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| DEPARTMENT OF ENERGY, MINES AND RESOURCES Mines Branch Ottawa |
| THE ROLE OF GAS BUBBLES |
| IN THE FLOTATION OF QUARTZ |
| H. P. DIBBS, L. L. SIROIS AND R. BREDIN MINERAL SCIENCES DIVISION AND MINERAL PROCESSING |
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Research Report R 248

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Mines Branch Research Report R 248

THE ROLE OF GAS BUBBLES IN THE FLOTATION OF QUARTZ

by

H.P. Dibbs*, L.L. Sirois** and R. Bredin***

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ABSTRACT

A method has been developed to measure the streaming current of gas bubbles in aqueous solutions of inorganic electrolytes and of dodecylamine hydrochloride. The streaming current data obtained in dodecylamine hydrochloride solutions has been compared with the zeta potential and the flotation recovery of quartz for the same solution conditions. The significance, in the flotation recovery of quartz, of the relative surface charges on the gas bubbles and on the quartz is discussed.

*Research Scientist, Mineral Sciences Division, and **Research Scientist and ***Technician, Mineral Processing Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada. Direction des mines

Rapport de recherches R248

LE RÔLE DES BULLES DE GAZ DANS LA FLOTATION DE QUARTZ

par

H.P. Dibbs*, L.L. Sirois**, et R. Bredin***

RÉSUMÉ

Les auteurs ont développé une méthode pour mesurer le courant d'écoulement des bulles de gaz dans les solutions aqueuses d'électrolytes inorganiques et de chlorure de dodécylamine. Ils ont comparé les données obtenues, sur le courant d'écoulement des solutions de chlorure de dodécylamine, avec le potentiel zêta et le recouvrement de quartz par flotation pour les conditions de solution. Ils ont discuté de l'importance, dans le recouvrement de quartz par flotation, des charges de surface relatives sur les bulles de gaz et sur le quartz.

*Chercheur scientifique, Division des sciences minérales, et **Chercheur scientifique et ***Technicien, Division du traitement des minéraux, Direction des mines, ministère d'Énergie, des mines et des Ressources, Ottawa, Canada.

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INTRODUCTION

The froth flotation process for the separation of minerals in a suitably conditioned aqueous suspension depends upon the establishment of contact between a solid, liquid, and gas phase. Because gas bubbles and mineral particles in an aqueous solution acquire a surface charge, which depends in sign and magnitude upon the solution composition and upon their time of contact with the solution, the efficacy of a given flotation process must be related to the properties of the gas-solution and mineral-solution interfaces before their mutual interaction. The properties of the mineralsolution interface have been widely studied from the flotation viewpoint, consequently, much is now known about the effects of flotation reagents and of other solution components on the properties of the electrical doublelayer at the mineral-solution interface (1,2). However, relatively little attention has been given to the role of the gas-solution interface in flotation and on how its properties facilitate the effective attachment of a gas bubble to a mineral particle. Nevertheless, there is evidence from surface tension and adhesion tension measurements with collectors of different chain lengths⁽³⁾, from contact angle measurements^(4,5), and from various flotation studies⁽⁶⁻⁸⁾ that the amount of collector adsorbed per unit area at the gas-solution interface may well be greater and more significant for good flotation recoveries than the amount of collector adsorbed at the mineralsolution interface. The present study was undertaken to investigate the relative effect of changes in solution pH and collector concentration on the electrical current (streaming current) which is developed, through the adsorption of ions, by gas bubbles as they ascend the flotation column, and to attempt to correlate this streaming current data with the electrokinetic and flotation properties of quartz. Quartz was selected for this work because it is readily available in a state of high purity and because extensive

- 1 -

background information is available on its electrochemical and flotation behaviour.

The electrical properties of gas bubbles in aqueous solutions have been the subject of intermittent study for over a hundred years (9-17). The results from these studies indicate that gas bubbles acquire a negative charge in pure water and in solutions of simple inorganic electrolytes, the magnitude of the charge depending on the electrolyte concentration and on the duration of contact. Similar electrical behaviour of bubbles has been observed with air, nitrogen, and other gases. Surface active agents (surfactants) in solution also produce charges on air bubbles, according to the concentrations of the surfactants and on the sign of the ionic group's charge in the hydrocarbon chain. Gilman and $Bach^{(18)}$, from electrophoretic measurements, found that tetra-substituted ammonium salts, at molar concentrations above 10^{-6} , produced a positive charge on an air bubble, whereas sodium palmitate solutions produced a negatively charged bubble whose charge increased with the solute concentration. Samygin et al. (14) measured the Dorn potential produced while air bubbles rise through an aqueous solution of inorganic salts, or of ionic surface active agents. It was found that the sign and magnitude of the Dorn potential was dependent on the ion adsorbed on the bubble and, if the ions in solution showed no appreciable tendency to adsorb, increasing their concentration gave a steady decrease in potential.

Bubble coalescence measurements^(15,16) also give information related to the properties of individual bubbles. It is found that, in pure water, air bubbles coalesce readily but that, in aqueous electrolyte solutions, coalescence becomes progressively more difficult with increase in electrolyte concentration; this effect is particularly marked in solutions containing small, multi-valent cations. These results were attributed to the "structure-forming" characteristics of inorganic ions which produce an increase in the viscosity of water that retards the draining of the interfacial film between two air bubbles. It may be expected that similar coalescence effects would result from the presence of frothing agents in solutions.

- 2 -

EXPERIMENTAL

The experimental arrangement which was developed to measure the streaming current of gas bubbles in an aqueous solution is shown in Figure 1. The cell was made of glass and was in two sections, joined by a 40/50 standard taper joint. A medium porosity frit in the lower section was used to generate the gas bubbles, and the upper section consisted of a 50 x 3.2-cm tube. High-purity nitrogen was used in all the measurements and a flow-rate of 100 ml/min was employed for most of the runs. The two silver-silver chloride electrodes (Figure 1) were prepared from loops of silver wire which were lightly chloridized before $use^{(19)}$. The silver wire from each electrode was passed to the measurement circuit through a closely fitting glass tube and was insulated from the solution, at the lower end, by an epoxy-resin seal or by a Teflon plug. The lower electrode was placed around the frit just below the bubble stream, whereas the upper electrode could be adjusted to allow streaming current readings at various distances from the frit and, hence, to measure changes in the streaming current with the "age" of the bubbles. As shown in Figure 1, six standard measurement positions for the upper electrode were employed; Position 6 was 2.5 cm above the frit, and the other five positions were spaced successively 6.25 cm apart along the tube.

The streaming current developed by the gas bubbles was measured by the technique used in the determination of the zeta potential of minerals⁽²⁰⁾ and metals⁽²¹⁾. In this method, a high-precision variable resistance is placed in series with the two measurement electrodes; if the value of this resistance is negligible in comparison with the resistance of the solution between the electrodes, essentially all the charge displaced by the bubbles is returned to the lower electrode through the external circuit. The streaming current may then be calculated from the voltage developed across the

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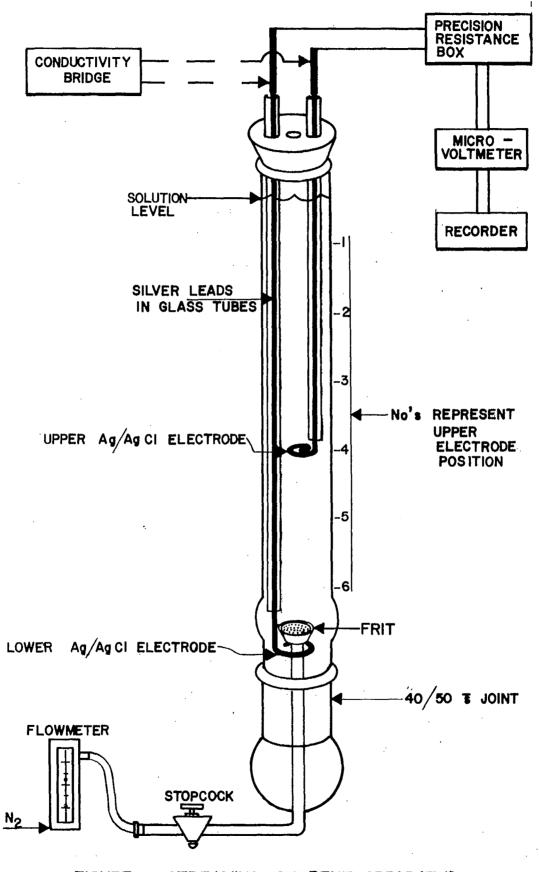


