

THE ACTION OF SODIUM SILICATE IN
THE FLOTATION OF CERTAIN CALCIUM
MINERALS

by

Grover Gutierrez B.

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A thesis respectfully submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment for the degree of Master of Science in Metallurgical Engineering.

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ABSTRACT

Microflotation studies were performed with calcite, fluorite, and apatite to determine, first, their response to oleate flotation, and second, the action of sodium silicate in the calcium mineral-oleate system. Electrokinetic and infrared spectrophotometric studies were undertaken to establish the mechanism of collector and silicate adsorption.

Chemisorption of the collector on the surface of these calcium minerals is inferred from flotation data and confirmed with infrared spectrophotometry.

The analysis of flotation and electrokinetic data shows that physical adsorption of the colloidal silica may be the mechanism of depression by an aqueous solution of sodium silicate.

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INTRODUCTION

The fatty acids and their derived soaps are not good selective flotation reagents. All minerals are more or less completely floated by them. If the mineral is liberated and if sufficient soap is used, the success or failure of flotation can be attributed to the choice and amount of the gangue depressing reagent.

Selective flotation between calcium minerals, using oleate as collector, has been investigated and practiced in the past. The reagents used in separation consist of a variety of chemical compounds, which have been added to the flotation pulps individually or as mixtures.

The soluble silicates, particularly sodium silicate, are used most of the time in nonmetallic mineral flotation. Sodium silicate acts as a depressant and as a dispersant for fine particles. In early studies, Patek⁽¹⁾ and Goghil and Clemer⁽²⁾ showed that calcite can be depressed either with solutions of acidified sodium silicate or with combinations of sodium silicate and heavy metal salts. Copper sulfate was the most used, but many other metal salts were just as effective. Redwood

tannin (quebracho) was used as depressant for calcite and quartz in the flotation of fluorspar⁽³⁾. In this system metallic salts had to be kept at a minimum because metal tannates also depress fluorspar. The quantity of carboxylic acid and quebracho required for this separation appears to be influenced to some extent by the pulp density⁽⁴⁾.

Selective flotation of scheelite from apatite and quartz has been effected using a fatty acid together with an alkaline reagent such as caustic soda, soda ash, or sodium silicate⁽⁵⁾. The same investigators pointed out that inorganic acids such as hydrochloric, nitric, etc., and short-chained organic acids are also effective in the depression of apatite.

Separation of phosphate and carbonate is achieved by using short-chained saturated fatty acids such as capric or naphthenic acid⁽⁶⁾. Separations of scheelite and calcite have been reported with sodium silicate at temperatures from 60 to 80 degrees centigrade⁽⁷⁾.

The role of sodium silicate in these separations is rather poorly understood for a number of reasons: first, its dissolution process is very complex, giving rise to the presence of many ions in solution. Second, the adsorption of silicate on the surface of some calcium minerals may modify their surfaces so as to result in the flotation of certain species and the depression of others.

Some investigators believe that when sodium silicate is dissolved, it may form polysilicates colloidal aggregates (polymers) in the solution.

These colloidal aggregates may coat the surface of a mineral, modifying its properties. The formation of a possible film of colloidal particles on the surface of a calcium mineral can be attributed to the chemical similarity between a siliceous surface and the polymers. Studies on slime coating have shown that this phenomenon is related to surface charge^(8,9). Generally speaking, a coating is possible when the mineral and slime or colloidal aggregate possess opposite electrical charge.

On the basis of the previous information, the present work was directed to study the role of aqueous solution of sodium silicate in the flotation of calcite, apatite, and fluorite with potassium oleate as collector.

FLOTATION EXPERIMENTS

A standard microflotation technique⁽¹⁰⁾ was used in the present study to determine, first, the response of these three calcium minerals to oleate flotation, and second, the action of sodium silicate in these systems.

Experimental Materials

The following materials were used in this investigation:

Minerals: Pure crystals of calcite, apatite, and fluorite were used in these experiments. The purity of each mineral was confirmed by X-ray diffraction. Some characteristics of these minerals are given below.

<u>Mineral</u>	<u>Chemical Composition</u>	<u>Specific Gravity</u>
Calcite	CaCO_3	2.7
Fluorite	CaF_2	3.0-3.3
Apatite	CaFPO_4	3.2

Sample Preparation: To avoid sample contamination, the crystals of

these minerals were ground by hand using a porcelain mortar and pestle. These ground minerals were sized by dry screening to the desired particle size of 48x150 mesh. Before each flotation experiment, the sized material was deslimed by being decanted several times with conductivity water.

Water: Conductivity water was used in all of the experimental work. This water was prepared by passing distilled water through an ion exchange column (Amberlite). The average measured conductivity was about 1.0 micromho.

Reagents: Pure potassium oleate was used as collector. The characteristics of the sodium silicate solution (water glass) were the following:

<u>Chemical Composition</u>	<u>Degree Baume</u>	<u>Equivalent Concentration</u>
$\text{Na}_2\text{O} \cdot 3.36\text{SiO}_2$	41	529 gram/liter

Dowfroth 250 was used as frother. Chemically pure hydrochloric acid and potassium hydroxide were used for pH adjustments.

Flotation Apparatus

A small microflotation cell was used in the experimental work. The cell was constructed by removing the stem of a 150 cc Buchner funnel and placing another stem parallel to the filter for gas introduction. A microscope slide was introduced into the cell as a baffle, while the pulp

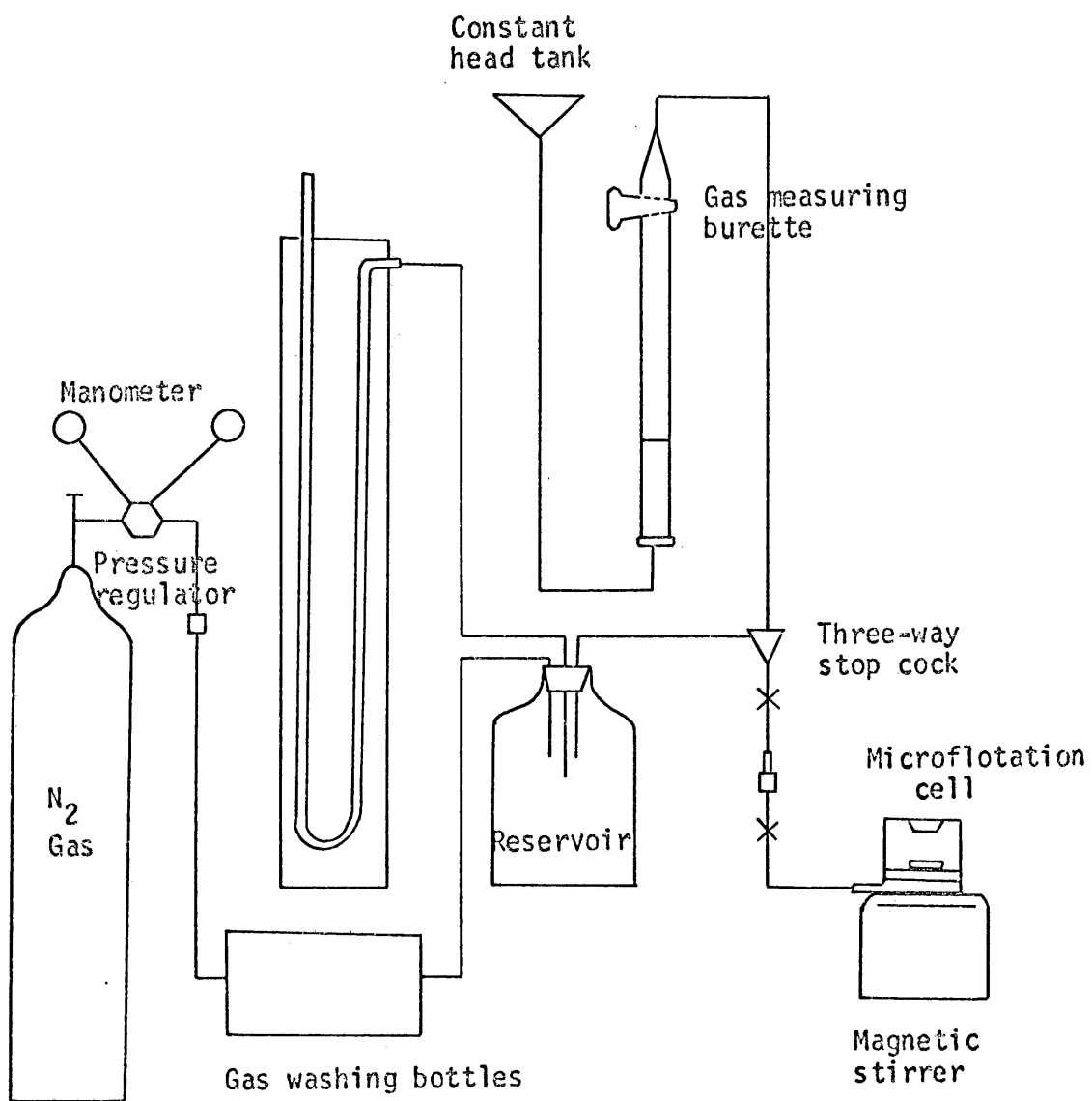


Figure 1: Schematic diagram of Microflotation apparatus.

was agitated with a magnetic stirrer.

Figure 1 is a schematic representation of the complete experimental apparatus used in this study.

The apparatus used has two principal advantages:

- 1) Contamination of the system is kept to a minimum because no metallic components are involved.
- 2) Small charges of a pure mineral can be used.

Experimental Procedure

All microflotation experiments were conducted at room temperature. The following sequence of steps was followed in the calcium mineral-oleate system.

- 1) A predetermined volume of conductivity water was added to the beaker.
- 2) The desired amount of collector was pipetted into the same beaker, so that the final volume of the solution was 130 ml (volume of the glass cell).
- 3) Two and one-half grams of the mineral was added.
- 4) The pH was adjusted to the desired value.
- 5) One drop of Dowfroth 250 was added.
- 6) The system was conditioned for 3 minutes.
- 7) The pH of the system was measured again. This value was termed flotation pH.

- 8) The suspension was transferred to the flotation cell.
- 9) Thirty milliliters of purified nitrogen was passed through the pulp in 15 seconds. During this time the froth was collected.
- 10) The pH of the pulp was remeasured and the value termed final pH.
- 11) The concentrates and tailings were dried and weighed, and the flotation recoveries were calculated.

One step was added to the described procedure when the calcium mineral-oleate-silicate system was studied, this being the addition of the desired amount of sodium silicate, which was made between steps 1 and 2 of the above procedure.

Flotation Results

The experimental results obtained in this study show the flotation response of the calcium minerals as a function of pH and of collector concentration. The data also show the role of sodium silicate in oleate flotation as a function of pH. The following results were obtained:

Calcite-Oleate System: The oleate concentration and the pH were varied in this system. The pH range considered was 6 to 13. The results are shown in figure 2. With a concentration of 5×10^{-6} mole per liter potassium oleate, complete flotation was obtained at pH 6, 92 percent flotation recovery at pH 7, 56 percent flotation recovery at pH 8, and almost no flotation at pH 8.4.

With a concentration of 1×10^{-5} mole per liter KO1, complete flotation

was obtained at pH 7; the flotation response gradually diminished, so that, at pH 12.7 the flotation recovery was only 20 percent.

A concentration of 1×10^{-4} mole per liter KOI gave complete flotation up to pH 8.5, 90 percent flotation recovery at pH 10, 52 percent flotation recovery at pH 12, and 22 percent at pH 13.

Complete flotation of calcite was obtained in the pH range investigated when the KOI concentration was 5×10^{-4} M.

In general, as the oleate addition was increased from 5×10^{-6} to 5×10^{-4} mole per liter, the highest value of pH at which complete flotation occurred was also increased.

Calcite-Oleate-Silicate System: Two parameters were investigated here: namely, concentration of sodium silicate added and the pH of its solution. As shown in figure 3, these experiments were conducted with a concentration of 1×10^{-4} M KOI. For a concentration of 1×10^{-6} M sodium silicate, complete flotation was obtained until pH 7.4, 90 percent flotation recovery at pH 8.0, 23 percent flotation recovery at pH 9.0, and almost no flotation at pH 9.4.

