This has been explained by the compression of the electrical double layers surrounding both the mineral particles and the air bubbles, which makes it easier for them to approach each other. Figure 3.4 shows the effect of KCl concentration on the induction time and the flotation for the quartz/DAH system. The induction time measurements have been carried out at pH 6.75 and three different levels of DAH concentrations. At a low collector concentration, i.e., 5×10^{-6} moles/l, the induction time decreases steadily with increasing KCl concentration, demonstrating that the presence of electrolyte accelerates the rupture of the wetting film. Similar results have been obtained by Laskowski and Iskra (1970) with methylated quartz.

At higher DAH concentrations, i.e., 5×10^{-4} and 5×10^{-3} moles/l, the induction time remains constant initially with increasing KCl concentration, as shown in Figure 3.4. However, as the KCl concentration reaches approximately 10^{-3} moles/l, it increases sharply

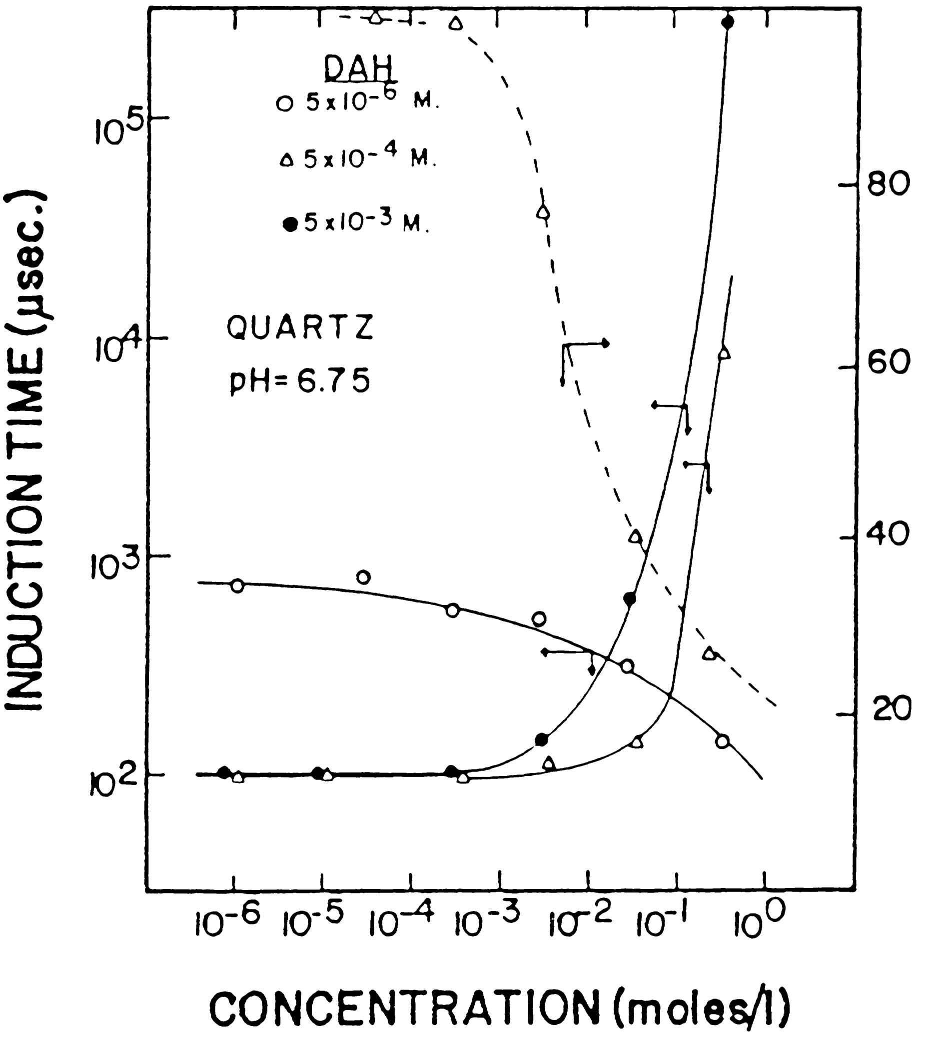


Figure 3.4. Effect of KCl concentration on the induction time and flotation recovery of quartz particles using different concentrations of DAH at pH 6.5.

and the flotation recovery drops significantly with increasing concentration. This finding may be attributed to the possibility that at high concentrations of KCl, the collector ions begin to associate with each other well before the CMC is reached and adsorb on the mineral surface in the form of micelles or form bi-molecular layers. This phenomenon is related to the lowering of the CMC of ionic surfactants in the presence of electrolyte. (Phillips, 1955)

3.4.4.- Effect of Temperature

Figure 3.5 shows the results of the induction time measurements conducted on the quartz-DAH system as a function of temperature at pH 6.1. Four different sets of experiments were conducted using 2×10^{-6}, 2×10^{-7}, 2×10^{-8} and 0 moles/l DAH solution. One can see that induction time decreases with increasing collector concentration. Note also that at a given concentration, the induction time decreases with increasing temperature. The effect of temperature becomes less significant with increasing DAH concentration. Eigeles and Volova (1960) obtained similar results, from which activation energies have been calculated using the Arrhenius-type equation:

$$t = t_o \exp(E/kT) \qquad [3.1]$$

in which t is the induction time, t_o is a constant, E is the activation energy for bubble-particle adhesion, k is the Boltzman constant, and T is the absolute temperature. Rearranging Eq. [3.1], one can obtain a