FIGURE I STREAMING CURRENT APPARATUS

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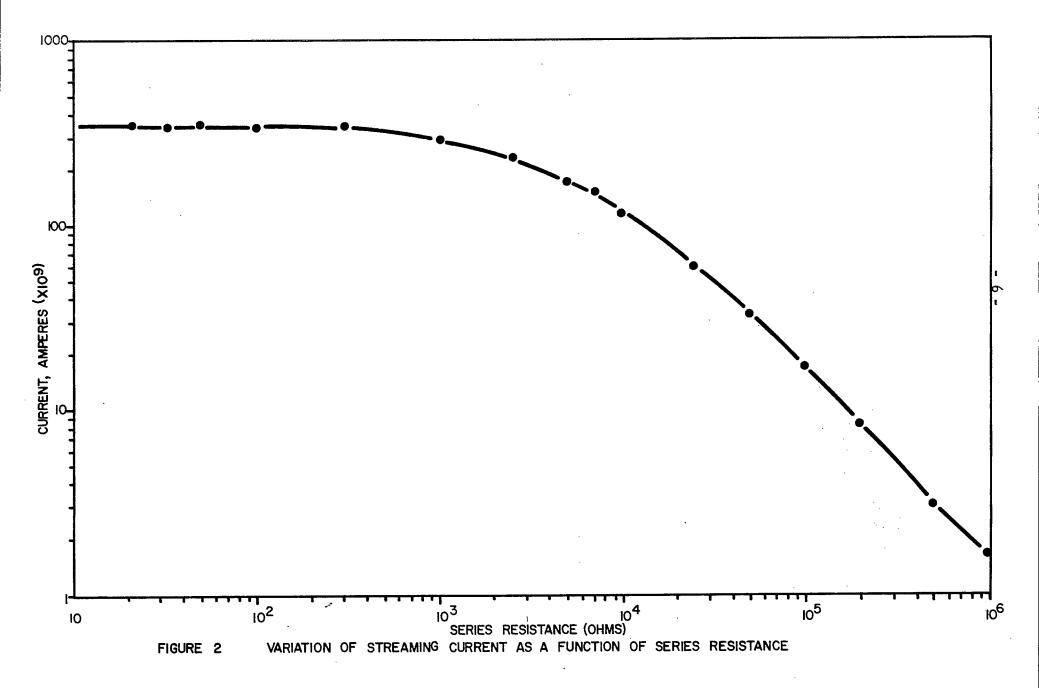
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known resistance. The resistance of the solution between the electrodes was measured with a conductivity bridge (Beckman Instrument Co., Model RC 18) before each run and a value of the external resistance was selected to be less than about two per cent of this resistance. In general, the streaming current was of the order of 10^{-8} amp and the voltage developed across the external resistance was measured with a microvoltmeter (Keithly Instrument Co., Model 150B) and displayed on a chart recorder. All voltage readings were converted to streaming currents for plotting. The effect of changing the value of the external resistance on the calculated value of the streaming current, for a solution resistance of about 4,000 ohms, is shown in Figure 2. It will be seen that, for low values of the external resistance, the calculated current is independent of this resistance.

The flotation cell (Figure 3) was similar in design to the streamingcurrent cell, with the addition of a feed port corresponding to Position 4 of the bubble tube, i.e., at 15 cm above the frit. The top of the cell was capped with a Hallimond-tube head to collect the floated quartz. For flotation measurements, a five-gram sample of quartz was conditioned for five minutes in the conditioner-feeder with the same solution as that in the flotation column. By applying a small gas pressure to the feeder, feed was added cyclically to the flotation column through an electrically actuated hosecock. A similar hosecock, at the base of the flotation column, was used to control the level in the flotation column by releasing non-floats and some solution. Flotation was carried out for seven minutes at a nitrogen flow-rate of 100 ml/min. Dodecylamine hydrochloride (DAC) was used as the flotation reagent for all the tests, and no additional frothing agent was used.

The zeta potential of quartz was determined by a modified streaming-potential method⁽²²⁾, in which the streaming potential and the pressure difference across the cell were measured simultaneously and plotted on an X-Y recorder. The zeta potential was calculated from the slope of the streaming potential/pressure difference curve, using the standard Smoluchowski relationship.

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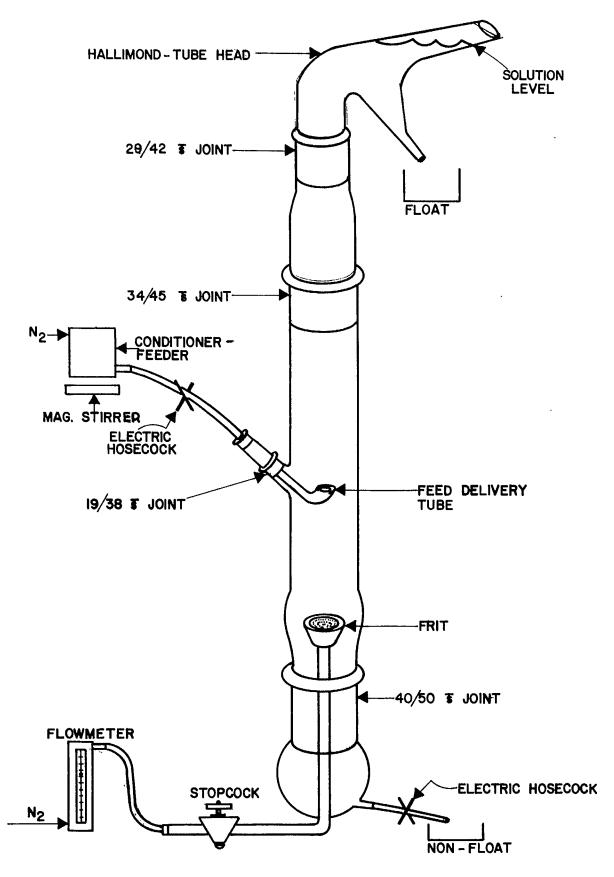


FIGURE 3 FLOTATION APPARATUS

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The quartz used for the flotation and the zeta-potential measurements was prepared from selected crystals of Brazilian quartz. These were crushed; the minus 150 plus 200-mesh fraction was retained and leached with constant boiling hydrochloric acid for twenty-four hours. The cleaned quartz was then elutriated with distilled water until the effluent solution was free of chloride ions. The cleaned and washed quartz was stored under triple-distilled water, which was changed frequently.

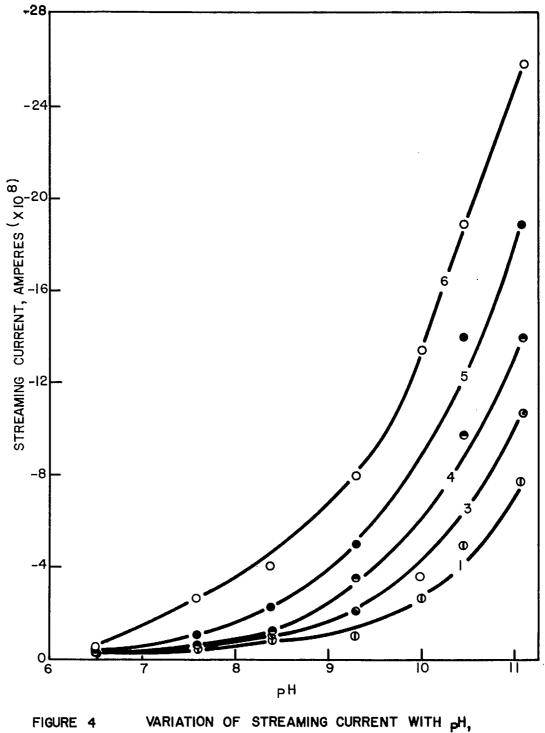
All measurements were made at room temperature and tripledistilled water was used to prepare the solutions for the streaming-current measurements.