In general, as the sodium silicate increased, the complete flotation region moved to lower values of pH.

Figure 4 shows the effect of the pH of the silicate solution in the flotation of calcite. These experiments were run with a silicate concentration of 5×10^{-4} M and an oleate concentration of 1×10^{-4} M. The pH of the solution of sodium silicate was adjusted to the desired value before

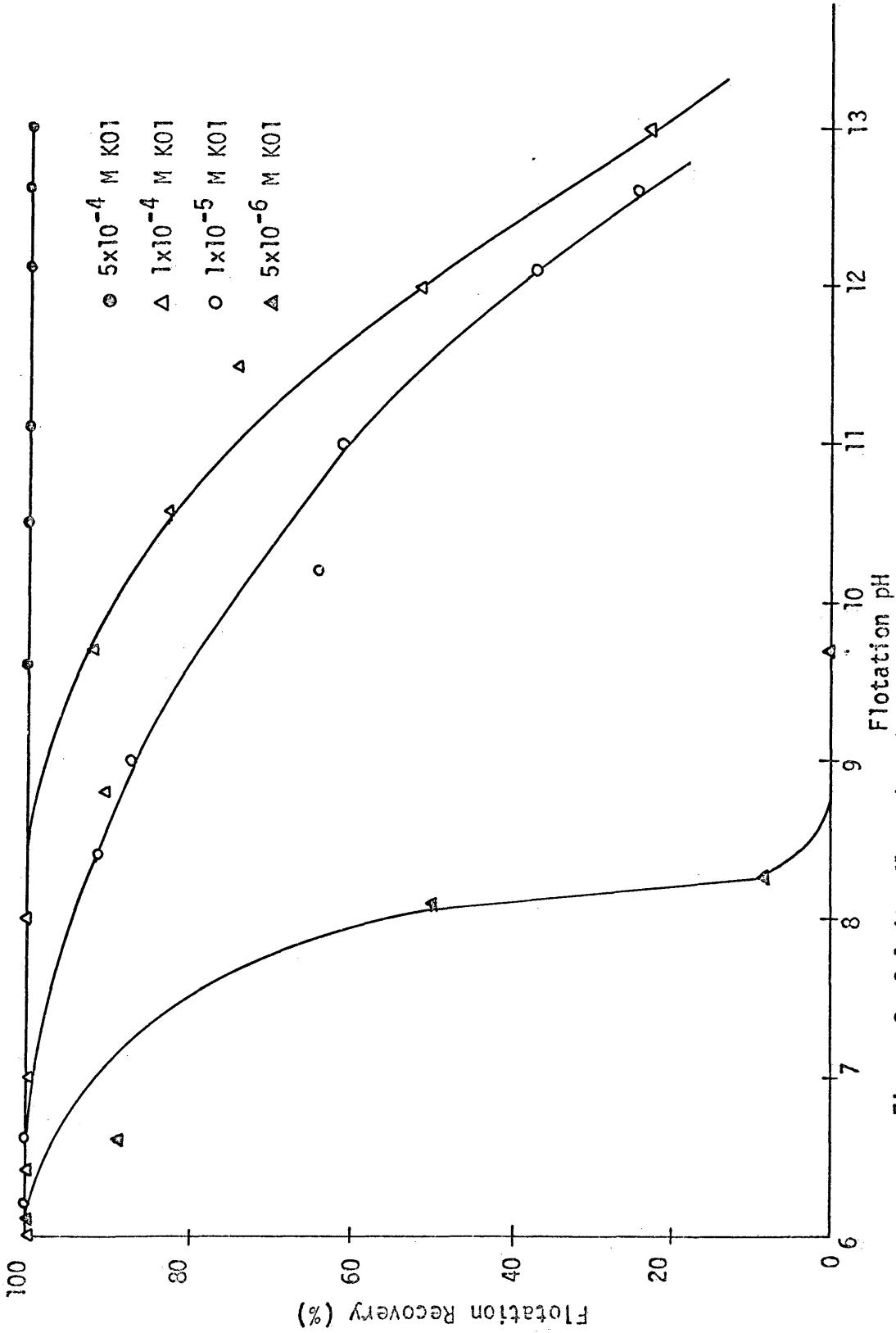


Figure 2: Calcite flotation data, recovery vs pH as a function of oleate concentration.

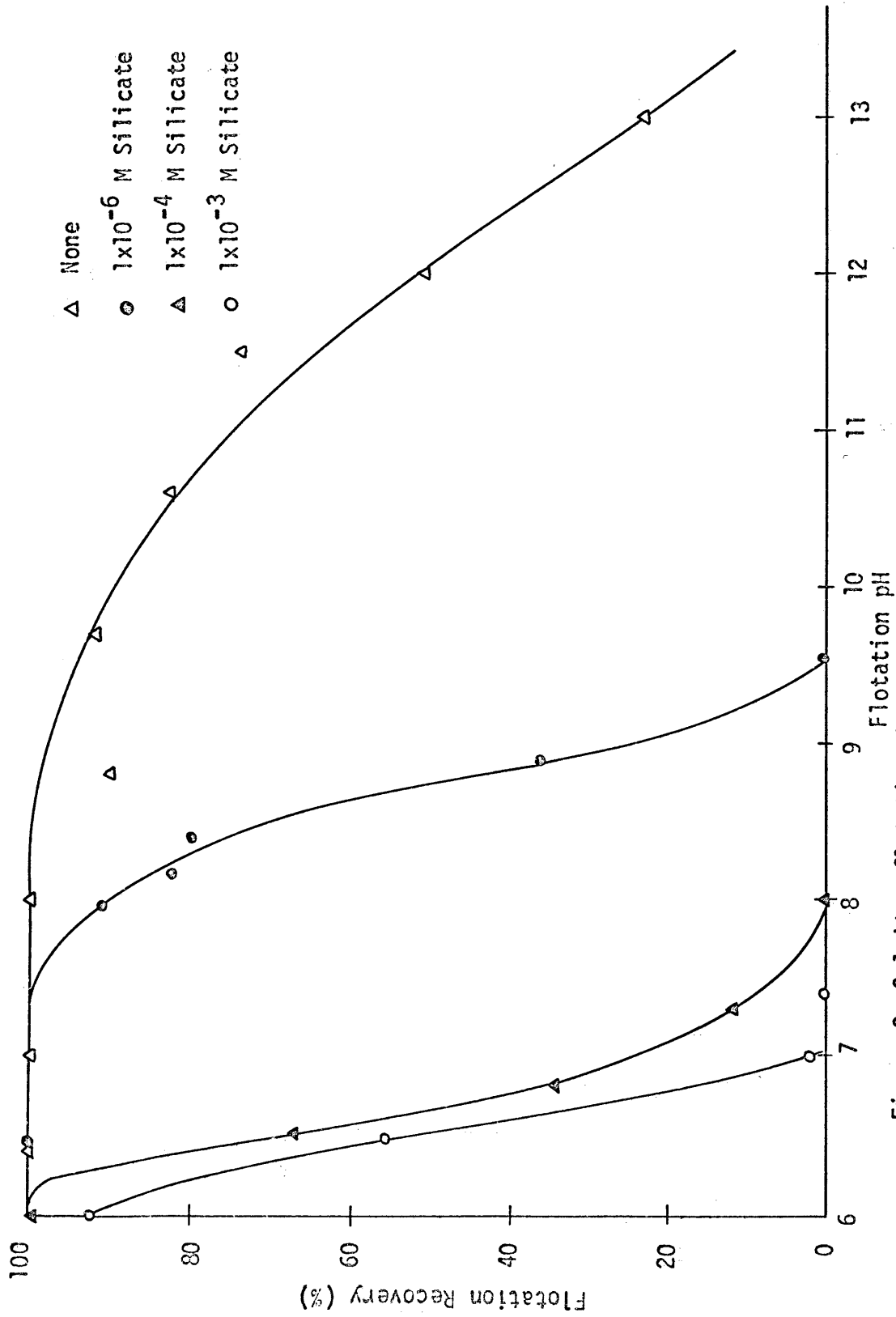


Figure 3: Calcite flotation data, recovery vs pH as a function of silicate concentration in the presence of 1x10⁻⁴ M KOI.

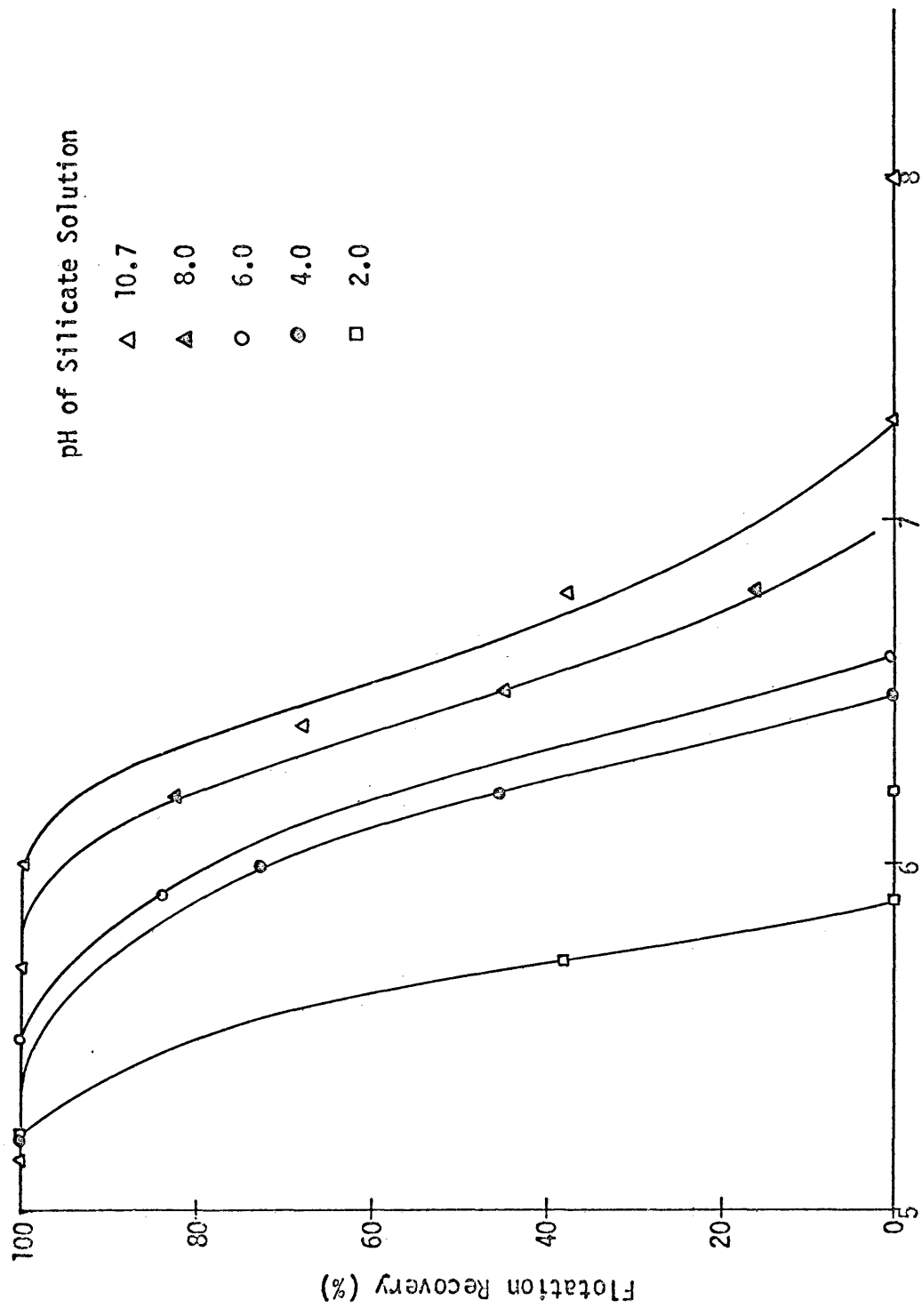


Figure 4: Calcite flotation data, recovery vs pH as a function of pH of silicate solution in the presence of 1×10^{-4} M KOI and 5×10^{-4} M silicate.