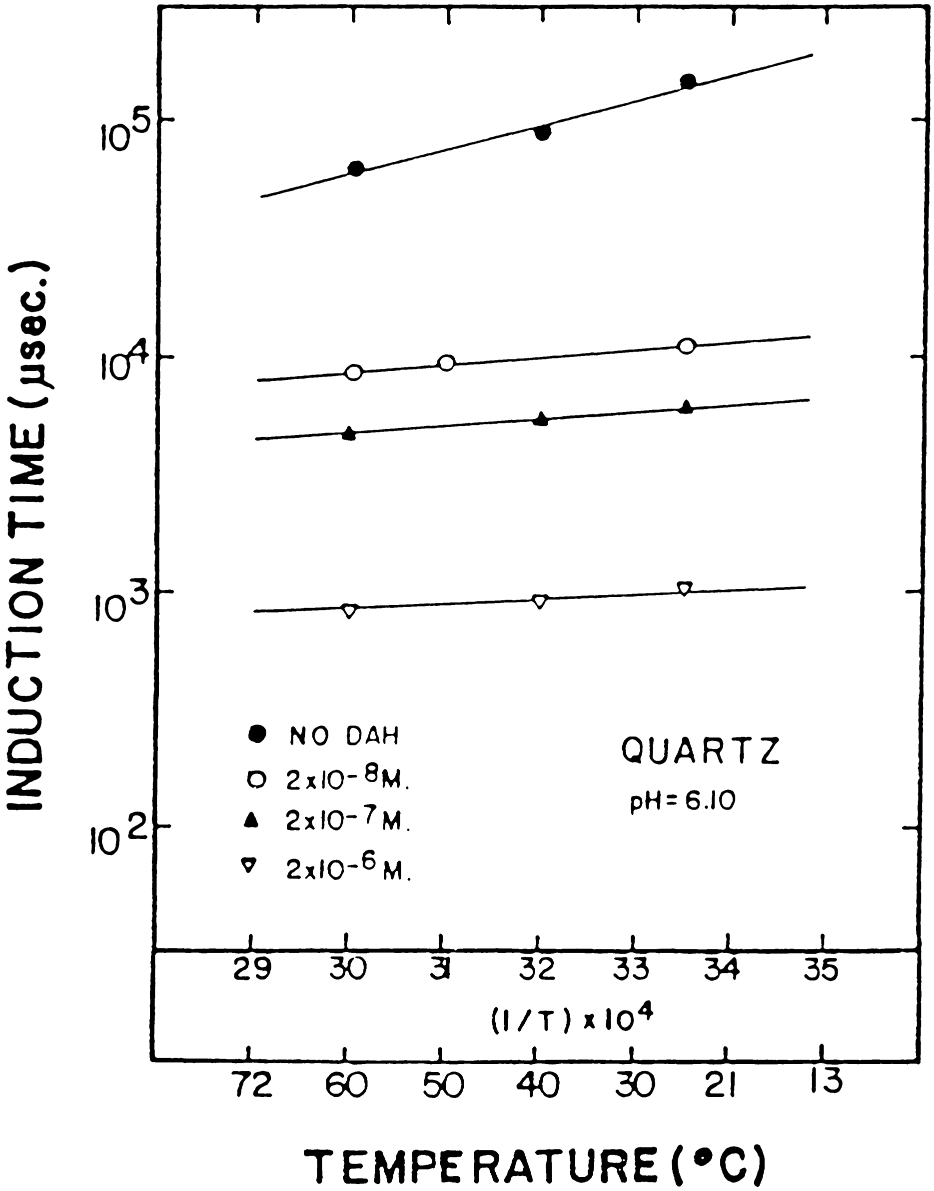


Figure 3.5 Effect of temperature on the induction time of quartz particles using different concentration of dodecylamine hydrochloride at pH 6.1

convenient expression

$$\log t = E/2.3kT + \log t_o \qquad [3.2]$$

in which $E/2.3k$ is the slope of the log t vs. (1/T) plot. Table 3.1 gives the activation energies calculated from the slopes of the plots shown in Figure 2.5. The activation energies are shown to decrease with increasing collector concentration.

3.4.5.- Effect of Particle Size

Figure 3.6 shows the results of the induction time measurements obtained as a function of particle size using 10^{-6} moles/l of DAH solution at pH 2.0. As shown, the induction time increases linearly with increasing particle size for the particle size range investigated. Eigeles and Volova (1960) observed the same trend, and attributed it to the greater weight of the larger particle which requires larger attraction force to balance it.

TABLE OF RESULTS 3.1

Activation energy of bubble-particle adhesion for the quartz/DAH flotation system calculated from experimental data

[DAH] (Moles/l)	[ACTIVATION ENERGY] (Kcal/mol)
0	5.07
2x10-8	1.40
2x10-7	1.53
2x10-6	0.93