RESULTS

The flotation, zeta potential, and streaming-current measurements on the quartz/aqueous DAC solution system were made in neutral or alkaline solutions, and pH adjustments were made by adding potassium hydroxide solution. However, before undertaking measurements of the variation of streaming current with DAC concentration in solutions of various pH's, preliminary measurements were made to determine the influence of pH alone on the streaming current. The results obtained (Figures 4 and 5) show that the streaming current was negative over the pH range examined (pH 6.5 to 11.1), that the current increased in an approximately exponential manner with pH (Figure 4) and that, for a given pH, the streaming current decreased (Figure 5) as the upper electrode was moved away from the frit, i.e., with the "age" of the bubbles. Some streaming-current measurements were also made at pH 6.3 in solutions of the chloride salts of mono-, di-, and tri-valent cations. Here again the streaming current was always negative (Figure 6) and, as has been noted in bubble coalescence measurements⁽¹⁵⁾, appeared to be closely related to the ionic strength of the chloride solution (Figure 7). As with the hydroxide solutions (Figure 5), the streaming current also decreased with increasing distance from the frit (Figure 8).

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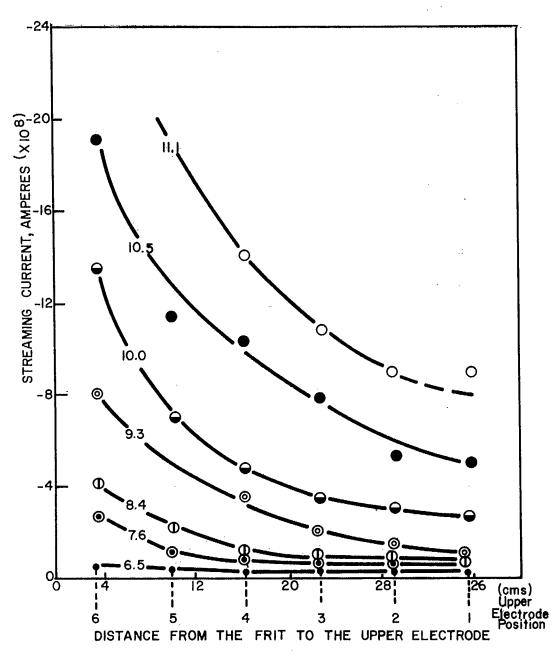
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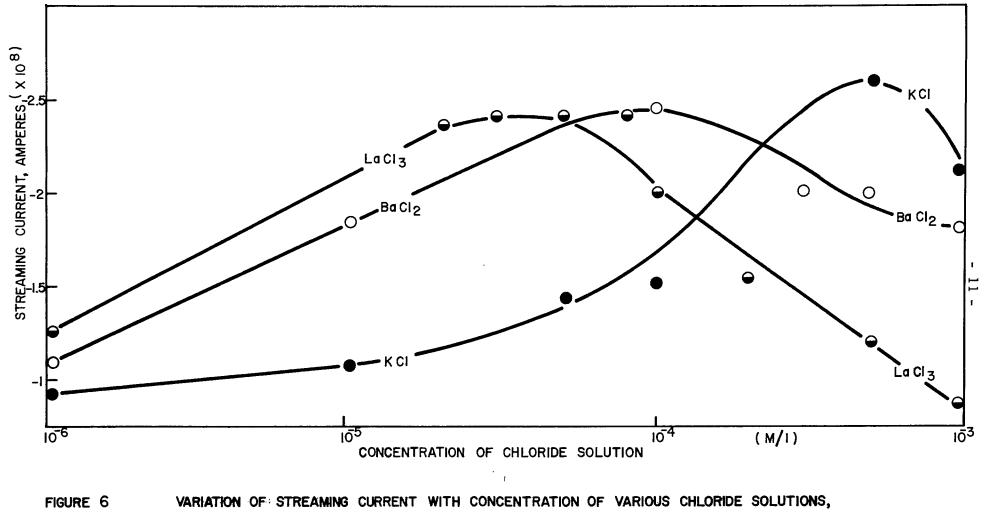
AT VARIOUS UPPER ELECTRODE POSITIONS







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FOR UPPER ELECTRODE POSITION NUMBER 6, AT PH 6.3

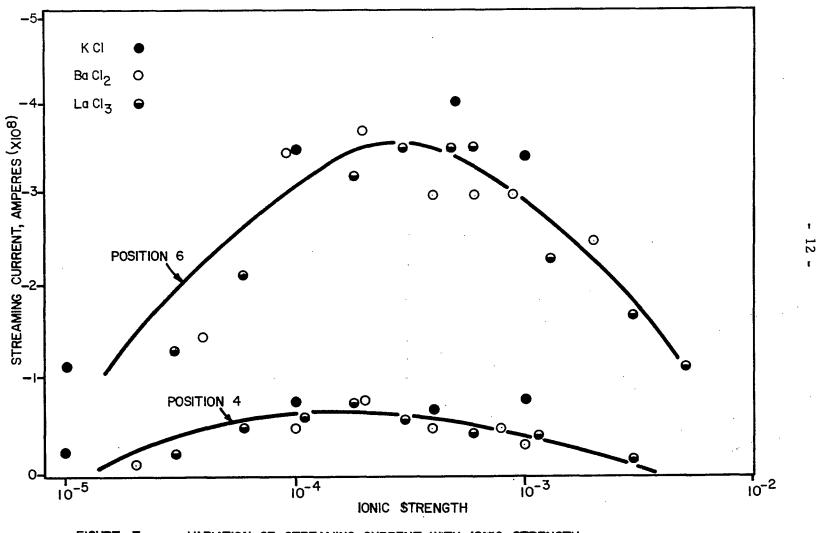
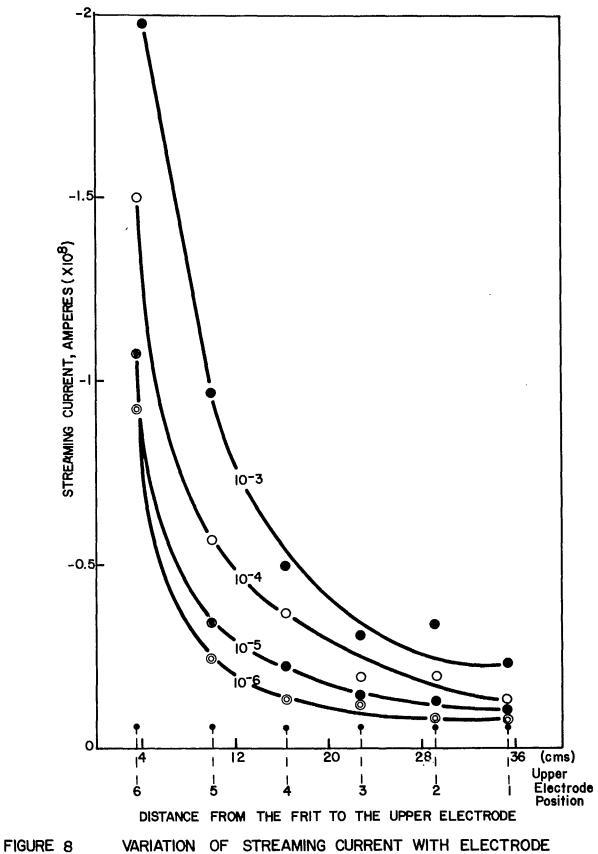


FIGURE 7 VARIATION OF STREAMING CURRENT WITH IONIC STRENGTH . FOR K CI, Ba CI₂, AND La CI₃ SOLUTIONS, AT _PH 6.3

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POSITION IN VARIOUS POTASSIUM CHLORIDE MOLAR SOLUTIONS, AT $\,$ pH $\,6.3$

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- 7

Detailed measurements were made, at the six standard positions in the cell, of the streaming current of bubbles in solutions of DAC over a molar concentration range of 10^{-6} to 10^{-4} at pH's of 6.3, 9.0, 9.5, 10.0, and 10.5, and 11.0. Most of these runs were made with a nitrogen flowrate of 100 ml/min. However, some studies were made at pH 6.3 on the effect of flow-rate on the streaming current for various concentrations of DAC (Figures 9 and 10), which indicated that the streaming current was not particularly flow-rate dependent for DAC concentrations below about 10^{-5} molar.