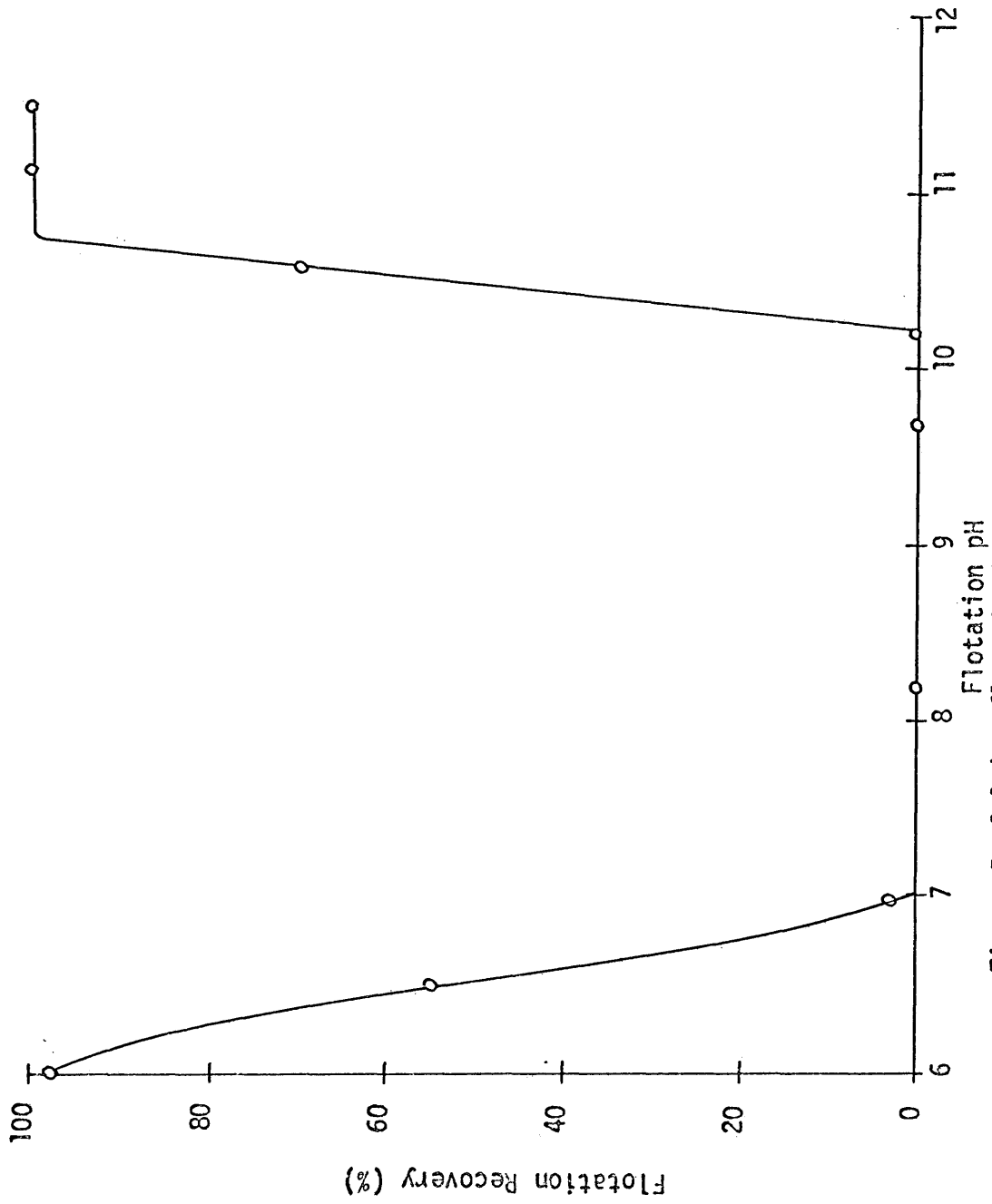


Figure 5: Calcite flotation data, recovery vs pH in the presence of 5×10^{-4} M K01 and 5×10^{-4} M silicate.

flotation. The figure shows that depression is enhanced when the pH of the solution is lowered from 10.7 to 2.0.

An interesting phenomenon was noted when the flotation of calcite was studied in solutions containing 5×10^{-4} M KOI and 5×10^{-4} M silicate, which solution pH was 6. As figure 5 shows, flotation is restored in the high pH region.

Fluorite-Oleate System: Experiments similar to those for calcite were also performed with fluorite; that is, the effect of oleate additions and pH were examined.

Figure 6 shows that an oleate concentration of 1×10^{-6} mole per liter, the flotation of fluorite is possible only in a narrow range, namely, from pH 6.0 to 9.6. The optimum flotation pH observed was the range 7.4-8.5. It was also noted that as the concentration of the collector was increased the pH range of complete flotation was wider. With additions of 1×10^{-5} mole per liter KOI, complete flotation was achieved in the pH region 4-13.

Fluorite-Oleate-Silicate System: The variables considered in this system for an oleate addition of 1×10^{-4} M were as follows:

- a) the effect of sodium silicate addition, and
- b) the effect of the pH of the silicate solution.

The response of fluorite to oleate flotation was not diminished even with a silicate concentration of 1×10^{-4} M. Additions of 1×10^{-3} silicate resulted in depression in the high pH region. Complete

flotation was obtained up to pH 8.7, 85 percent recovery was obtained at pH 10, and no flotation at pH 11.3.

In this system, as in the preceding one, higher additions of silicate enhanced the depression. See figure 7.

Figure 8 shows the effect of the pH of the solution of sodium silicate. This effect was studied for oleate and silicate additions of 1×10^{-4} and 5×10^{-4} mole per liter, respectively. As before, the flotation response of fluorite was diminished as the pH of the silicate solution was lowered.

Apatite-Oleate System: As shown in figure 9, the flotation response of apatite is very sensitive to pH and to the amount of collector present. With an addition of 5×10^{-6} M KOI, optimum flotation recovery was achieved between pH values of 6.0 and 8.6. At 1×10^{-5} M KOI, the flotation response in the acid region was only slightly improved. On the other hand, the flotation response of apatite is increased appreciably on the basic side. With this addition, the optimum recovery was noted between pH 5.8 and 9.8. No flotation was obtained at pH values below 5.0 and above 11.1.

The flotation characteristics of apatite are improved as the amount of the collector is increased. With 1×10^{-4} M KOI, complete flotation was observed in the pH region between 5.0 and 13. No flotation was obtained at pH values lower than 3.0.

Apatite-Oleate-Silicate System: The effect of silicate additions

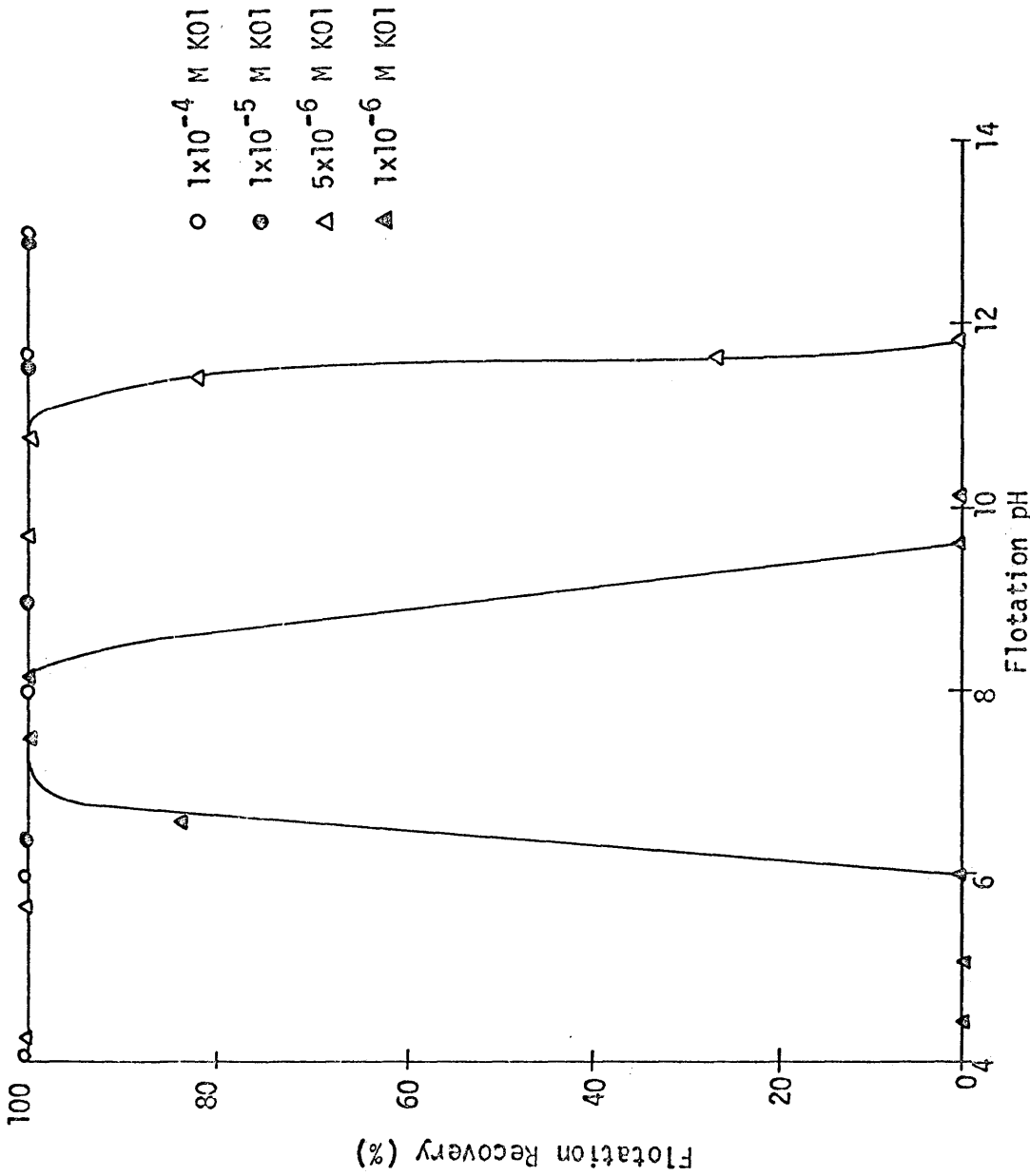


Figure 6: Fluorite flotation data, recovery vs pH as a function of oleate concentration.