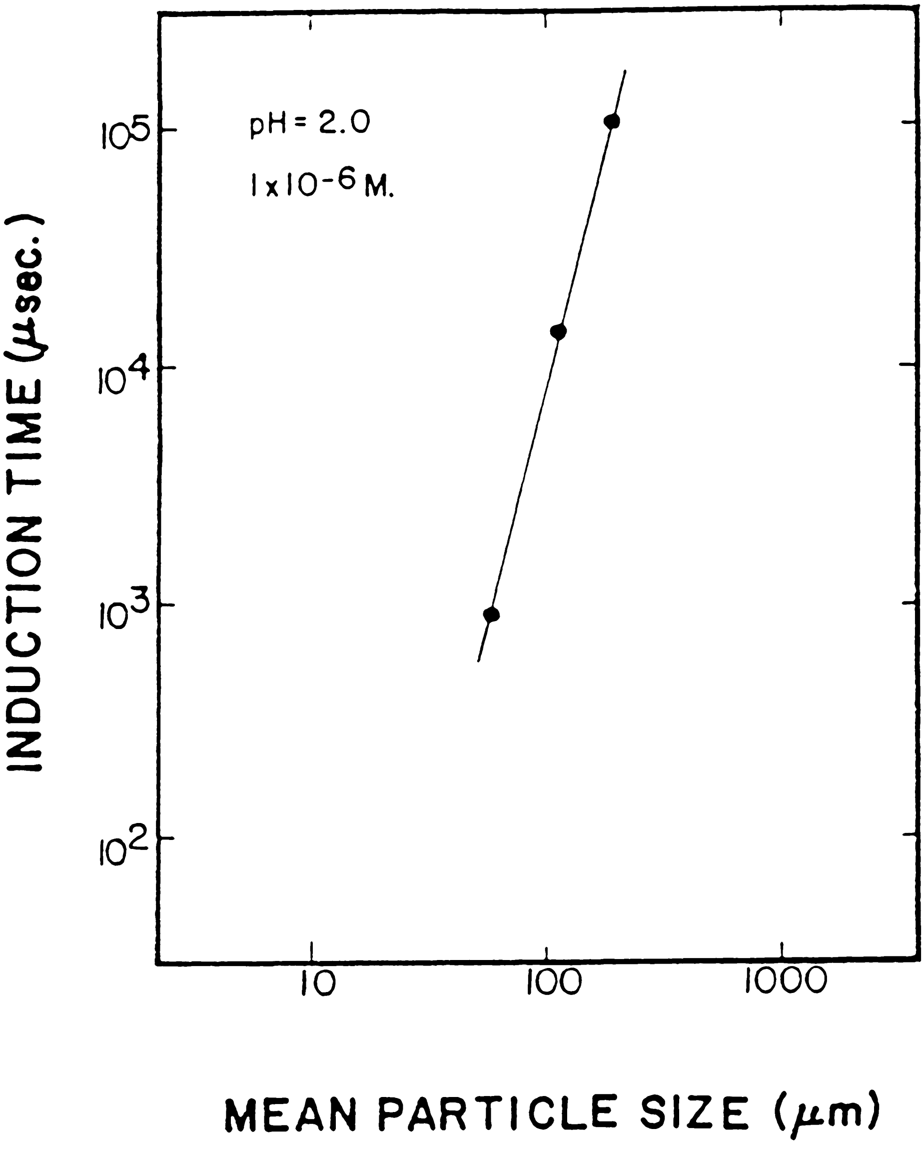


Figure 3.6 Effect of particle size on the induction time of quartz particles using 1×10^{-6} moles/l of dodecylamine hydrochloride at pH 2.0

3.5. Discussion

The results presented in the foregoing section have shown that the induction time apparatus constructed in the present work offers a convenient method of studying the flotation chemistry of the quartz-DAH system. It has been shown that increasing the DAH concentration results in a reduction in induction time and a corresponding increase in flotation recovery. When the concentration is increased further, approaching the CMC, the induction time increases drastically and the flotation recovery decreases accordingly. It has also been found that the induction time measurements were useful in studying other variables such as pH, temperature, particle size and the concentration of indifferent electrolytes.

Information that can be obtained from induction time measurements may be similar to that obtainable from contact angle measurements. However, the induction time measurements have the following advantages. Firstly, the induction time is a much more sensitive measure of flotation chemistry than the contact angle. It has been shown that induction time varies by three or four orders of magnitude in a single series of experiments. On the other hand, the contact angle usually varies from 0 to 80 degrees. Secondly, the induction time measurements can be made on particles rather than on polished specimens. There is no doubt that information obtained using particles is more relevant to flotation, making it possible to study the effect of particle size. Finally, induction time is a measure of both the chemistry and the hydrodynamics of flotation, while contact angle is only a thermodynamic quantity.

Smith and Lai (1966) showed that the equilibrium contact angles measured for the quartz-DAH system failed to explain the flotation at high pH values and that only the dynamic contact angles showed any relevance to their flotation experiments. They suggested that the interfacial tensions at the liquid/vapor and solid /vapor interfaces change as a function of time. Also, Finch and Smith (1972) showed that good flotation of magnetite can be obtained with DAH when the equilibrium contact angle is zero. These investigators found that at a high pH and a high DAH concentration, the surface tension ($\gamma_{l/v}$) varies significantly with time, and suggested that aged bubbles have surface tensions that are too low to give a finite contact angle. According to Young's equation, a high value of $\gamma_{l/v}$ is necessary to have a large contact angle. However, the bubbles generated in flotation cells present relatively fresh surfaces to the particles to be collected and, therefore, magnetite can still be floated even when the equilibrium contact angle is zero. One may have noticed that the single bubbles used for the induction time measurements are also aged just as the captive bubbles used in the equilibrium contact angle measurements. Note, however, that during the induction time measurements, the bubbles move quickly toward the bed of particles. This causes the surfactant molecules at the front end of the bubble to move toward the back side of the bubble, thereby exposing a fresh bubble surface and, hence, giving a large value of $\gamma_{l/v}$. This situation resembles, more closely than the equilibrium contact angle measurements, the actual flotation process in which bubbles and particles are colliding each other by turbulent agitation.

The complex flotation phenomenon that occurs in a flotation cell may be represented by the following equation:

$$P = P_cP_a(1-P_d), \qquad [3.3]$$

in which P is the probability of flotation, P_c is the probability of collision, P_a is the probability of adhesion, and P_d is the probability of detachment. P_c is primarily a function of particle size, bubble size (Weber and Paddock, 1983; Yoon and Luttrell, 1985) and impeller speed, while P_a is known to be a function of chemistry (Dobby and Finch, 1985). A proper collector addition will make the particle more hydrophobic and increase P_a. What this means is that during the time when bubble and particle are in contact with each other, the disjoining film between them is more readily thinned and ruptured by the collector addition to form a finite contact angle. In flotation, the contact time is determined by the time it takes for a particle to slide along the surface of a bubble before it reaches the back side, while in induction time measurements, the contact time is artificially controlled.

It appears that the rate of film thinning is determined initially by the hydrodynamics of the system. The Reynolds lubrication theory may be useful in describing the initial film thinning process (Schulze, 1984),

$$v = -\frac{hF}{6\pi\eta R}, \qquad [3.4]$$

which states that the drainage velocity (v) of the thin film between a sphere and an infinitely large plate is proportional to the driving force (F), i.e., the force of approaching two bodies of solids, and the film thickness (h), and is inversely proportional to the viscosity (η) of the film and the radius of the sphere (R). Thus, induction time should be a function of the force applied in moving the bubble toward the particle bed and also the initial distance separating the stationary bubble and the particle bed. Although these factors have been ignored in the present work, the results presented here show the relative changes in time required for thinning the film between the bubble and the particle.