The variation of streaming current with distance from the frit for various molar DAC concentrations at pH 6.3 is shown in Figure 11. It is of interest to note that for the lower DAC concentrations the current direction changes sign - from negative to positive - as the bubbles ascend the tube. In Figures 12 to 16 the variation of streaming current with DAC concentration is shown for various values of pH at different upper electrode positions. In Figure 17, these data are summarized for Position 4 in the bubble cell for the range of DAC concentrations and pH values which were studied. For a pH up to about 9.5, the streaming current was positive for all but the lowest DAC concentrations but, at a pH above 9.5, the streaming current changed to a negative value at a DAC molar concentration of about 10^{-5} . Because - at a given DAC concentration and pH - a change in size of the bubbles, as they ascend the tube, could influence the electrical data, measurements of bubble diameters were made by a photographic technique at different positions in the cell. The measurements indicated that changes in bubble diameter were small and that they would not influence the electric current; for example, at a 10^{-4} -molar concentration of DAC, at pH 10, the average size of the bubbles at Position 6 was 750 µm and at Position 1 was 770 µm. Separate bubble experiments using glass and stainless steel capillaries indicated that the charge on the bubble was independent of the nature of the capillaries and that applying an external potential between the steel capillary and the solution had no effect on the bubble charge.

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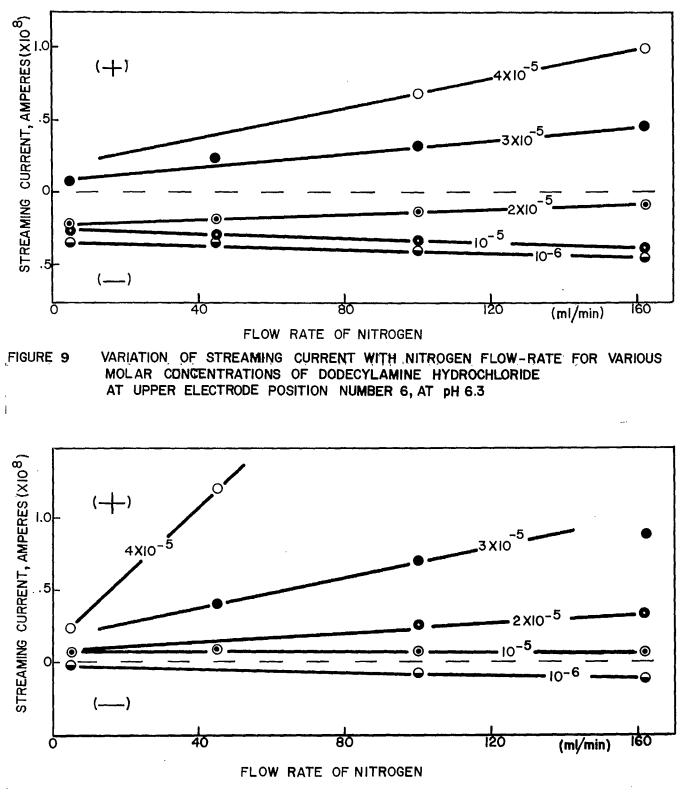


FIGURE IO VARIATION OF STREAMING CURRENT WITH NITROGEN FLOW-RATE FOR VARIOUS MOLAR CONCENTRATIONS OF DODECYLAMINE HYDROCHLORIDE AT UPPER ELECTRODE POSITION NUMBER 1, AT pH 6.3

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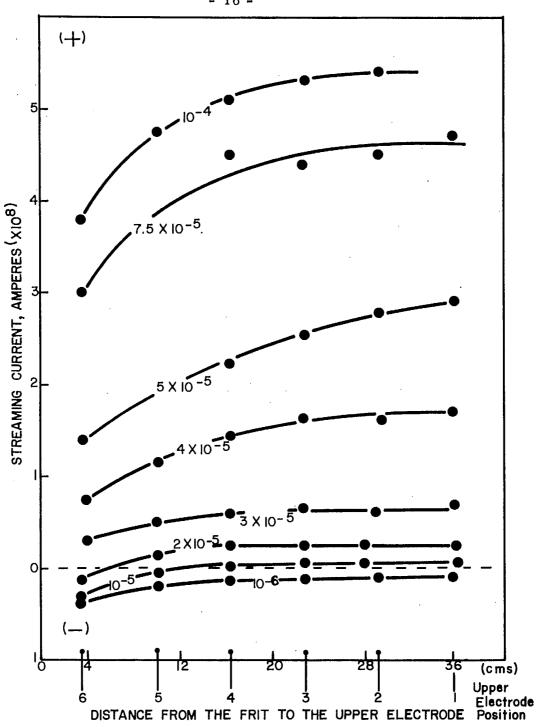
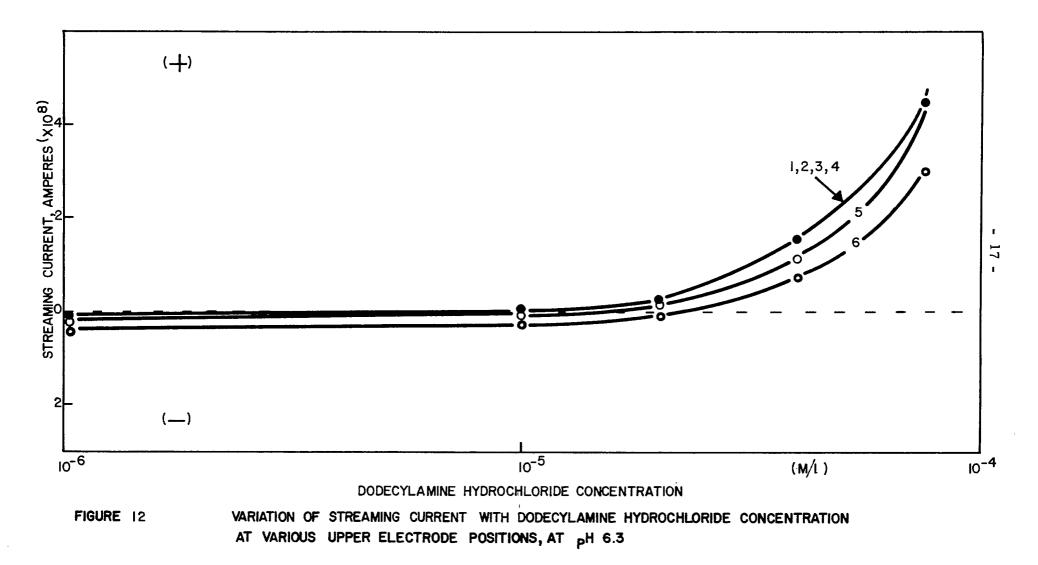