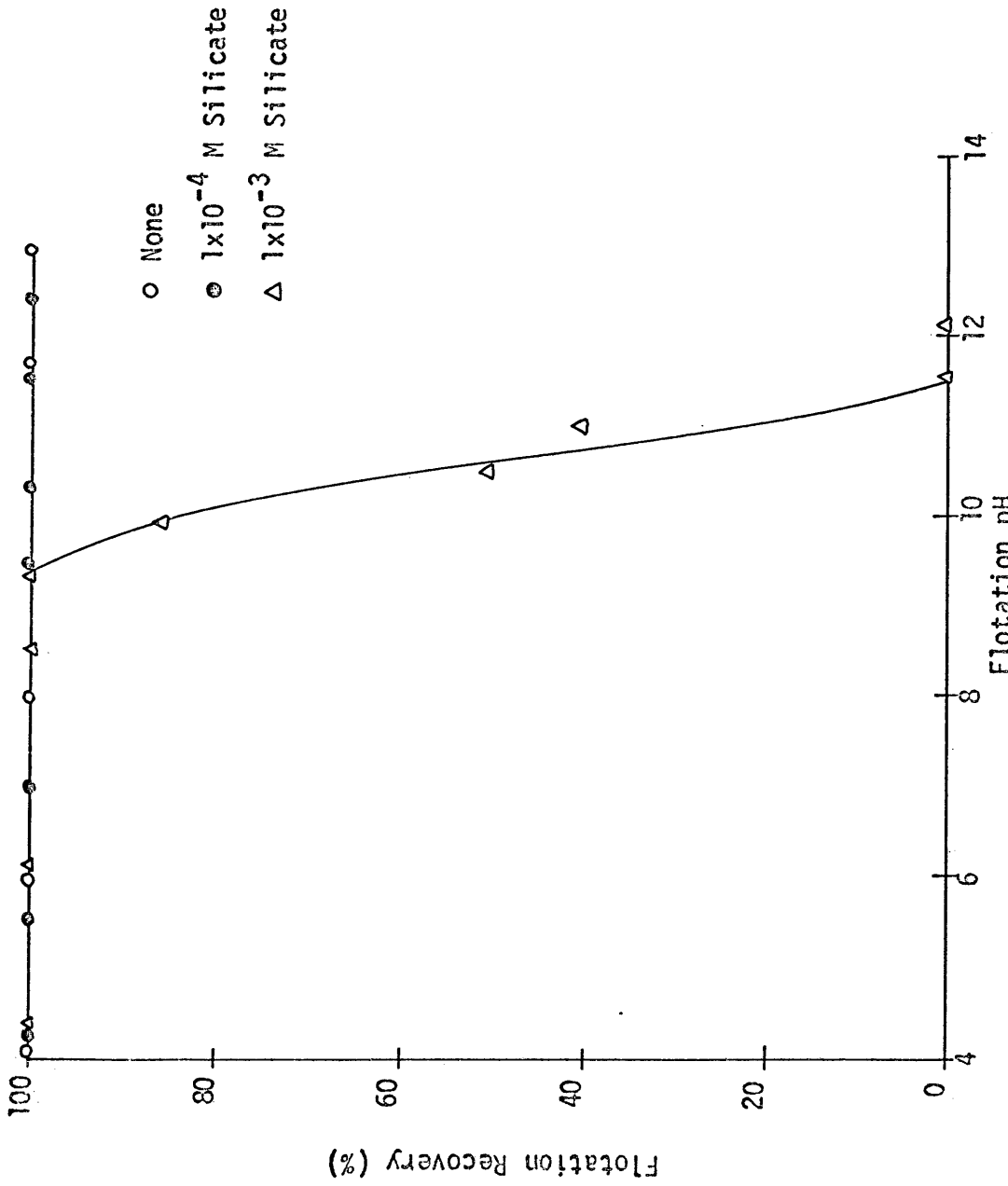


Figure 7: Fluorite flotation data, recovery vs pH as a function of silicate concentration in the presence of 1x10⁻⁴ M KOI.

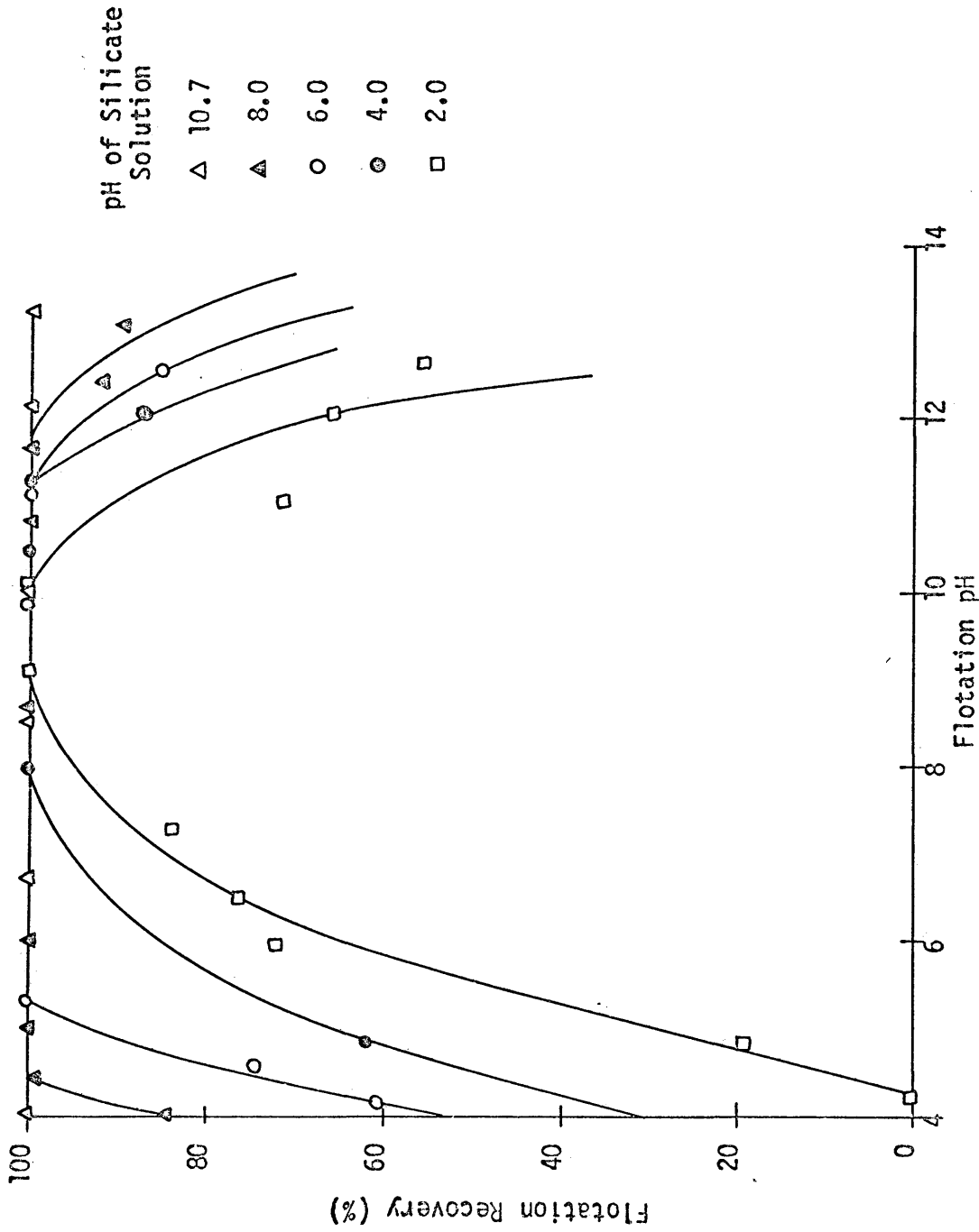


Figure 8: Fluorite flotation data, recovery vs pH as a function of pH of silicate solution in the presence of oleate and silicate concentrations of 1×10^{-4} and 5×10^{-4} M, respectively.

and the pH of its solution were the parameters investigated in the flotation of apatite using a constant addition of collector. Figure 10 shows the effect of the addition of silicate, and it can be seen that flotation recovery is diminished as the concentration of silicate is increased. The depressing action is only on the acid side.

The effect of the pH of the silicate solution is shown in figure 11. For silicate and oleate additions of 5×10^{-4} and 1×10^{-4} mole per liter, respectively, the depression is enhanced as the pH of the silicate solution is lowered.

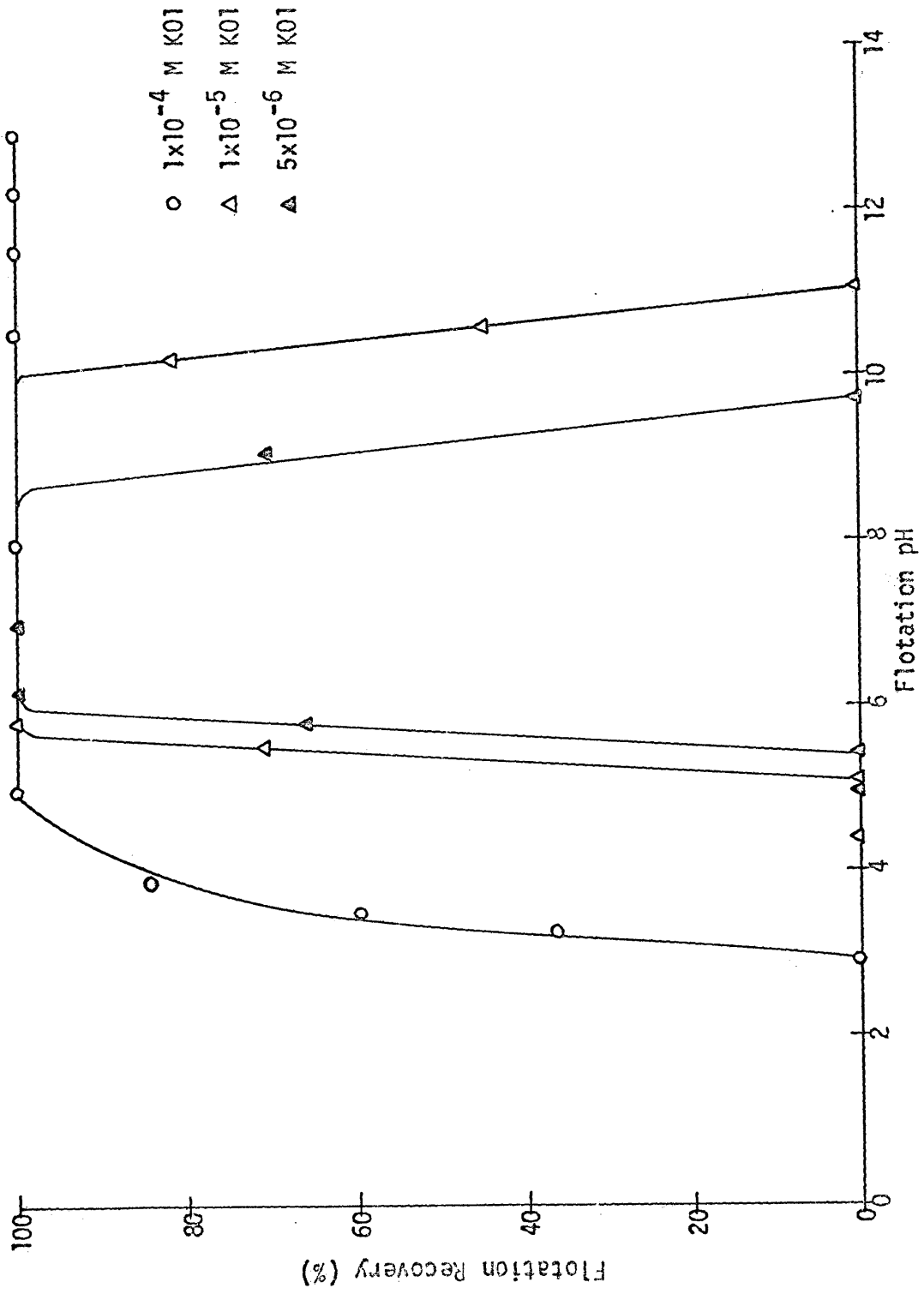


Figure 9: Apatite flotation data, recovery vs pH as a function of oleate concentration.