When the film becomes sufficiently thin in the 100-200nm range (Schulze, 1984), interfacial surface forces come into play and influence the rate of thinning. Three major types of surface forces are important at this stage, i.e., electrostatic, dispersion and structural forces. Depending on the nature and the relative magnitudes of these forces, the thin film can rupture spontaneously at a certain critical thickness (h_{crit}). It has been shown by Schulze (1984) and Read and Kitchener (1969) that h_{crit} varies with the chemistry of a system such as pH and collector concentration. In general, h_{crit} increases as the mineral becomes more hydrophobic and the flotation condition becomes more favorable. It has long been recognized that the **electrostatic force** is important in flotation. However, not enough information is available regarding the charge of air bubbles used in flotation. In chapter IV of the present study is clearly shown that the induction time is reduced drastically when the bubble and the particle have opposite charges. The drastically when the bubble and the particle have opposite charges. The **dispersion force** affecting the film thickness is controlled in flotation by collector and frother additions. deBruyn (1955) and Fuerstenau (1957) showed how DAH adsorption on quartz affects the contact angle and, hence, flotation. The collector coating also reduces the zeta-potential, which may contribute to reducing the electrostatic energy barrier against film thinning. The major component of **structural force** is the cohesive energy of water in the film. The hydrocarbon tails of the adsorbed collector molecules will help break the hydrogen bonds and thereby reduce the cohesive energy between water molecules. This will increase the rate of film drainage and rupture process.

Like any other rate process, bubble-particle adhesion can occur only when the total energy available for thinning and rupturing the wetting film exceeds the activation energy barrier (E). Table 3.1 shows the values of E determined from the induction time measurements as a function of temperature. When no collector is added, the activation energy is 5.07 Kcal/mole. It is shown to decrease with increasing collector addition. For example, when the collector addition is 2×10^{-6} moles/l, the activation energy is reduced to 0.93 Kcal/mole. The difference between the two activation energy values, i.e., 4.14 Kcal/mole, may be considered to have been provided by the collector adsorption. As suggested by Rao (1974), this reduction in activation energy should correspond to the free energy of the collector adsorption. Ball and Fuerstenau (1971) determined the free energies of adsorption for the quartz-dodecylammonium acetate system from the adsorption isotherms using the Stern-Grahame equation. Their values range between -3.1 and -4.3 Kcal/mole, depending on the collector concentration and temperature. This close correspondence between the two sets of data elucidates the role of collector in the bubble-particle adhesion process.

3.6.-Conclusions

1. The induction time apparatus constructed in the present work has been found to be useful in studying both the chemistry and the hydrodynamic aspects of flotation in the quartz-DAH system.
2. At a given DAH concentration, the induction time reaches a minimum at approximately pH 10.5 where the collector molecules hydrolize to form neutral amine. The flotation recovery reaches a maximum at the same pH, suggesting that the iono-molecular species formed between the neutral amine and the charged amminium species is the most surface-active species responsible for flotation.
3. Induction time is found to decrease with increasing DAH concentration until the CMC is reached. A corresponding increase in flotation recovery with decreasing induction time has been observed. Above the CMC, the induction time increases drastically, and the flotation recovery is reduced to zero.
4. At a low DAH concentration, the presence of an indifferent electrolyte (KCl) reduces the induction time and promotes flotation. At a relatively high DAH concentration, however, KCl increases the induction time and retards the flotation. This phenomenon has been

explained by the lowering of CMC.

5. Activation energies of the bubble-particle adhesion process have been determined. The values range between 5.07 and 0.93 Kcal/mole at DAH concentrations ranging between 0 and 2×10^{-6} moles/1. It has been found that these values are comparable with the free energies of the collector adsorption reported in the literature.

CHAPTER IV

Role of Bubble Charge in the Bubble-Particle Adhesion Process

4.1.-General

In spite of the fact that a good deal of research has been devoted to study the role of the electrostatic contribution of the disjoining pressure in the adhesion process, the results obtained have mostly been explained in terms of the electrical properties of charged mineral particles, with little or no reference to the charge at the liquid/gas interface. However, it has been shown in chapter II of the present study that air bubbles stabilized in surfactant solutions acquire electrical charge in a similar way as mineral particles do. Therefore, the bubble charge should influence the kinetics of capture. In this regard, it has been the objective of this chapter to study the role of bubble charge in the attachment process. To meet this goal, induction time experiments have been conducted on quartz particles using air bubbles of known electrical properties.

4.2.-Literature Review

Dibbs, et al (1974) were the first to study the role of bubble charge in flotation using the data on bubble charge from the streaming current measurements. They have shown that for quartz-DAH flotation system, the best flotation results are obtained when the colliding bubble and particle carry opposite charges. Collins and Jameson (1977) reported an increase in the flotation rate of small latex particles with decreasing bubble charge which was explained in terms of a reduction in the electrostatic repulsive force, which opposes film thinning. In their experiments, the bubble charge was reduced by the addition of sodium sulfate.

There has not been much evidence given to date that the electrostatic attractive force between particles and bubble alone can make hydrophilic solids floatable. Fukui and Yuu (1980) showed, however, that small latex particles can be floated with no frother or collector; it was shown that the latex particles could be floated by controlling the conditions in such a way that the particles and the bubbles had opposite charges. Sato, et al (1979) floated emulsified particles with maximum efficiency when the electrical charge on both particles and bubbles were minimal or nonexistence. This was done simply by keeping the pH of the pulp near the i.e.p of the colliding interfaces.

4.3.-Results and Discussion

The results of the induction time and microflotation experiments conducted on quartz particles using bubbles of different electrical charges are presented in the following sections.

4.3.1.-In the absence of surfactant

Figure 4.1 shows the results of the induction time measurements of quartz particles (-100 + 150 mesh) conducted as a function of pH in the absence of collector. As shown, the induction time increases with increasing pH, suggesting that film rupture becomes more difficult as the pH of the solution rises. These results are similar to those reported by Laskowski and Iskra (1970) using methylated quartz. These investigators also observed a good correlation between flotation response and induction time.

It has been well established that in pure water, the electrical charge of both air bubbles (Mcshea and Callagham (1983), Schulze (1984)) and quartz particles (Fuerstenau (1957)) becomes increasingly negative as pH goes from the acidic to the alkaline region. Therefore, the results shown in figure 4.1 demostrate the effect of the electrical charges between the approaching particle and bubble.