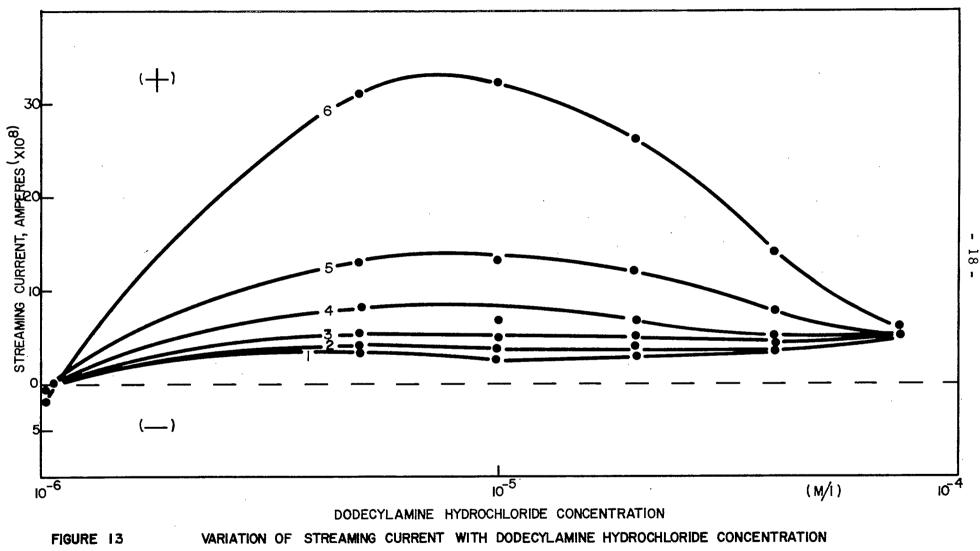
FIGURE II VARIATION OF STREAMING CURRENT WITH ELECTRODE POSITION IN VARIOUS DODECYLAMINE HYDROCHLORIDE MOLAR SOLUTIONS, AT PH 6.3

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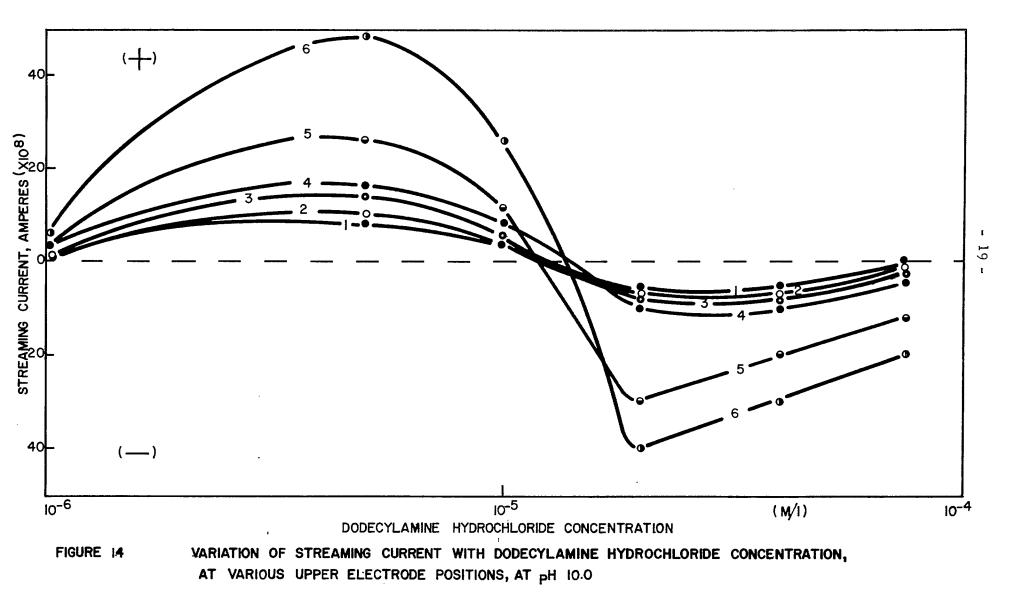


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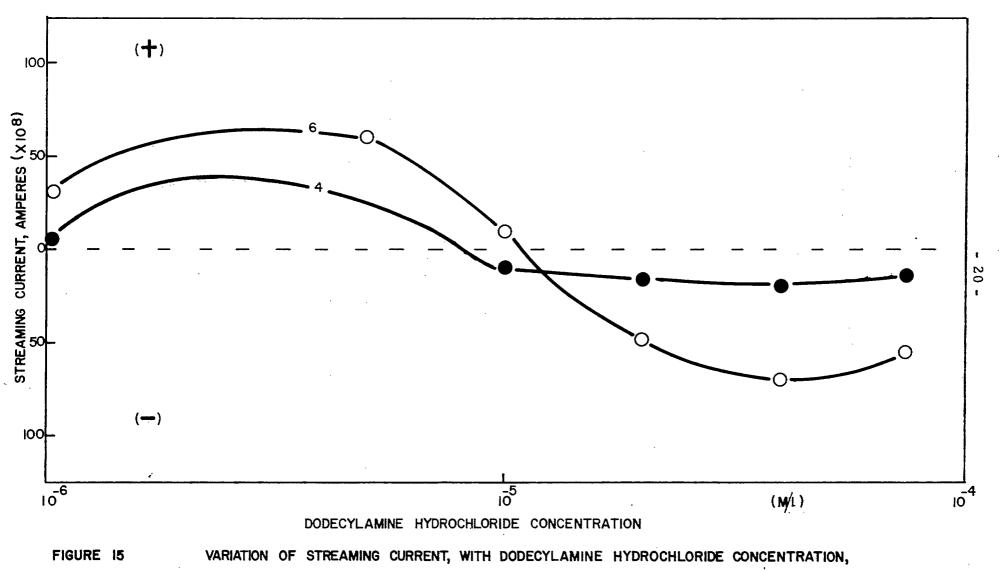
AT VARIOUS UPPER ELECTRODE POSITIONS, AT pH 9.0

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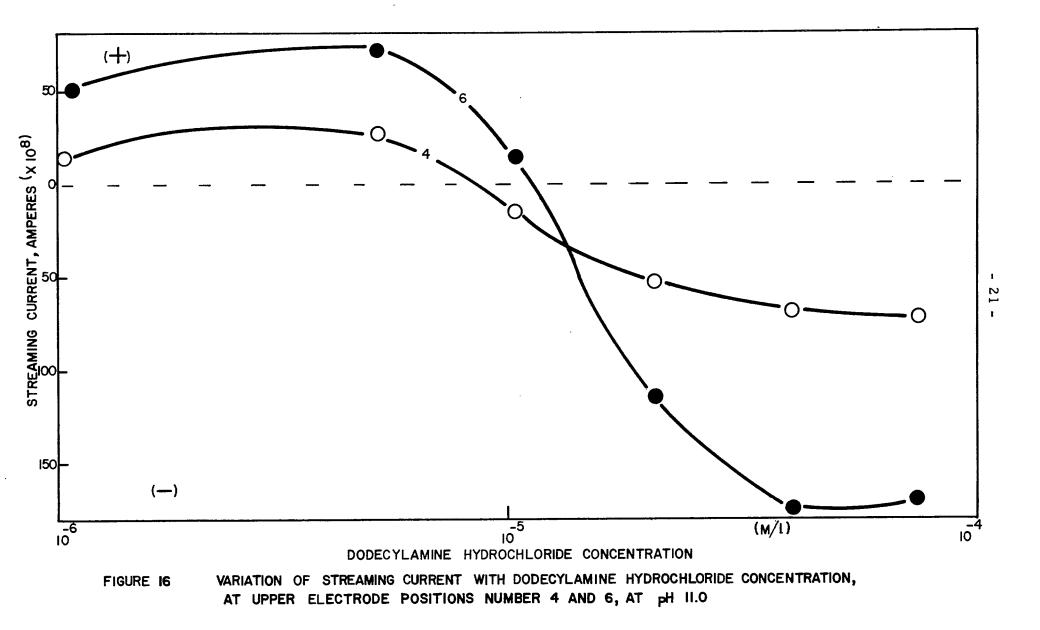
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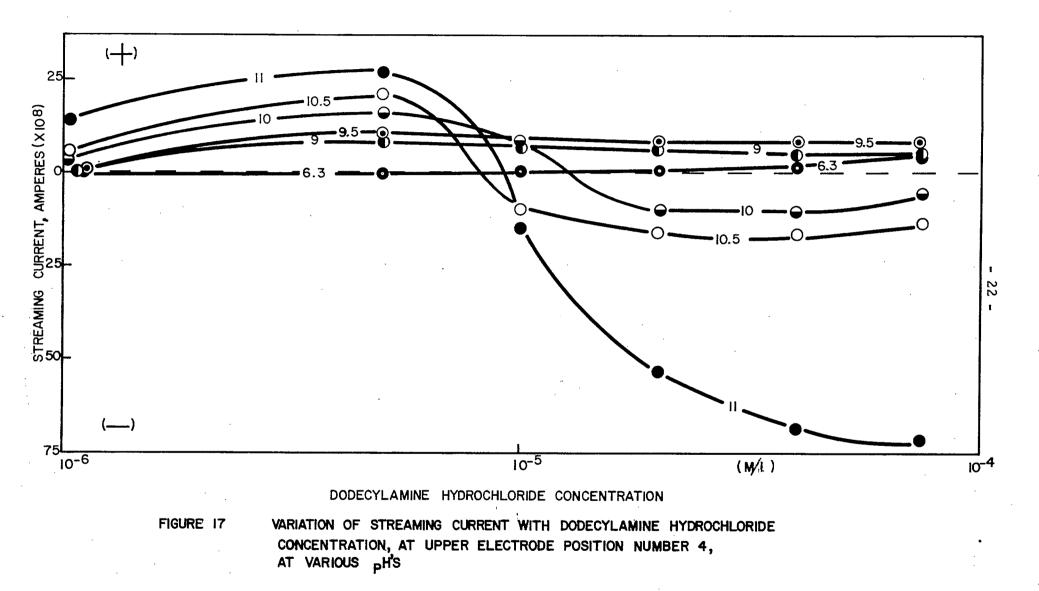
AT UPPER ELECTRODE POSITIONS NUMBER 4 AND 6, AT PH 10.5