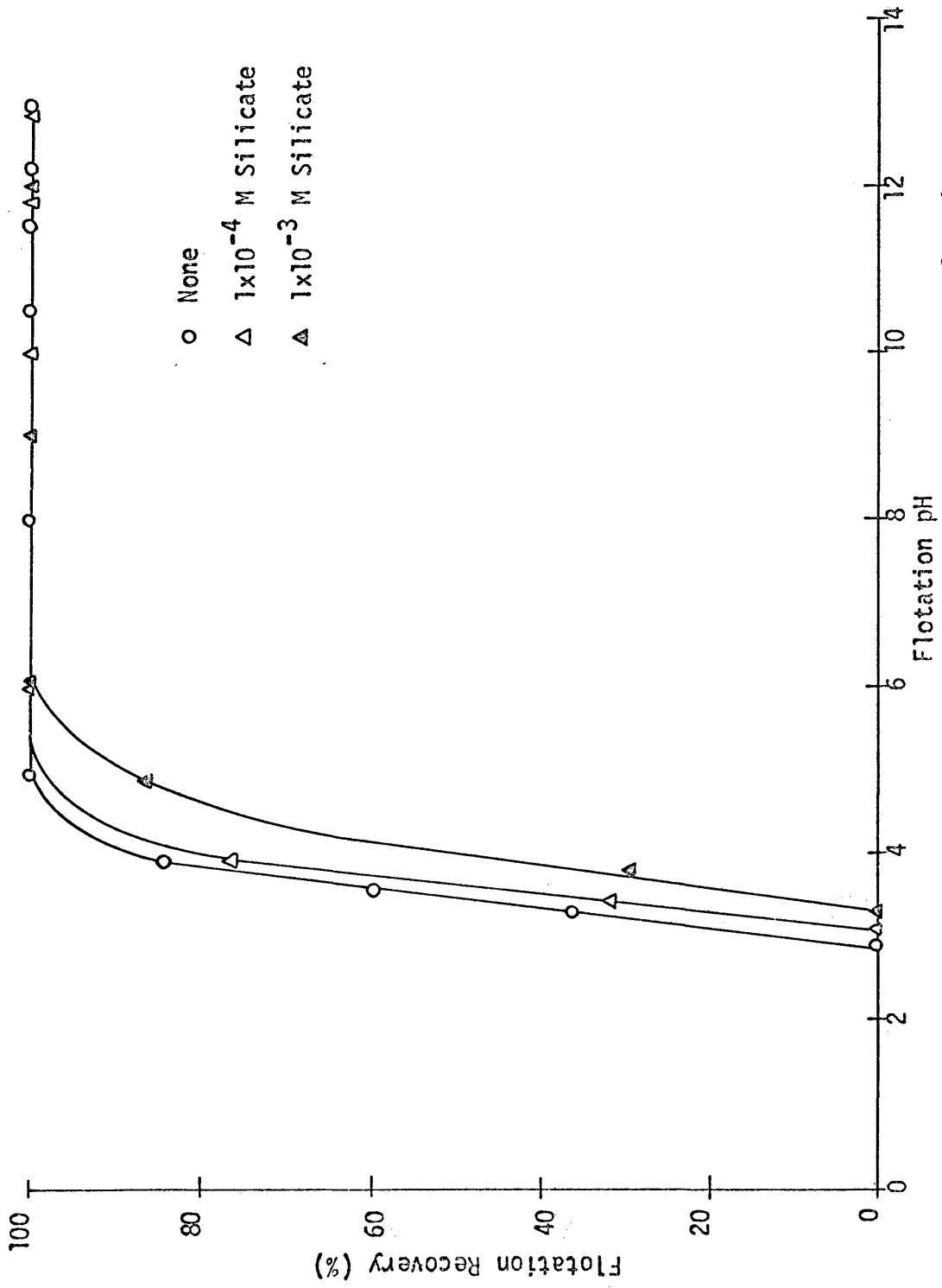


Figure 10: Apatite flotation data, recovery vs pH as a function of silicate concentration with oleate concentration of 1x10⁻⁴ M.

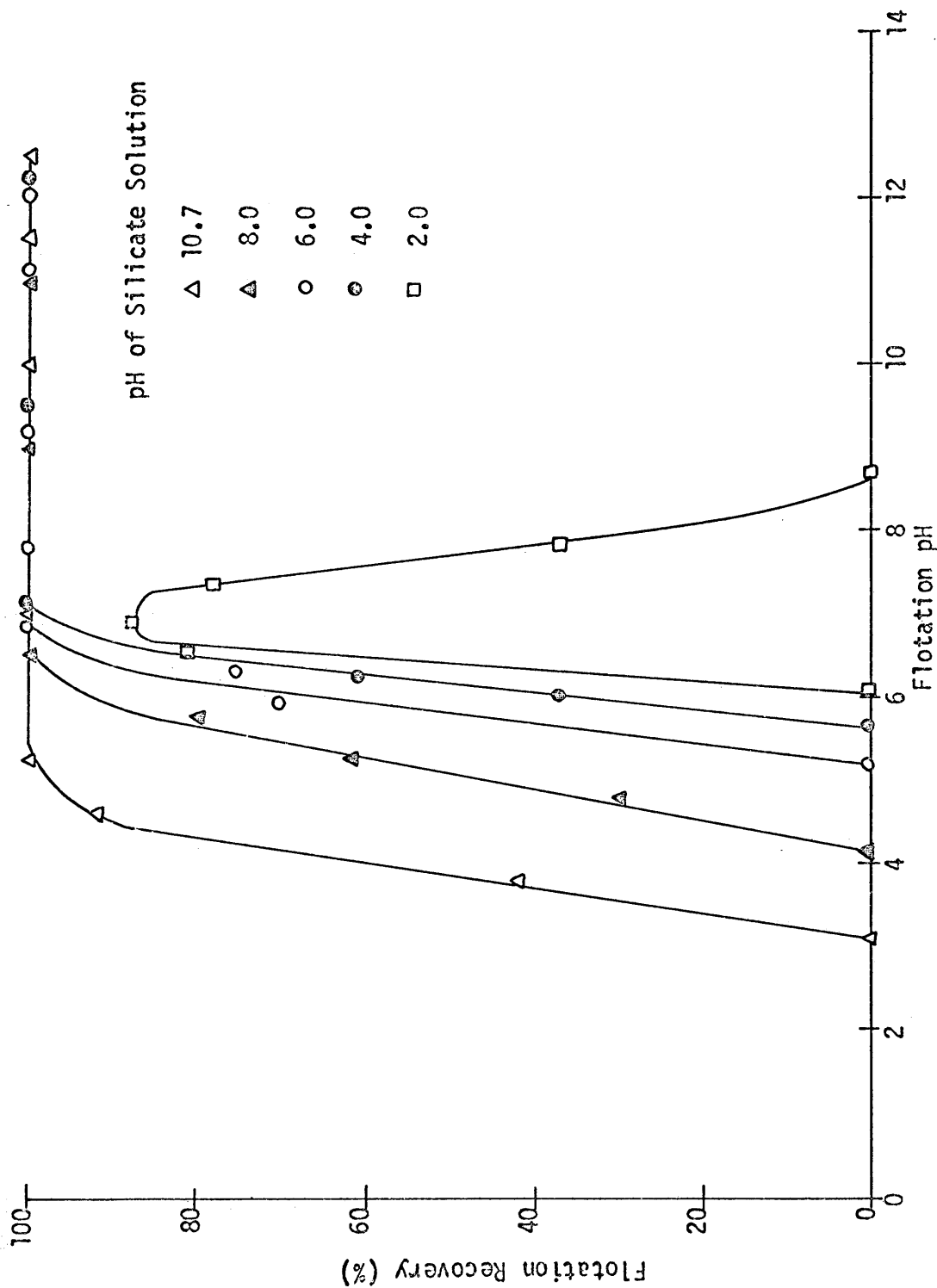


Figure 11: Apatite flotation data, recovery vs pH as a function of pH of silicate solution with oleate and silicate concentrations of 1×10^{-4} and 5×10^{-4} mole per liter, respectively.

ELECTROKINETIC STUDIES

It is known that in aqueous solution of sodium silicate, the bulk of the silica exists in a colloidal form. The properties of this colloidal silica, as was pointed out earlier, are similar to those of quartz. H^+ and OH^- are potential determining ions for quartz; consequently, their concentrations in solution determine the type of electrical charge that a quartz particle may have. In the same manner, H^+ and OH^- may be considered potential determining ions for calcite, fluorite, and apatite because they control the hydrolysis of the surface species. Since the flotation experiments were conducted over a wide pH range, the kind of electrical charge on the surface of both colloidal silica and calcium minerals can change in the investigated region.

As a consequence, electrophoretic measurements are important in this study, because these data provide an insight into the interactions that take place between a certain reagent and the surface of the mineral.

Experimental Materials

Minerals: The minerals used in this step of the investigation were the same used in the microflotation experiments.

Sample Preparation: The required particle size for electrophoretic measurements is about 5 microns. This particle size was obtained by the following procedure:

- 1) A small amount of the sample was ground for 2 hours with a porcelain mortar and pestle.
- 2) A stable suspension of 300 ml was made with 2 grams of this finely ground sample and conductivity water.
- 3) The suspension was allowed to settle for 20 minutes.
- 4) 100 ml of the upper part of the solution was removed. This was the standard solution used, which contained the required particle size.
- 5) 6 ml taken from the solution of part 4 was used for each electrophoretic measurement.

Reagents: Sodium silicate ($\text{Na}_2\text{O} \cdot 3.36\text{SiO}_2$), with the characteristics specified earlier, pure hydrochloric acid, and potassium hydroxide were used.

Apparatus and Procedure

Electrophoretic mobility of mineral particles was measured with a zeta meter. The apparatus consists of a microscope-cell combination

and a control panel for applying DC voltage.

The microelectrophoresis cell, with the mineral suspension placed into it, is placed on the stage of a microscope. The suspension is used as the electrolyte, and a certain voltage is applied to the electrodes of the cell. The movement of the particles is observed by means of a scale in the ocular of the microscope. According to the electrophoretic mobility of the particles, zeta potentials were determined by means of tables prepared for the instrument, or they could be calculated using the Helmholtz-Smoluchowski equation.

Experimental Results

Figures 12, 13, and 14 show the zeta potential as a function of pH for calcite, fluorite, and apatite respectively. Curve a is the zeta potential curve for the minerals in conductivity water and curve b is for a solution containing 5×10^{-4} mole per liter sodium silicate.

The pH corresponding to the zero point of charge (zpc) is also depicted in these figures. Below this pH movement of the particles was toward the cathode, which means that the particles were positively charged; whereas above this pH, the movement was toward the anode, which means that the surface was negative.

With calcite, the measurements were conducted in the pH range 6 - 10.5. The surface charge of calcite in this zone was found to be positive. In solutions containing sodium silicate, the surface charge

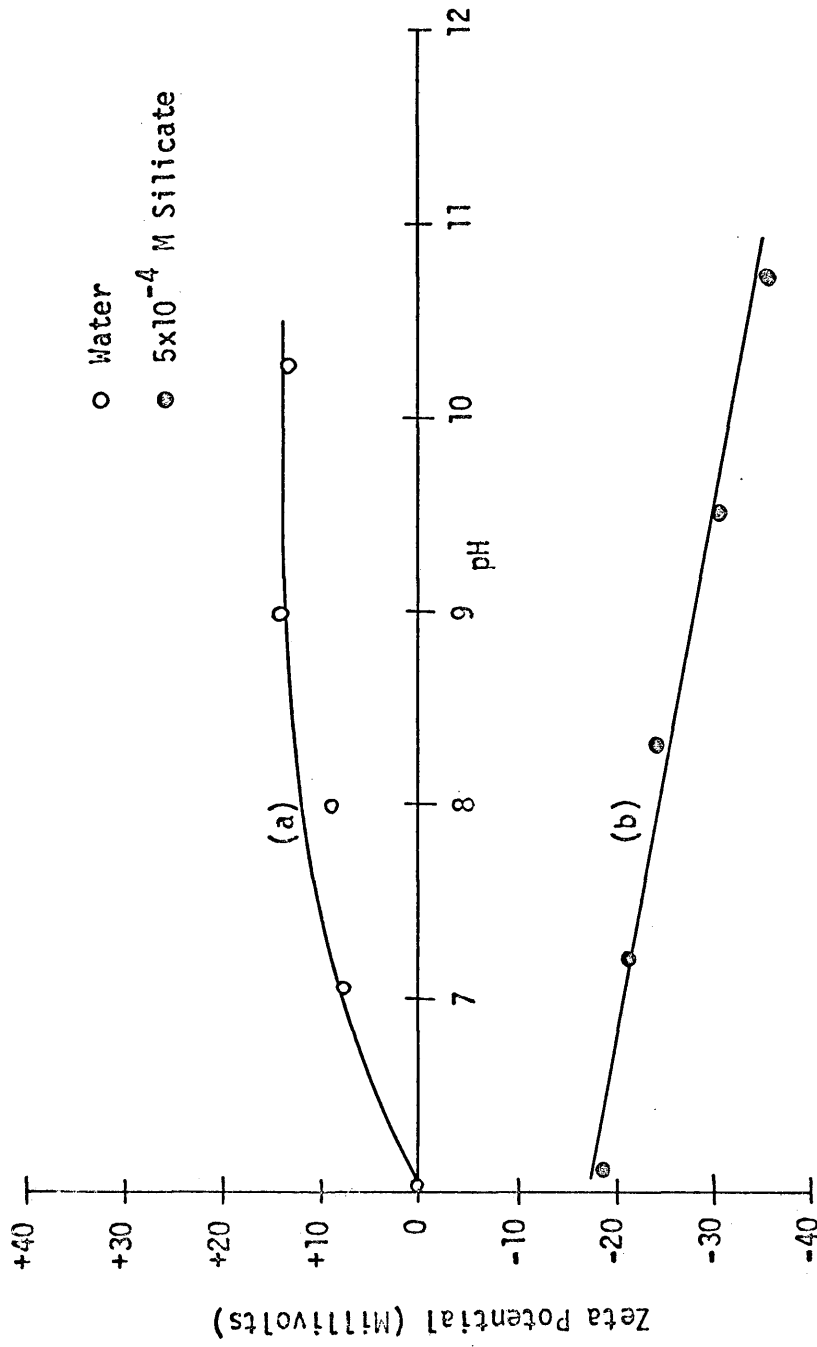


Figure 12: The zeta potential of calcite as a function of pH.