4.3.2.-In the presence of sodium dodecyl sulfate

Table 4.1 shows the results of the induction time of quartz particles (-60 +100 mesh) conducted as a function of sodium dodecyl

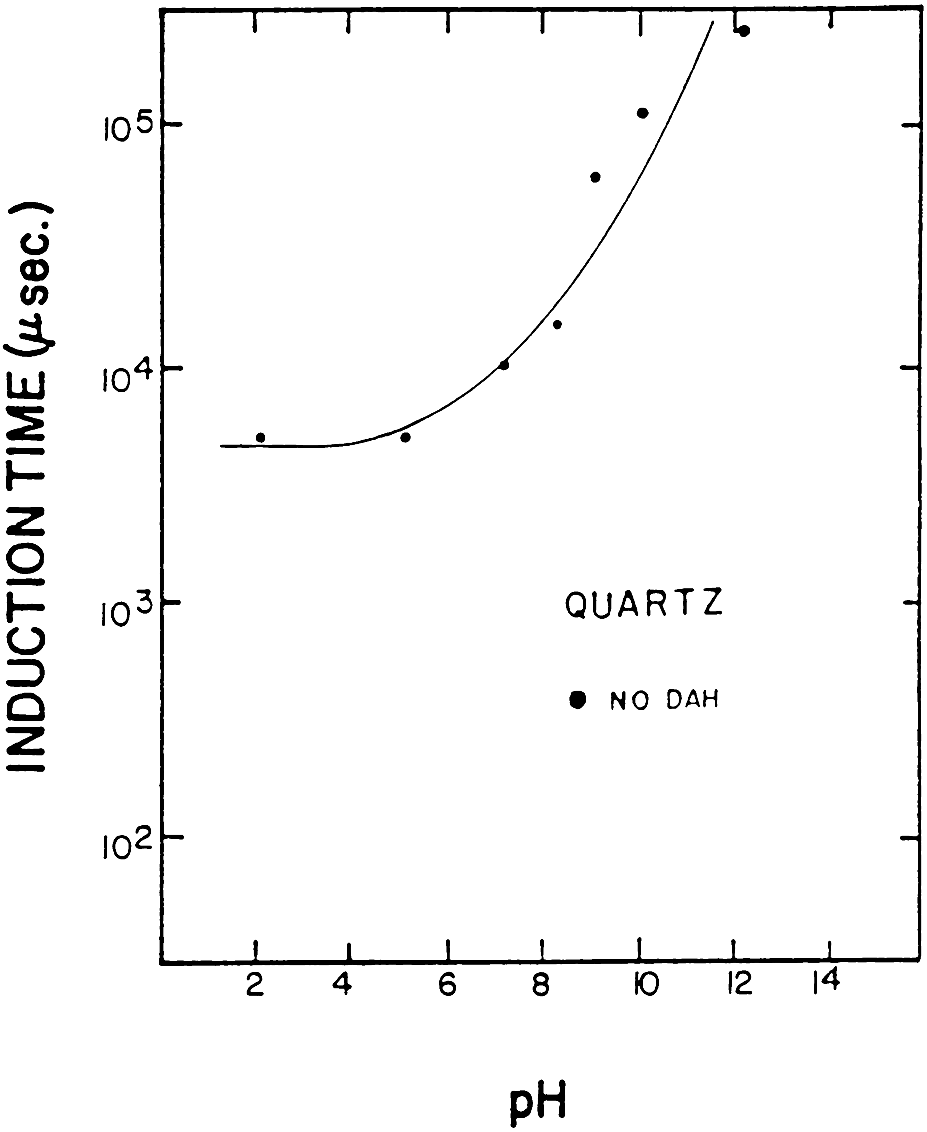


Figure 4.1 Effect of pH on the induction time of quartz particles in the absence of surfactant

TABLE OF RESULTS 4.1

Effect of sodium dodecyl sulfate concentration on the induction time of quartz particles at pH 4.5.

[SDS] (moles/l)	Induction Time (micro-seconds)
0	100,000
1×10^{-4}	250,000
1×10^{-3}	no contact (>10 Sec.)

sulfate concentration. The pH was kept constant at 4.5. Three sets of experiments were done using 0, $1x10^{-4}$ and $1x10^{-3}$ moles/l of SDS.

It can be seen that the induction time is critically affected by the addition of SDS. The fact that it increases from 100,000 micro-seconds in the absence of SDS up to more than 10 seconds at a concentration of $1x10^{-3}$ moles/l of SDS, indicates that upon addition of SDS a strong repulsive force develops, which opposes film rupture. It is important to point out that at the pH of 4.5 employed in the tests, quartz particles are known to be negatively charged and, therefore, it is highly unlikely that adsortion of SDS molecules takes place at the solid/liquid interface. In this respect, Schulze (1984) has noted that regardless the SDS concentration employed, the electrokinetic behaviour of quartz particles remains unchanged. On the other hand, it has been shown in chapter II (figure 2.2) that in SDS solutions, air bubble are negatively charged and that the charge increases with SDS addition. It appears, thus, that this increase in bubble charge with SDS addition is responsible for the observed induction time behavior. These results may be correlated to the findings of Anfruns and Kitchener (1977), who reported a reduction in the collection efficiency of methylated quartz when $1x10^{-4}$ moles/l of SDS were added to the system. They suggested that the charge developed on the bubble leading to electrostatic repulsion was responsible for the reduced collection efficiency.

4.3.3.-In the presence of polyoxyethylene methyl ether

It has been shown in chapter II (figure 2.12) that the electrical charge acquired by air bubbles generated in solution of polyoxyethylene methyl ether is a function of solution pH, with the i.e.p. occuring at pH 6.1. In order to see if the sign of the charge existing at the air/liquid interface has any infuence on the adhesion process, two sets of induction time and microflotation experiments were conducted using $1x10^{-4}$ moles/l POEME solution at pH 4.8, where bubbles are positively charged, and at pH 9.8, where they are negatively charged. Quartz particles, on the contrary, are negatively charged throughout the pH range studied. The results obtained are presented in table 4.2.