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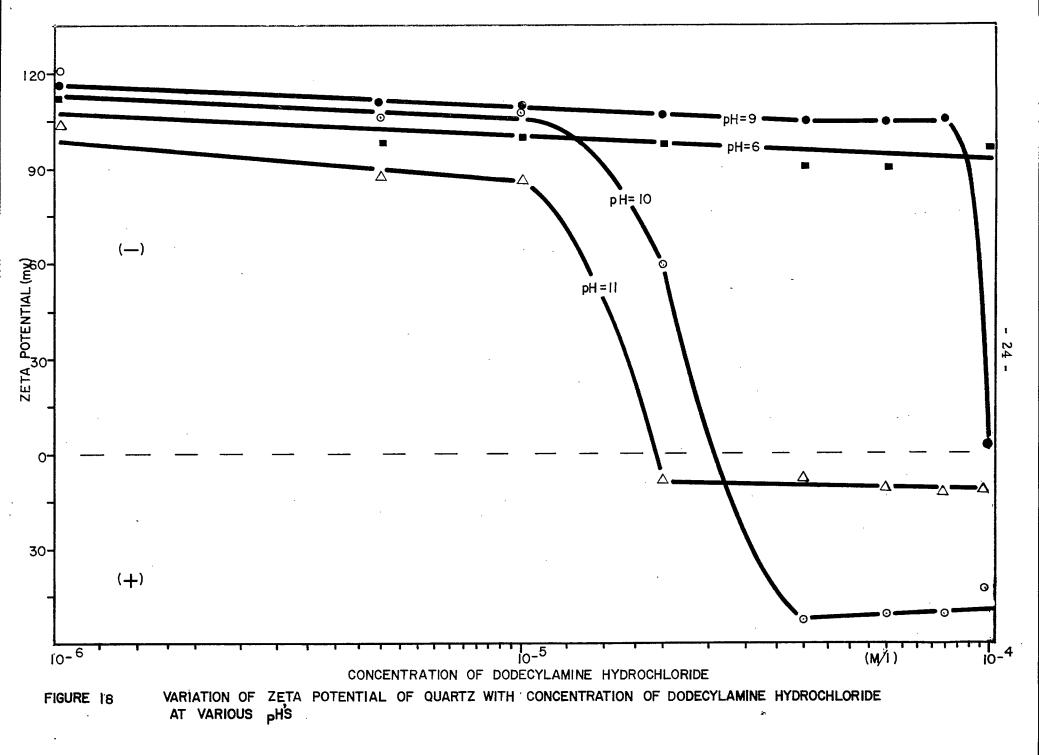
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The zeta potential of the quartz used in the flotation measurements was determined in DAC solutions at molar concentrations between 10^{-6} and 10^{-4} at different pH's and is shown in Figure 18. These data compare well with similar measurements reported by other authors^(23,24).

Flotation tests with quartz were made at pH 6, 9, 10, and 11 and at DAC molar concentrations of 1×10^{-6} , 5×10^{-6} , 1×10^{-5} , 5×10^{-5} , and 8×10^{-5} . The flotation recoveries are shown, in Figures 19 to 23, with the streaming current of the bubbles and zeta potential of the quartz for the same solution conditions.

DISCUSSION

The properties of the static air/water interface have been the subject of numerous studies (25, 26) which have indicated that the interfacial water layer possesses considerable "structure" (25) and that the first layer of water molecules consists of oriented dipoles whose positive ends are directed towards the bulk solution (27). It is also known from surface tension measurements in solutions of inorganic electrolytes that, in all but very dilute solutions, there are less solute ions in the interfacial layer than in the bulk solution (25, 28). At the moment of formation of a gas bubble in an aqueous solution, the composition of the solution at the gas-solution interface must be similar to that in the bulk and must consist of an equal number of positive and negative ions in a "matrix" of water molecules. However, immediately after bubble formation, a re-arrangement of ions in the vicinity of the bubble surface must occur to give an interfacial structure approaching that of the static gas-solution interface. Previous studies of the electrical properties of gas bubbles in aqueous solutions of inorganic electrolytes^(11-14,29) have shown that the bubble always has a net negative charge, indicating an excess of negative ions (or deficiency of positive ions) associated with the bubble surface. For the inorganic electrolyte solutions