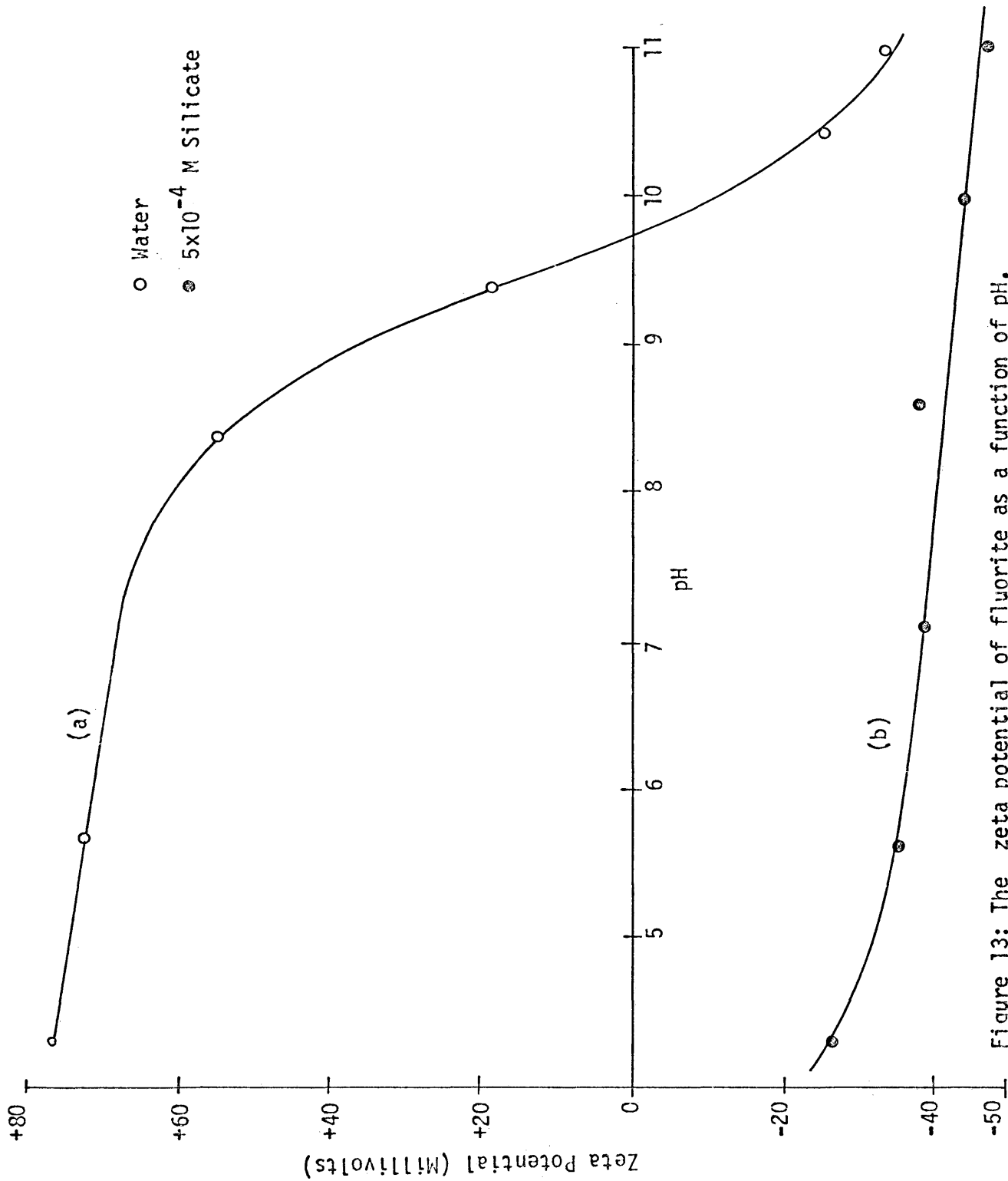


Figure 13: The zeta potential of fluorite as a function of pH.

was reversed.

The zpc of apatite, when placed in conductivity water, was found to be at pH 6.8. Apatite placed in solution containing sodium silicate acquires a negative surface charge in the pH range 4.0 - 11.0.

The zpc of fluorite in pure water was determined to be at pH 9.8. The surface charge was reversed when silicate was present in the solution.

In general, additions of sodium silicate to the solution change the surface charge from positive to negative, but almost no change was noted in the region where the calcium minerals already had a negative surface charge.

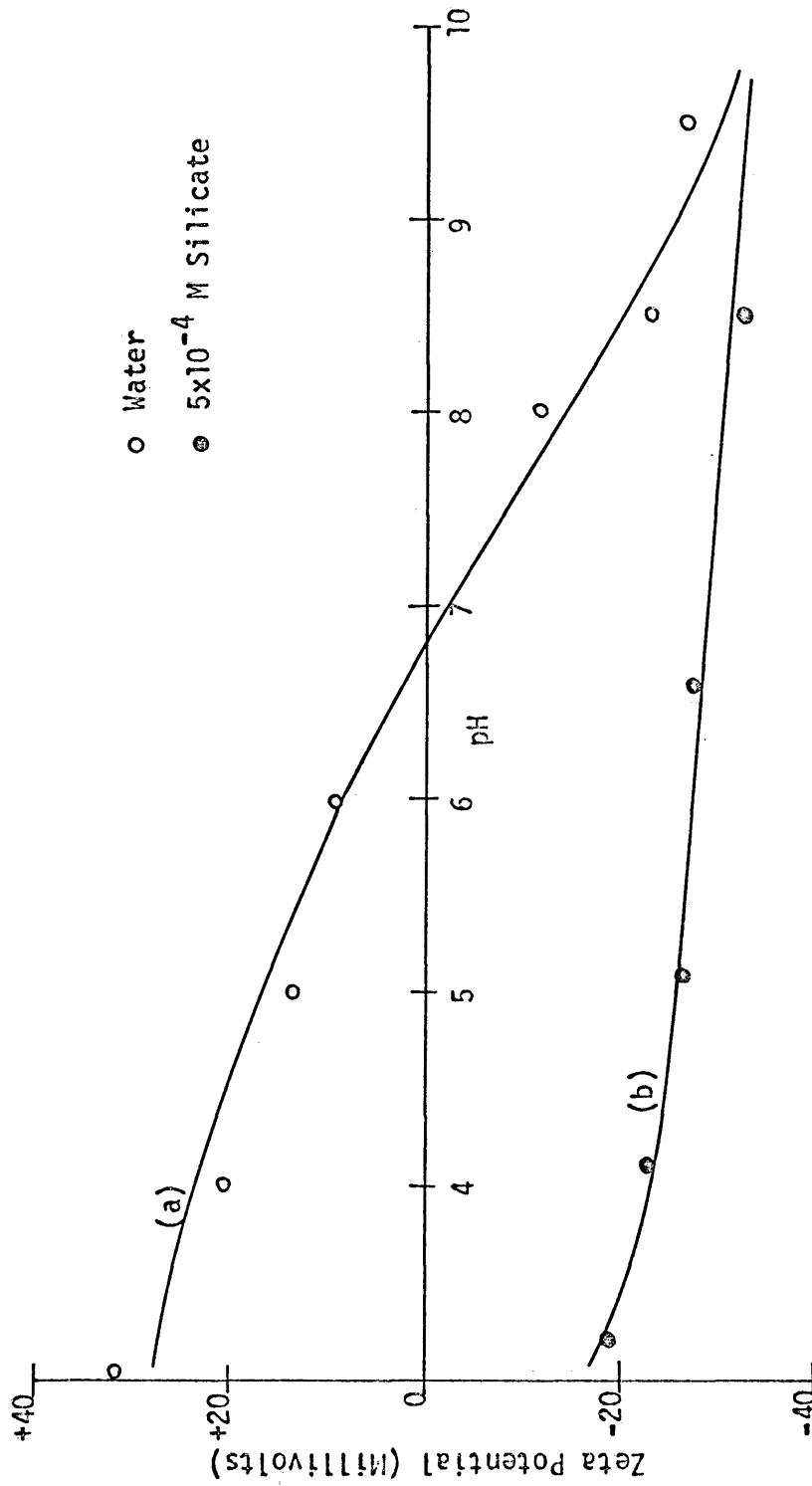


Figure 14: The zeta potential of apatite as a function of pH

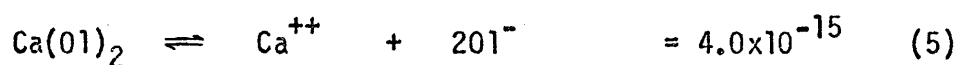
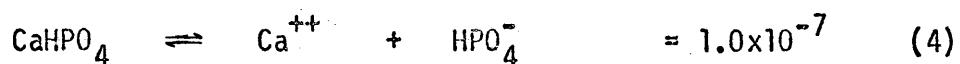
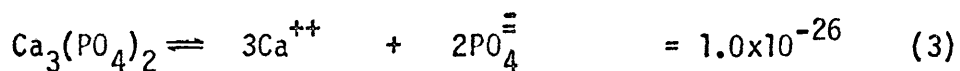
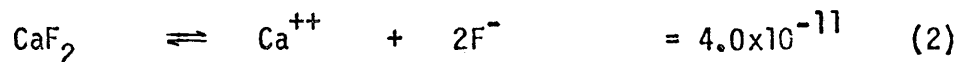
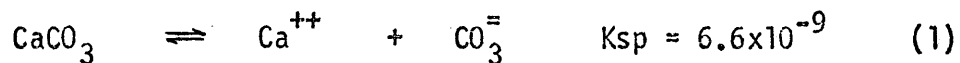
DISCUSSION OF RESULTS

The analysis of the experimental results are considered separately for the calcium mineral-oleate system and the calcium mineral-oleate-silicate system.

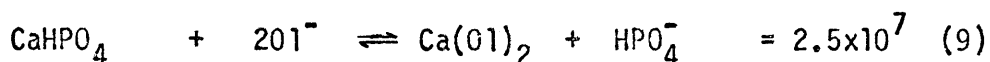
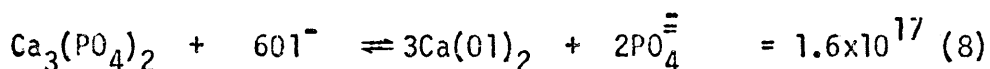
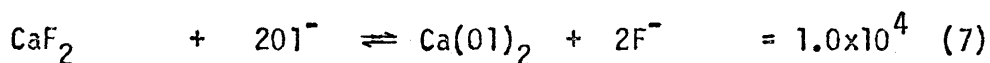
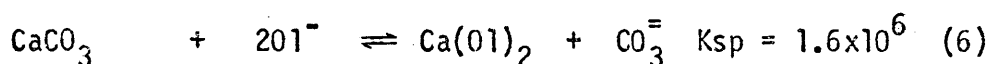
Calcium Mineral - Oleate System

In order to relate the experimental results with the action of the collector, one must find the mechanism by which adsorption occurs. Infrared spectrophotometry measurements^(11,12), and confirmed in this study, show that chemisorption of the collector is the mechanism involved. That is, oleate ions are adsorbed on the calcium minerals to form a surface calcium oleate. This chemical bonding between the oleate and the mineral surface was found to be present in the region where flotation is obtained.