As shown, the induction time is significantly shorter at pH 4.52, where the quartz particles and bubbles have opposite charge, than at pH 9.80 where both of them bear similar charge. The microflotation results clearly indicate that flotation response is also affected. The low recovery obtained when the interacting bodies were oppositely charged indicates that the existing electrostatic attractive force is not sufficient to render the hydrophilic quartz particles completely floatable.

TABLE OF RESULTS 4.2

Effect of pH on the induction time and recovery of quartz particles using 1×10^{-4} moles/l polyoxyethylene methyl ether solutions.

pH	Induction Time (micro-seconds)	Flotation Recovery (%)
4.52	10,000	22.21
9.80	125,000	0

4.4.-Summary and Conclusions

1.- The experimental results obtained indicate that the bubble charge indeed has an important bearing in the rate of collection of particles by bubbles.

2.- It has been shown that the adhesion process is favored when the electrical charges on the solid and bubble are of opposite sign and retarded when the interacting bodies carry electrical charge of the equal sign.

CHAPTER V

General Conclusions and Recomendations for future work

5.1.-General Conclusions

The major findings of the present work may be summarized as follows:

1.- It has been shown that air bubbles produced in aqueous solutions acquire electrical charge in the same way as mineral particles do. The sign and magnitude of the zeta potential depend on the type and concentration of surfactant employed. In the case of ionic surfactants the charge is almost invariably determined by the sign of the polar head, i.e., positive for cationic and negative for anionic. Nonionic surfactants, on the other hand, produce negative bubbles at neutral and alkaline pH and positive ones in acidic solutions.

2.- The flotation chemistry of the quartz/dodecylamminium hydrocloride has been studied using the induction time technique. A good correlation always exists between flotation recovery and induction time of the disjoining film. For example, floatability is good when the induction time is short and viceversa. It has been found that the induction time is affected by physical variables such as particle size and temperature, as well as chemical ones such as pH, collector concentration and ionic strength.

3.- The effect of the bubble charge in the bubble-particle adhesion process is very important. The experimental results have indeed shown that a change in the electrostatic forces of attraction produced by a modification of the bubble charge can accelerate or retard the kinetics of capture. For example, when the charge on the air/water is opposite to that on the solid/liquid interface the induction time is short; conversely, if the potential of the air bubbles is of the same sign as that of the mineral particles the induction time is long. These effects are undoubtedly caused by electrical double layer forces.

5.2.-Recomendations for future work

Based upon the experience and information obtained during the course of this investigation, additional research in the following areas is suggested.

1.- Further research should be conducted on the zeta potential of air bubbles. It would be useful to study in a more systematic way the effect of bubble size, hydrocarbon chain length and substitution, different types of electrolytes, frother-collector interaction, etc. The modified electrophoresis technique can also be employed to study the electrokinetic behaviour of oil droplets produced with different types of fuel oils.

2.- On the basis of the results of zeta potential of air bubbles, it would be useful to derive using double layer theory mathematical models to describe the bubble charging mechanisms. The development of such models would allow a more indepth treatment of the role of bubble charge in the adhesion process.

3.- Using the induction time technique employed in the present work, it is possible to study the physico-chemistry of any flotation system. Particular attention should be paid to the effect on the attachment process of depressants, activators and any other reagent that are typically present in a flotation pulp. In addition, the induction time apparatus can be somewhat modified to study the effect of bubble size.

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APPENDIX I

Calculation of Activation Energies for Quartz/DAH Flotation System from Experimental Data

The apparent activation energy of passage of the wetting film into the labile state has been obtained from experimental data using the approach employed by Eigeles and Volova (1960). The experimental dependence of the induction time on the temperature can be derived from the Arrhenius equation in the following manner.

$$k = A \exp [-E/KT] \qquad [1]$$

where k is the rate of reaction in sec^{-1}, A a constant, E the activation energy in Kcal/mol, K the Boltzman constant and T the absolute temperature. One can invert equation [1] to obtain.

$$t = t_o \exp [E/KT] \qquad [2]$$

where $t = 1/k$ is the induction time and $t_o = 1/A$ remains a constant. Equation [2] can be expressed in a more convenient form as follows.

$$\log t = E/2.303KT + \log t_o \qquad [3]$$

therefore

$$\log t = A/T + B \qquad [4]$$

where $A = E/2.303k$ is the slope of a t vs 1/T plot and $B = \log t_o$ the intercept. Therefore one can calculate E from the value of A obtained using the following equation.

$$E = 4.58\times10^{-3} \times A \qquad [5]$$

The results of the activation energies calculations are shown in table A.1

TABLE OF RESULTS A.1

Medium	Temperature (^{o}C)	Induction Time (Micro-sec)	Slope	Activation Energy Kcal/mol
Distilled water	60	60,000	1116.4	5.11
	40	85,000		
	25	150,000		
$2x10^{-8}$ DAH	60	8,500	300.41	1.38
	50	9,700		
	25	11,000		
$2x10^{-7}$ DAH	60	4,500	337.15	1.54
	40	5,300		
	25	6,900		
$2x10^{-6}$	60	800	205.51	0.94
	40	925		
	25	1,000		

APPENDIX II

Determination of Ranks Brothers Electrophoresis Apparatus Parameters

1.- Determination of the eyepiece graticule

A stage micrometer was employed to obtain the distance measured by the eyepiece graticule. The distance was determined to be 77 um.

2.- Determination of flat cell thickness

This was determined as the difference in micrometer reading from measurements taken at the inner back wall and inner front wall. The thickness was determined to be 73 um.

3.-Determination of inter-electrode distance

The interelectrode distance, 1 , was determined using the following relationship

$$1 = R\ K\ A\ C$$

Where R is the resistance of the cell for a given solution of known specific conductance K, A the cross-section area of the cell and C the correction for refraction. In this particular case the values for the above parameters were:

$R = 5.405 \times 10^{-4}$ ohms

$K = 1.23 \times 10^{-3}$ 1/ohms-cm

$$A = 0.0725 \text{ cm}^2$$

$$C = 1.33$$

therefore

$$L = 6.4 \text{ cm.}$$

4.- Determination of stationary levels

The position of the stationary levels were obtained using the Komagata's equation

$$s/d = 0.500 - [\ 0.0833 + 32d/\ 3.14^5 \times L]^{1/2}$$

This expression can be approximated to

$$S = 0.20s/d = 0.20 \times [\text{Thickness}]$$

Therefore the two stationary levels are located at a distance 0.2xThickness from the inner back and front walls.