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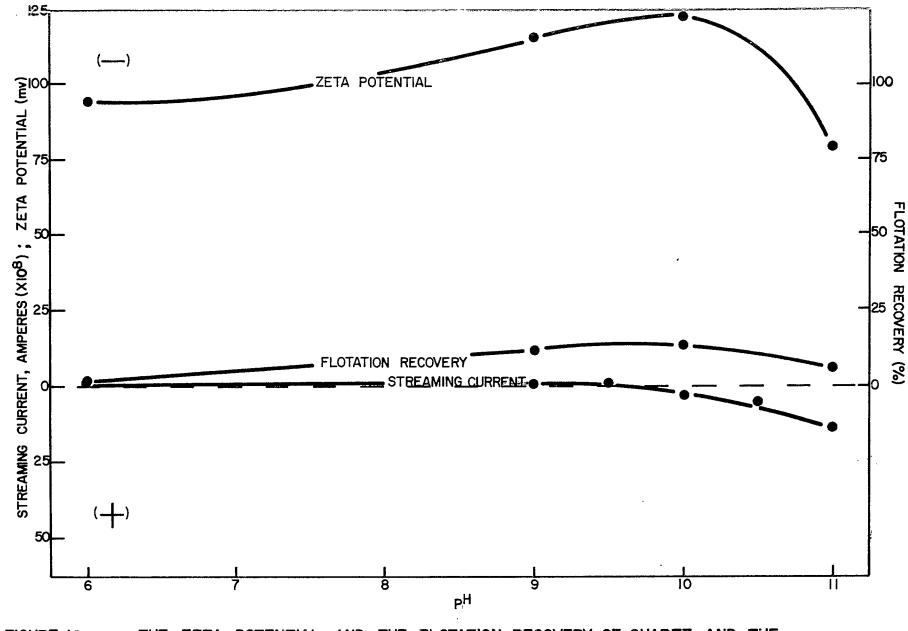
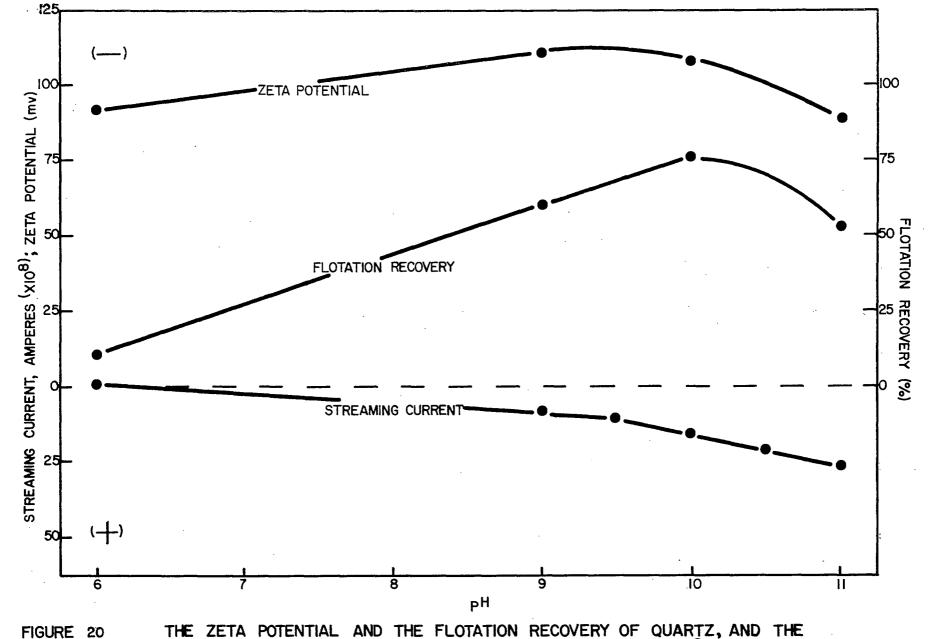


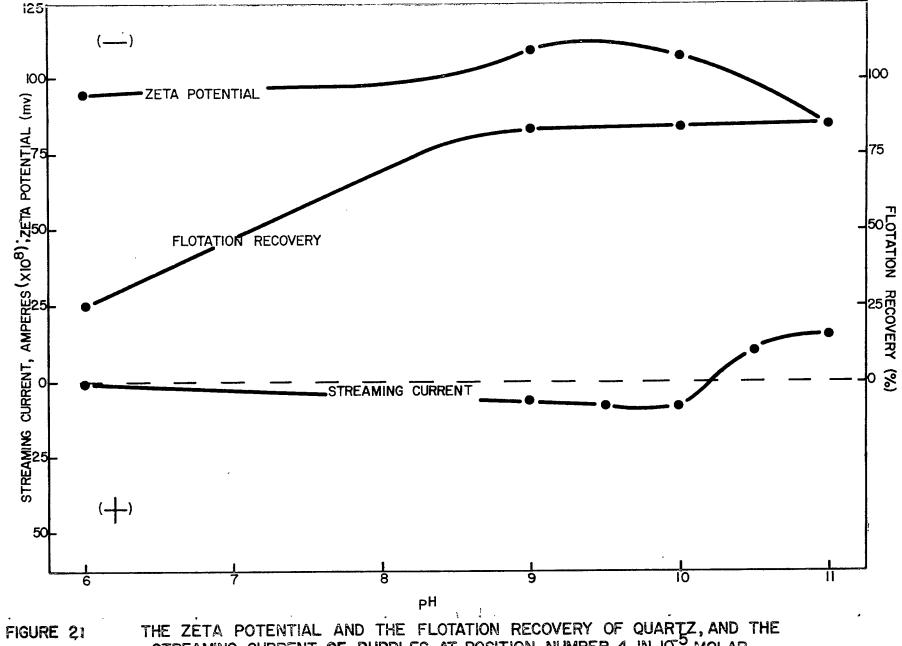
FIGURE 19 THE ZETA POTENTIAL AND THE FLOTATION RECOVERY OF QUARTZ, AND THE STREAMING CURRENT OF BUBBLES AT POSITION NUMBER 4, IN 10⁻⁶ MOLAR DODECYLAMINE HYDROCHLORIDE SOLUTION, AT VARIOUS PHS

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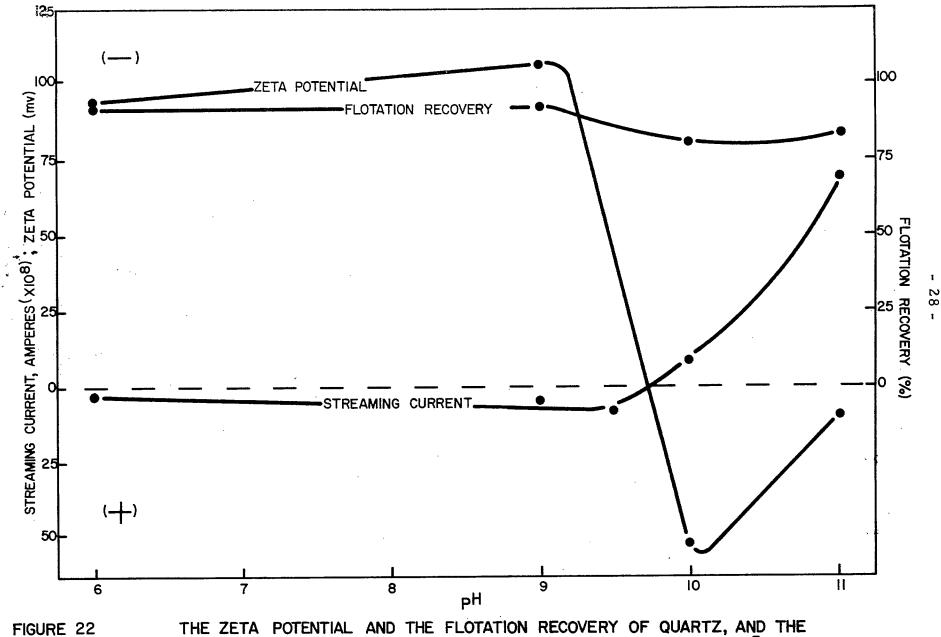
THE ZETA POTENTIAL AND THE FLOTATION RECOVERY OF QUARTZ, AND THE STREAMING CURRENT OF BUBBLES, POSITION NUMBER 4, IN 5 X 10⁻⁶ MOLAR DODECYLAMINE HYDROCHLORIDE SOLUTION, AT VARIOUS PH'S.

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THE ZETA POTENTIAL AND THE FLOTATION RECOVERY OF QUARTZ, AND THE STREAMING CURRENT OF BUBBLES AT POSITION NUMBER 4, IN 10⁵ MOLAR DODECYLAMINE HYDROCHLORIDE SOLUTION, AT VARIOUS PHS THE