That chemisorption of the collector is the process involved can also be predicted from thermodynamic considerations, because calcium oleate is a more stable compound than calcium phosphate, carbonate, and fluoride, respectively, as can be seen from the following equilibria^(13,14).



The possible reactions by which adsorption of the collector takes place are:



Thus, the above reactions are spontaneous ones in the direction written.

On the other hand, the mechanism by which depression takes place in the acid and basic regions can be explained as follows: Depression of calcite in the basic region may be due preferentially to the action of the carbonate ions. Reasons for this postulate are that CaCO_3 and Ca(OH)_2 are stable at high values of pH and that the concentration of

carbonate ions in solution increases more rapidly than the OH^- ions with the pH. Thus, at pH 9.0 the carbonate activity is 2×10^{-4} (calculated from CaCO_3 , CO_2 equilibria) and that of OH^- is 1×10^{-5} . When the pH is raised to 10, the activity of $\text{CO}_3^{=}$ and OH^- are 2×10^{-2} and 1×10^{-4} , respectively. Therefore, the above statements certainly indicate that CaCO_3 can be formed again on the surface of the mineral. So, depression probably results from a competition between carbonate and oleate ions for the surface. For an addition of 1×10^{-5} M KOI, the amount of $\text{CO}_3^{=}$ ions present in solution -- for instance, at pH 10 -- is 2,000 times greater than the oleate; as a consequence, a competition should be expected, and reaction 6 can be driven from right to left.

In the case of fluorite and apatite, depression in the basic side may result from a repulsion between the charge on the mineral surface and that of the oleate ions or from a competition between OH^- ions and the collector, because at high values of pH the only ions present in large amounts are the OH^- and $\text{CO}_3^{=}$.

Depression of these three species in the acid region can be attributed to the hydrolysis of the collector ions to oleic acid, which takes place at low pH.

Calcium Mineral-Oleate-Sodium Silicate System

In relating the experimental results to a certain specific mechanism in the adsorption of the reagent sodium silicate, one must know

the behavior of its aqueous solutions. It is well known that the dissolution process of sodium silicate is complex. Hence, a knowledge of it may help in the interpretation of the experimental data. In the past, the properties of aqueous solution of sodium silicate have been studied by some investigators. The common conclusion was that such dissolution process gives rise to the formation of colloidal hydrated silica, also called silicic acid.

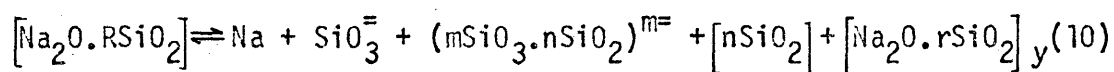
Probably the more complete study of the solution of sodium silicate was that conducted by Harman⁽¹⁵⁾, who through measurements of the conductivity, transport number, sodium ion activity, hydrolysis, phase rule, etc., was able to analyze aqueous solutions of ratios of $\text{Na}_2\text{O}:\text{SiO}_2$ ranging from 2:1 to 1:4. The following were his conclusions:

- 1) The ratio of Na_2O to SiO_2 is one important factor in the dissolution process. Thus, the monosilicate corresponding to the ratio 1:1 is strongly hydrolyzed. The sodium disilicate is less soluble in water and, hence, less hydrolyzed than the monosilicate. Solutions of tri- and tetrasilicates; that is, ratios of 1:3 and 1:4, respectively, contain complexes of mono and disilicates with excess of SiO_2 or hydrated silica. The fact that there is an increasingly lower percentage hydrolysis as the proportion of silica increases in the ratio until hydrolysis is practically negligible in 1:4 ratio, favors very much the view that these higher ratios are complexes of the two salts

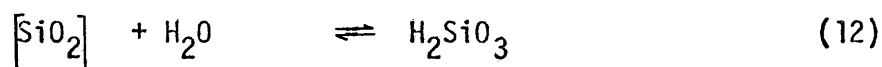
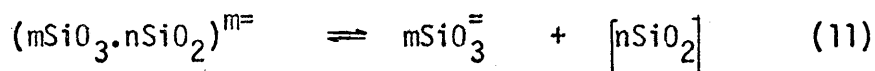
mentioned above. The substantial differences in the properties of sodium silicate solutions with the ratio present, were also found, for a specific ratio, to be a function of the concentration. Thus, it is interesting to note that for dilute solutions of sodium silicate, particularly those of 1:3 and 1:4 $\text{Na}_2\text{O}:\text{SiO}_2$ ratios, the measurements of conductivity, sodium ion activity, etc., are much higher than for concentrated solutions of the same ratio. Such discrepancies are understandable if it is supposed that complex silicate ions exist in the stronger solution and split up into simpler ions in dilute solutions.

- 2) The amount of silica present in these solutions in the colloidal or crystalloidal (ionically active) depends upon the ratio $\text{Na}_2\text{O}:\text{SiO}_2$ and upon the concentration. The colloidal silica content for a solution also increases with the ratio for a fixed concentration and with the concentration for a fixed ratio.
- 3) The fundamental nature of silica in solution appears to depend upon the existence of only one acid, metasilicic acid, in which the equilibrium between the crystalloidal and the colloidal constituents depends upon the concentration.

As a result, the dissolution process can be represented in some such manner as the following:



As was pointed out, breakdown of these complex silicates ions takes place as the solution is diluted. This process can be represented as follows:



where aggregates included in square brackets are colloidal.

The preceding equilibrium reactions will tend to go in such direction depending on the concentration in any ratio or on the ratio at any one concentration.

Harman's conclusions were checked later by other investigators. Main⁽¹⁶⁾, through viscosity studies, also suggests that above the ratio of $1\text{Na}_2\text{O} : 2\text{SiO}_2$ colloidal aggregates are formed in aqueous solution; these aggregates undoubtedly correspond to polysilicate ions. Nauman and Debye⁽¹⁷⁾ also confirmed these points by light-scattering studies.

The above considerations on the aqueous solution of sodium silicate appear to agree with the behavior of silicon or silica and its hydrates if the fact is considered that silica forms complexes, molecular compounds and aggregates, colloidal solutions and gels. Then, these resemblances in properties can also be extended to the surface charge on the colloidal particles, which will be useful later in the discussion of the experimental results, because it is intended to

correlate them with surface charge effects.

Since in solutions of high ratios, $1\text{Na}_2\text{O} : 3.36\text{SiO}_2$ used for the present investigation, the products of the above reactions (10 to 12) are present, the possibilities of the depression of calcium minerals can be due to the action either of silicate ions or of the colloidal hydrated silica.

The action of the silicate ions with surface calcium ions possibly can take place through the formation of CaSiO_3 . This compound will be formed if its stability under actual flotation conditions is greater than that of the calcium mineral itself. Furthermore, flotation can be diminished by its action only if the corresponding silicate is more stable than the surface calcium oleate. The solubilities of the different compounds (calcite, apatite, fluorite, and calcium oleate) already given and compared with that of calcium silicate (7×10^{-7}) suggest that the formation of calcium oleate should be the favored reaction.

That CaSiO_3 is a relatively soluble compound can also be concluded from the analysis of figures 15 and 16. Figure 15 shows the zeta potential of quartz as a function of pH; the effect of calcium and silicate ions is also considered in the same figure. In figure 16 the values of the zeta potential of quartz are charted against pH for a constant addition of 5×10^{-4} mole per liter sodium silicate with several additions of Ca^{++} . It can be seen that the action of Ca^{++} on the zeta potential is independent of the silicate addition; that is, formation

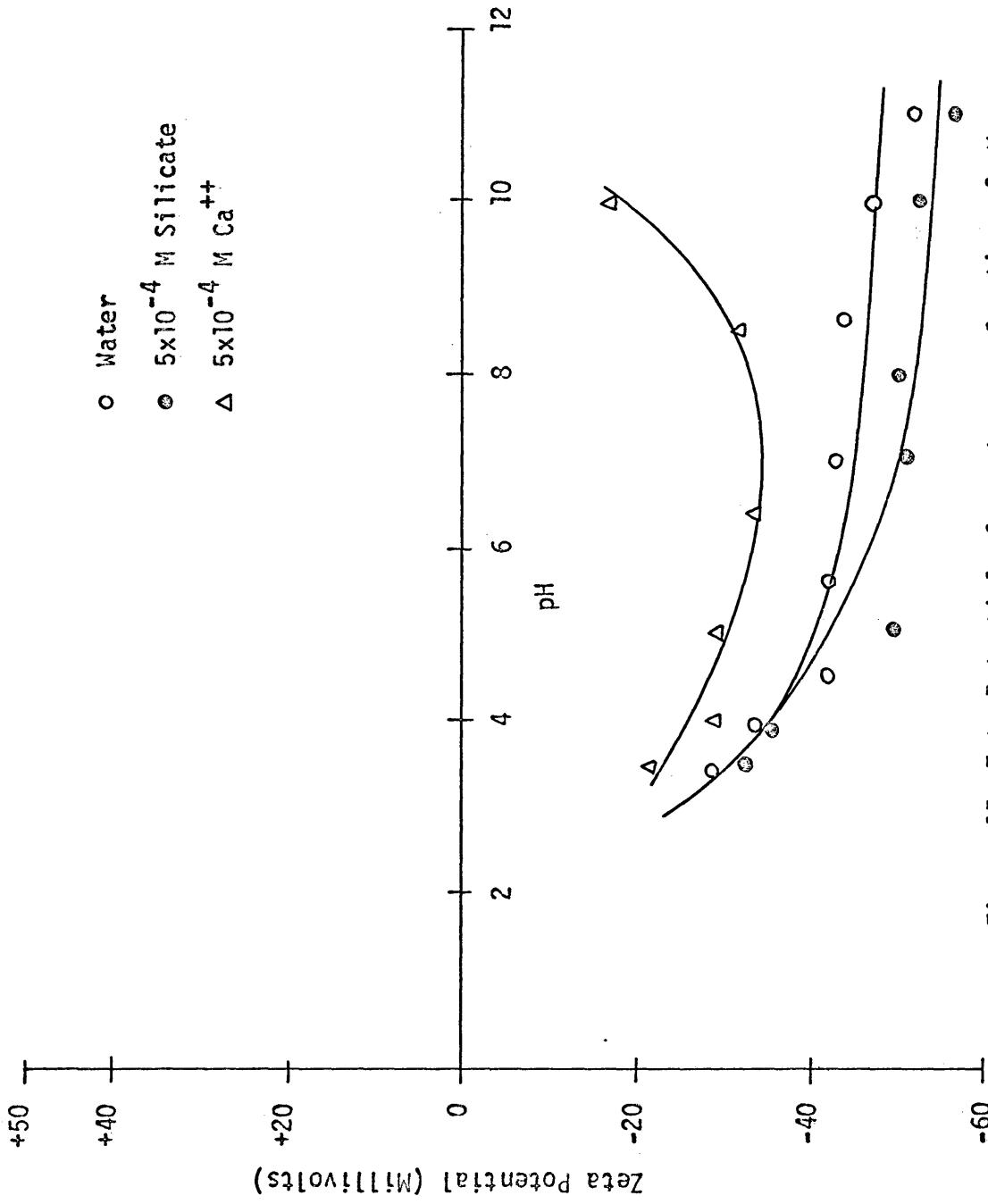


Figure 15: Zeta Potential of quartz as a function of pH.