APPENDIX III

Tables of Experimental Results

Presented in Figures

Figure No.2.2

Effect of concentration on the zeta potential of microbubbles generated using sodium dodecyl sulfate solution at pH 10.3.

CONCENTRATION (moles/L)	ZETA POTENTIAL (mV)
$1x10^{-5}$	-41.42
$1x10^{-4}$	-40.73
$1x10^{-3}$	-58.50
$1x10^{-2}$	-67.65

Figure 2.3

Effect of pH on the zeta potential of microbubbles generated using different concentrations of sodium dodecyl sulfate solution.

	pH	Zeta Potential (mV)
1x10^{-4}	2.1	-28.31
	4.6	-42.33
	7.7	-36.52
	8.3	-39.25
	10.0	-41.74
1x10^{-3}	2.1	-40.17
	3.4	-48.34
	4.8	-53.27
	7.7	-59.87
	8.2	-59.62
	10.0	-57.93
1x10^{-2}	2.1	-60.51
	5.0	-74.25
	7.7	-70.00
	10.1	-75.10

Fig. 2.4

Effect of KCl concentration on the zeta potential of microbubbles generated using 1×10^{-5} mole/l sodium docecyl sylfate solution at pH 10.6.

CONCENTRATION (KCl)	ZETA POTENTIAL (mV)
1×10^{-4}	-40.35
1×10^{-3}	-34.71
1×10^{-2}	-27.25

Fig. 2.5

Effect of pH on the zeta potential of microbubbles generated using different concentrations of sodium oleate solution.

1×10^{-5} M

pH	Zeta Potential (mV)
6.4	-29.25
8.4	-44.75
9.3	-46.08
10.3	-50.00

1×10^{-4} M

6.4	-43.91
7.2	-72.05
8.8	-70.70
10.3	-68.43

Fig. 2.6

Effect of concentration on the zeta potential of microbubbles generated using dodecyl amine hydrochloride at pH 7.1.

Concentration (Moles/l)	Zeta Potential (mV)
1×10^{-4}	24.50
1×10^{-3}	43.00
1×10^{-2}	59.88

Fig. 2.7

Effect of pH on the zeta potential of microbubbles generated using different concentrations of dodecylamine hydrochloride solution.

	pH	Zeta Potential (mV)
2.5×10^{-4} M		
	2.9	31.25
	4.0	30.75
	6.0	33.00
	6.9	29.75
	8.0	23.50
	10.5	-11.70
	11.4	-18.95
5×10^{-4} M		
	3.3	38.34
	4.2	34.71
	6.6	33.80
	7.9	29.54
	9.0	25.00
	10.7	-9.40
1×10^{-3} M		
	2.9	50.05
	6.0	53.27
	8.0	40.31
	10.0	23.75

Fig. 2.8

Effect of pH on the zeta potential of microbubbles generated using different concentrations of cetyl pyridinium chloride solution.

	pH	Zeta Potential (mV)
1×10^{-4} M.		
	2.0	41.00
	3.0	38.75
	5.0	40.73
	7.0	44.15
	10.0	40.21
	10.5	39.00
1×10^{-3} .M		
	3.0	60.35
	6.0	58.75
	8.0	65.00
	10.5	71.85

Fig. 2.9

Effect of concentration on the zeta potential of microbubbles generated using polypropylene glycol solutions of different pH.

	Concentration	Zeta Potential (mV)
pH 2.0	1×10^{-4}	10.15
	1×10^{-3}	13.72
	5×10^{-3}	10.00
	1×10^{-2}	10.00
pH 4.0	1×10^{-4}	16.85
	1×10^{-3}	19.75
	4×10^{-3}	17.33
	9.5×10^{-3}	17.87
pH 7.0	1×10^{-4}	24.22
	5×10^{-4}	25.31
	1×10^{-3}	21.77
	5×10^{-3}	27.15
	1×10^{-2}	21.81
pH 10.4	9×10^{-5}	36.37
	4.5×10^{-4}	33.45
	2×10^{-3}	37.00
	5×10^{-3}	35.22
	9.5×10^{-3}	35.97

Fig. 2.11

Effect of concentration on the zeta potential of microbubbles generated using polyoxyethylene methyl ether solutions of different pH.

	Concentration (Moles/l)	Zeta Potential (mV)
pH 3.2	2.5×10^{-4}	41.67
	1.5×10^{-3}	48.25
	3×10^{-3}	50.71
	8×10^{-3}	50.03
	1×10^{-2}	49.87
pH 5.3	2.5×10^{-4}	18.97
	1.5×10^{-3}	19.35
	5×10^{-3}	21.72
	1×10^{-2}	20.68
pH 6.8	2.5×10^{-4}	-22.69
	1.5×10^{-3}	-26.88
	5×10^{-3}	-24.25
	1×10^{-2}	-24.00
pH 8.2	2.5×10^{-4}	-40.72
	3.5×10^{-4}	-43.00
	5×10^{-4}	-42.92
	1×10^{-2}	-56.25

Fig.2.11 (cont)

pH 10.2

Concentration (moles/l)	Zeta Potential (mV)
2.5×10^{-4}	-46.50
1×10^{-3}	-51.33
4×10^{-3}	-58.00
5×10^{-3}	-62.31
1×10^{-2}	-70.42

Fig. 2.12

Effect of pH on the zeta potential of microbubbles generated using different concentrations of polyoxyethylene methyl ether solution.

	pH	Zeta Potential (mV)
$6\text{x}10^{-4}$ M.		
	3.00	41.00
	5.25	17.50
	6.50	-29.66
	8.00	-42.11
	10.00	-43.25
$1\text{x}10^{-2}$ M.		
	3.00	45.55
	5.25	17.50
	6.50	-29.66
	8.00	-63.00
	10.00	-77.90

Fig. 2.13

Effect of concentration on the zeta potential of microbubbles generated using polyoxyethylene dodecyl ethers with different numbers of EO groups.