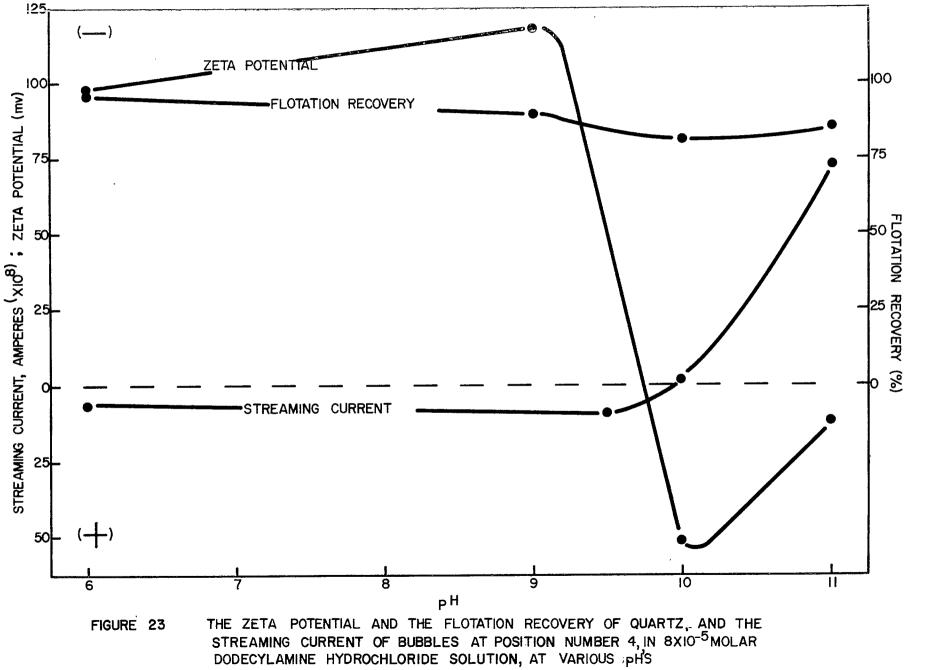
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THE ZETA POTENTIAL AND THE FLOTATION RECOVERY OF QUARTZ, AND THE STREAMING CURRENT OF BUBBLES AT POSITION NUMBER 4, IN 5X10⁻⁵ MOLAR DODECYLAMINE HYDROCHLORIDE SOLUTION, AT VARIOUS PHS.

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studied here, it is suggested that, on bubble formation, the ions in the vicinity of the bubble surface are attracted to the bulk of the solution. The degree of this attraction will be closely related to the extent of hydration of the individual ions and will be greater for more highly hydrated ions which act as "structure formers" in aqueous solutions (26) and will be influenced by the electric field of the oriented dipole layer of water at the gas-solution interface. Because, in general, cations have greater primary solvation sheaths than anions, they will be more strongly attracted than anions towards the bulk solution (30) and they will also be repelled from the interface by the dipolar field. Hence, on bubble formation, a re-arrangement of the ionic structure at the interface occurs which, in time and depending on the mobilities of the ions involved, will give rise to an equilibrium interfacialcharge distribution in which there is an excess of negative ions associated with the bubble surface. For the potassium hydroxide (Figures 4 and 5) and the chloride solutions (Figures 6 and 8) studied here, it is proposed that, shortly after bubble formation, a non-equilibrium excess of negative ions is present at the bubble-solution interface and that it later approaches an equilibrium charge distribution as the negative ions diffuse from the interface, i.e., as the bubble ages; this effect is reflected in the decrease in the negative streaming current as the upper electrode is moved away from the frit.

As may be seen from Figures 12 to 17, the behaviour of the streaming current of gas bubbles in solutions of DAC is more complex than in simple inorganic electrolyte solutions. Because dodecylamine salts are salts of a weak base, they are hydrolized in solution, and a considerable amount of the free base is present at alkaline pH's⁽³¹⁾. Both the dodecylamine ion (RNH_3^+) and the dodecylamine molecule (RNH_2) will have a structure-breaking effect on water. Further, the non-polar hydrocarbon chain favours a medium that has a low dielectric constant so that dodecylamine will be adsorbed at the gas/water interface with its hydrocarbon chain in the gas phase⁽³²⁾. Therefore, as distinct from inorganic electrolyte

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solutions, it would be expected that dodecylamine (in ionic or molecular form) present at the gas-solution interface on bubble formation would be preferentially adsorbed and that its concentration would be increased during the bubble lifetime by further adsorption from the solution by diffusion, and by collision processes.

The behaviour of the streaming current in DAC solutions at pH 6.3 (Figures 11 and 12), where all the dodecylamine is present as RNH_3^{\ddagger} , is as would be expected from this viewpoint. At low concentrations (<2 x 10⁻⁵ molar) of DAC, the streaming current is initially negative at Position 6 and is similar in value to that of water of the same pH (Figure 4). However, as the distance from the frit increases, the streaming current becomes positive, indicating a steady adsorption of RNH_3⁺ on the bubble as it ascends the tube. In general, the equilibrium value of the streaming current is greater, the higher the DAC concentration (Figure 10).

At any particular DAC concentration, as the pH of the solution is increased, the ratio [OH-]:[RNH⁺₃ + RNH₂] increases markedly, and it would be expected that the streaming current would initially increase in the negative direction with increase in pH (Figure 4). However, up to a DAC molar concentration of about 10^{-5} , no such effect is observed and, in all cases (Figures 13 to 16), the largest positive value of the streaming current is observed closest to the frit. The reasons for this behaviour are not clear, but it appears that the effect of increasing the hydroxide ion concentration is to increase the adsorption of RNH_3^+ on the bubbles. Depending on the pH, further increase in DAC molar concentration above about 10-5 leads to a decrease, or to a reversal in sign, of the streaming current. The latter behaviour at pH 10 and above can be attributed only to the build-up of counter hydroxyl ions in the plane of adsorbed RNH⁺₃ ions. This build-up has the dual effect of reducing the net charge on the bubble surface by coulombic interaction and of increasing the local hydroxide ion concentration at the gas-solution interface to a value greater than that in the bulk solution; the build-up thus modifies the $RNH_3^+ + OH^- \neq RNH_2 + H_2O$ equilibrium in

the interfacial region. It should be noted in this context that the streamingcurrent measurements reflect only the net charge on the bubbles and consequently can provide no data on the amount of RNH₂ adsorbed, although RNH₂ molecules would still be held on the bubbles by van der Waals forces.

The quartz/aqueous solution system has been widely studied^(23, 24, 33) and it is well established that hydrogen and hydroxyl ions are potentialdetermining ions for this system. Zeta potential measurements for quartz in sodium chloride solutions^(23, 24) have shown that, at a fixed pH, increasing the ionic strength of the solution leads to a decrease in the (negative) value of the zeta potential but not to a reversal of its sign. The zeta potential of quartz in dilute solutions of DAC is similar to that in sodium chloride solutions but, in the alkaline range at concentrations above about 10^{-5} molar, a reversal in sign of zeta potential is found (Figure 17). This effect has been attributed to the adsorption of more dodecylamine ions on the quartz surface than would be anticipated from simple electrostatic considerations; and this adsorption may be enhanced by the presence of neutral dodecylamine molecules on the quartz surface in the alkaline range⁽²³⁾.

For the successful flotation of quartz, it is necessary that the quartz particle and the gas bubble make "permanent" contact with each other, forming a three-interphase quartz-gas-liquid system which has to be energetically more favourable than the two separate systems, gas-liquid and solid-liquid. Because both the gas bubble and the mineral particle are moving in the flotation pulp, the distribution of charge at the quartz-liquid and gas-liquid interfaces will be similar to that determined by electro-kinetic measurements and the probability of favourable interaction between the solid and the gas bubble should be dependent on electrostatic and van der Waal's forces together with possible effects from steric interactions⁽³⁴⁾. With the exception of the flotation recoveries above pH 10 in the 10^{-5} molar DAC (Figure 21), the present studies show that the charges on the quartz and the gas bubbles are opposite over the range of DAC concentrations in which the flotation was conducted; the reversal in sign of zeta potential,

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and hence the surface charge on the solid side of the diffuse double layer, occurring under the same solution conditions as the reversal in sign of the streaming current of the bubbles (Figures 19 to 33). However, before the quartz and the gas bubble can join together the water layer between them has to be displaced. In general, the presence of a molecule containing a hydrocarbon chain in an aqueous phase will have a structure-breaking effect on the water in its vicinity and thus reduce its viscosity⁽¹⁵⁾. If it is assumed that dodecylamine is adsorbed on or near the quartz surface with its polar and directed towards the solid, then such adsorption should aid the draining of the quartz-bubble interphase water layer.

The present study shows that for fixed hydrodynamic-conditions, simple electrostatic interactions between bubbles and the quartz particles play a significant role in the flotation recovery of quartz in DAC solutions. To test the general applicability of this hypothesis, further studies are required in other flotation systems in which different surfactants, and modifiers and depressants, are used, associated with contact angle measurements for the same system.

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