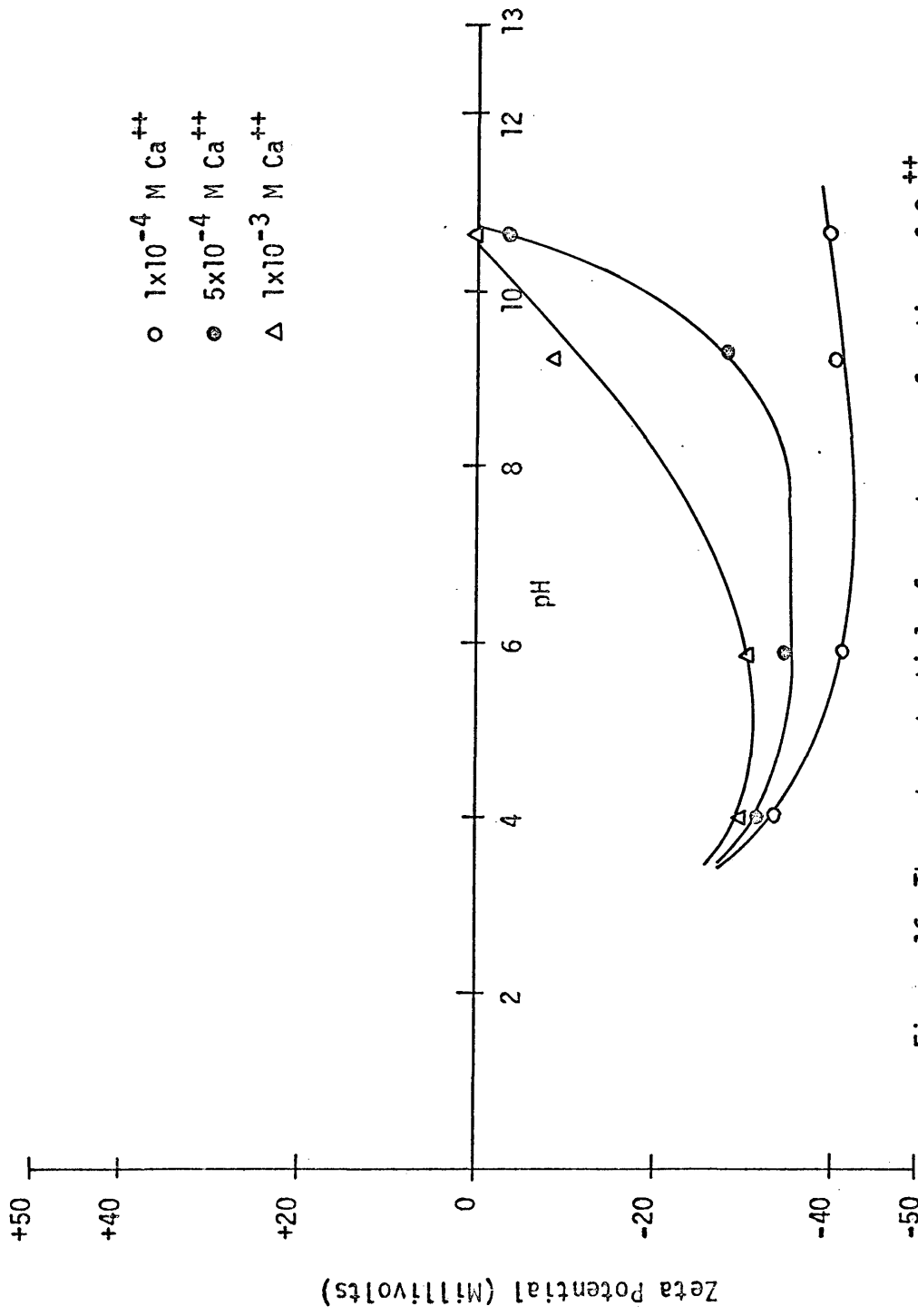


Figure 16: The zeta potential of quartz as a function of Ca^{++} additions in the presence of 5×10^{-4} M silicate.

of CaSiO_3 does not take place in the solution even at these high additions. Onoda and Fuerstenau⁽¹⁸⁾ have presented the variation of the zeta potential of quartz as a function of Ba^{++} concentration, and their results are similar to the values obtained in figure 16. These facts tend to confirm that there is no interference of the sodium silicate in the considered measurements.

From the preceding paragraphs, it can probably be concluded that the first possibility of the action of sodium silicate -- namely, the formation of CaSiO_3 on the surface-- may be discarded. Now the second possibility -- action of colloidal silica-- will be analyzed.

As was pointed out previously, because of common properties of the colloidal silica and quartz particles, it was expected that in the former there was a negative surface charge except in the very acid region. Electrophoretic measurements conducted on sodium silicate in the pH region 5 - 10 confirmed the kind of surface charge that was expected. Some values about surface charge of these colloidal particles were also reported^(19,20).

Studies on slime coating have shown that this phenomenon is related to surface charge. Generally speaking, a coating is produced when the mineral and slimes possess opposite electrical charges. Then, interaction between these colloidal charged aggregates and the mineral is expected if they have different kinds of surface charge. Once these colloidal aggregates coat the surface of a mineral particle, their

surface properties are modified.

The adsorption of colloidal silica on the calcium mineral particles and the consequent coverage is going to make them behave like quartz. It is known that quartz is not floated by oleate unless an activating ion in relatively high concentrations is present. Then, colloidal silica coverage might be responsible for depression in these systems.

In order to proceed further, it is convenient to point out at this stage that quartz particles have a zero point of charge (zpc) in the pH region 2.5 - 3.0. At pH values greater than the zpc, quartz particles have a negative electrical charge on their surface and at pH values below the zpc the surface charge is positive. The same charges are expected for the colloidal silica in the different pH regions.

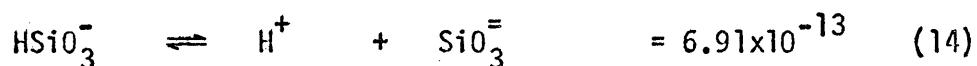
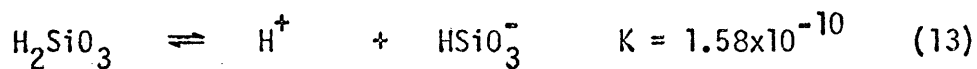
Figure 12 shows that calcite particles are positively charged above pH 6.0. Recent streaming potential studies have shown that calcite is positively charged up to a pH value of 10.7⁽²¹⁾. Above this pH, the charge is reversed to negative. The preceding range of surface charge on calcite was also confirmed by studying the flotation response with amine. As a consequence interaction between calcite particles and colloidal silica might be expected in that region due to coulombic attraction. This would coat the calcite particles with the colloids, and flotation with oleate as collector would not be possible. Figure 3 shows that flotation recoveries in the calcite-oleate-silicate system diminish above pH 6.0. These results tend to support

this proposed mechanism of depression. The same figure also shows that complete flotation is obtained at lower pH values as the addition of sodium silicate is increased. This may be due to the increase of colloidal silica in solution, which was shown to increase as the concentration is increased for a fixed ratio of $\text{Na}_2\text{O} : \text{SiO}_2$.

Figure 5 shows no interaction between the silicate solution and the surface of the mineral at pH values higher than 10.5 because flotation is restored. If physical adsorption is the mechanism of the action of silicate, no interaction between colloidal silica and calcite would be expected because both have the same type of surface charge.

Beside the action of different additions of sodium silicate in the flotation response of calcite, the effect of the pH of the sodium silicate solution added was also investigated. Figure 4 shows this effect for a constant addition of potassium oleate (1×10^{-4}) and silicate (5×10^{-4}). It is seen in the figure that depression is enhanced as the pH of the silicate solution is lowered. In order to explain these shifts in the flotation response it is convenient to point out that the state of the hydrated silica or colloidal silicic acid is altered by the concentration of H^+ and OH^- ions in solution. Thus, from a typical sol made from sodium silicate, it was found that the particles of colloidal silica pass into true solution to form silicate ions when the pH is increased to about pH 11. This can also be seen if

the following equilibria are considered:



The H_2SiO_3 or hydrated silica is the specie that polymerizes. With this in mind and for the simplification of calculations, only the two equations written above will be considered, as these are sufficient to estimate the amounts of silicic acid and silicate ions which are present at different values of pH. Table I shows the concentration of the different species for these simplified equilibria, considering an addition of 5×10^{-4} M sodium silicate.

Table I shows that the predominant specie in the aqueous solution of sodium silicate is colloidal silicic acid if the pH is lower than 9.0. The fact that depression was found to be stronger for low pH values of the silicate solution seems to support the proposed mechanism, namely, that the colloidal hydrated silica or silicic acid may be the responsible for depression and not the silicate ions.

Figure 14 indicates that the zero point of charge of the apatite used in this investigation is pH 6.8. Therefore, in the pH region 3 - 6.8 physical adsorption of colloidal silica on the surface of apatite should be possible. The formation of this colloidal coating does not permit the flotation of apatite using potassium oleate as collector. In figure 9 it is seen that depression occurs slightly

TABLE I.- Concentration of dissociation species of sodium silicate (modulus 1:3.36) at different values of pH.

<u>pH of solution</u>	<u>SiO₃⁻</u>	<u>HSiO₃⁻</u>	<u>H₂SiO₃</u>
6.0	5.48x10 ⁻¹⁴	7.90x10 ⁻⁸	5.00x10 ⁻⁴
7.0	5.48x10 ⁻¹²	7.90x10 ⁻⁷	5.00x10 ⁻⁴
8.0	5.38x10 ⁻¹⁰	7.80x10 ⁻⁶	4.92x10 ⁻⁴
9.0	4.71x10 ⁻⁸	6.83x10 ⁻⁵	4.32x10 ⁻⁴
10.0	2.41x10 ⁻⁶	3.10x10 ⁻⁴	1.90x10 ⁻⁴
11.0	3.10x10 ⁻⁵	4.50x10 ⁻⁴	5.00x10 ⁻⁵
12.0	2.00x10 ⁻⁴	2.94x10 ⁻⁴	1.86x10 ⁻⁶
13.0	4.38x10 ⁻⁴	6.25x10 ⁻⁵	4.00x10 ⁻⁸

on the acid side and it is enhanced as the addition of silicate is increased. The results of microflotation experiments for this mineral also agree with the proposed mechanism of the action of silicate.

As shown in figure 11, flotation of apatite diminishes when the pH of the silicate solution is lowered; this also supports the premise that colloidal hydrated silica may be the depressor. When the silicate solution is at pH 2, depression is observed in both acidic and basic media. An explanation can be the following: the surface of the colloidal silica at this pH may be positively charged. In the pH range from 6 to 8, apatite is very slightly charged (see figure 14); a clear interaction is hard to define and this may be the reason for that shape of curve. As the pH is increased, apatite acquires a definite negative surface charge, which can interact with the positive of the colloidal silica. As a result of this coulombic attraction, colloidal silica coverage can be present which gives rise to the depression of apatite.

In the case of fluorite, depression in the acid side is observed only when the pH of the silicate solution is lowered. This depression may also be attributed to the physical adsorption of the colloidal silica on the fluorite surface because they have different surface charges. On the basic side, depression is also observed, and the reasons for this are not still clear. Figures 7 and 8 show the experimental results.

CONCLUSIONS

The results of the preceding study based on microflotation experiments and on electrophoretic and infrared measurements can be summarized as follows:

- 1.- Flotation of calcite, fluorite, and apatite using potassium oleate as collector is due to the formation of calcium oleate on the surface of these minerals.
- 2.- The action of the aqueous solutions of sodium silicate in the calcium mineral-oleate system was found to be related to their colloidal silica content.
- 3.- The electrophoretic measurements show that interaction between colloidal silica and the calcium mineral particles may be attributed to surface charge effects.
- 4.- The depressing effect of an aqueous solution of sodium silicate is enhanced with the concentration for a fixed ratio of Na_2O to SiO_2 . As the concentration of silicate is increased, the amount of colloidal silica present in the system is also

increased; consequently, depression is more effective for the higher additions.

- 5.- For a constant addition of silicate, the depressing action is increased as the pH of the silicate solution is lowered. This is expected because the colloidal silica content increases as the solution is acidified.

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