4 EO

Concentration (moles/l)	Zeta Potential (mV)
4×10^{-6}	-38.75
9×10^{-6}	-37.61
1.25×10^{-5}	-46.25
6×10^{-5}	-36.00
9×10^{-5}	-33.90
2×10^{-4}	-43.17

23 EO

3.5×10^{-6}	-42.93
8.7×10^{-6}	-41.76
1×10^{-5}	-51.00
2.5×10^{-5}	-42.07
9×10^{-5}	-40.76

Fig. 2.14

Effect of pH on the zeta potential of microbubbles generated using polyoxyethylenes with 4 and 23 ethylene oxide groups.

4 EO

pH	Zeta Potential (mV)
2.3	-5.00
3.0	-5.00
3.7	-7.75
4.0	-21.32
6.0	-26.00
7.1	-41.61
8.2	-50.00
10.0	-57.00

23 EO

2.6	-7.14
2.9	-27.00
5.0	-41.51
7.0	-34.25
8.7	-41.00
9.4	-45.82
10.0	-45.24

Fig. 3.2 Effect of pH on the induction time and flotation recovery of quartz particles using different concentration of dodecylamime hydrocloride (DAH)

	pH	Induction Time (micro-seconds)
1×10^{-6} M.	2.0	150,000
	4.0	80,000
	5.0	7,525
	8.4	875
	10.0	625
	11.2	86,000
1×10^{-5} M	2.0	100,000
	3.1	62,500
	5.8	375
	6.4	250
	9.8	100
	10.2	100
	11.3	67,500

Fig.3.2. cont.

1×10^{-5} M.

pH	Flotation Recovery (%)
3.0	1.5
4.7	4.8
8.6	22.15
9.0	57.50
10.0	91.33
11.0	78.00
11.70	2.00

Fig. 3.3

Effect of DAH concentration on the induction time and flotation recovery of quartz particles at pH 6.6

Concentration (moles/l)	Induction Time (micro-seconds)
1×10^{-6}	6525
3×10^{-6}	1150
1×10^{-5}	500
1×10^{-4}	375
5×10^{-4}	100
1×10^{-3}	100
5×10^{-3}	100
1×10^{-2}	150,000

Concentration (moles/l)	Flotation Recovery (%)
1×10^{-6}	11.15
1×10^{-5}	22.70
5×10^{-5}	83.45
1×10^{-4}	97.00
5×10^{-4}	99.23
1×10^{-3}	91.50
2×10^{-3}	94.30
1×10^{-2}	16.00

Fig. 3.4

Effect of KCl concentration on the induction time and flotation recovery of quartz particles using different concentrations of CAH at pH 6.5.

5×10^{-6}

Concentration (moles/l)	Induction Time (micro-seconds)
1×10^{-6}	875
5×10^{-5}	960
5×10^{-4}	810
5×10^{-3}	775
5×10^{-2}	575
5×10^{-1}	200

5×10^{-4} M.

1×10^{-6}	100
1×10^{-5}	100
5×10^{-4}	100
5×10^{-3}	150
5×10^{-2}	250
5×10^{-1}	9,500

Fig.3.4. cont.

5×10^{-3} M.

1×10^{-6}	100
1×10^{-5}	100
5×10^{-4}	100
5×10^{-3}	175
5×10^{-2}	850
1×10^{-1}	175,000

Fig. 4.1

Effect of pH on the induction time of quartz particles in the absence of surfactant

NO DAH

pH	Induction Time (micro-seconds)
2.0	8,500
5.7	8,500
7.3	10,000
8.0	11,500
9.0	85,500
10.0	102,500
12.1	165,000

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KINETICS OF BUBBLE-PARTICLE ADHESION

by

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(ABSTRACT)

In order to study the role of electrical charge existing on air bubbles in the kinetics of the particle-bubble adhesion process in froth flotation, the zeta potential of microbubbles in the 40 -to 80-micron size range have been determined by means of a simple microelectrophoresis technique. In general, the bubble charge is determined by the charge of the polar head of the surfactants when ionic surfactants are used to produce bubbles. However, the magnitude of the zeta-potential is reduced when the surfactants are hydrolyzed. When using nonionic surfactants, the bubbles exhibit isoelectric points (i.e.p) in acidic and neutral pH ranges. It appears that the location of an i.e.p. is determined by the acid-base property of the surfactant molecule used. The negative charges observed with air bubbles and oil droplets in the absence of surfactants can be explained by the differences in the hydration energies of H^+ and OH^- ions. An increase in the concentration of ionic surfactants results in an increase in bubble charge. However, the increase is minimal or non-existant when nonionic surfactants are used.

The flotation chemistry of the quartz-amine system has been studied

using an induction time apparatus constructed in the present work which has a sensitivity limit of 100-150 micro-seconds. The basic unit is similar to the one used by Eigeles and Volova (1960) and Trahar (1983), but it operates with a micro-computer and has a greater sensitivity. It has been found that at a given dodecyl amminium hydrochloride concentration, the induction time is at a minimum at approximately pH 10.5. At this pH, the collector hydrolizes to form neutral amine and the flotation recovery reaches a maximum, suggesting that iono-molecular species are the surface-active species responsible for flotation. This finding confirms the earlier conclusions obtained using the surface tension (Somasundaran, 1976; Finch and Smith, 1973) and the contact angle (Smith, 1963) techniques. The induction time measurements have also been conducted as a function of particle size, collector concentration, indifferent electrolyte concentration and temperature. The results are compared with flotation data, bubble charge, particle charge and film thickness.

Results of the induction time and microflotation experiments conducted using bubbles and particles of known electrical properties indicate that if the potential on the air/water interface is increase to a high value with the same sign as that of the s/l interface (e.g. by adding a suitable surfactant) the flotation kinetic is retarded; conversely, surfactant of the opposite sign can enhance the adhesion process.