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LEAD ACTIVATION  
IN  
OLEATE FLOTATION OF QUARTZ

by

Bernard M. F. Perinne

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

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ABSTRACT

Micro-flotation studies with quartz were undertaken to determine, first, the response of quartz to flotation with oleate as collector and plumbous ion as activator and, second, the mechanism of collection involved.

The experimental results indicate that lead functions as an activator between pH 6 and 12. In this range, lead ions hydrolyze and react with oleate ions to form precipitated lead-hydroxy-oleate. Flotation of the quartz results from the formation of this compound which apparently hydrogen-bonds to an oxygen of the quartz surface.

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## INTRODUCTION

Quartz, being one of the most prevalent gangue minerals, has received extensive study to determine its flotation response with both cationic and anionic collectors. The works of Gaudin (1, 2, 3), Cook (4), Fuerstenau (3), de Bruyn (5), and Wadsworth (6), have contributed much to a general understanding of cationic (amine) flotation of quartz.

On the other hand, the flotation of quartz with anionic collectors, such as fatty acids, is poorly understood. It has been known, however, that pure quartz cannot be floated in conductivity water at any pH with oleate as collector (7). Further, various polyvalent cations, e.g.  $\text{Fe}^{+++}$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ , and  $\text{Cu}^{++}$ , have been known to function as activators in such a system (8, 9). The specific function that the various metal cations assume in these systems has long been an enigma; in fact Taggart (10) wrote in 1950: "Activation and depression in non-metallic flotation have not yet advanced to the point even of definite correlation of kind of effect with the reagent added, let alone to determination of the mechanism."

Recent investigations have revealed that these various cations function as activators when the pH is such that the metal cation hydrolyzes (11, 12). Further the necessity of the presence of a hydroxyl in a precipitated metal ion-organic compound, e.g. lead-hydroxy-sulfonate, was also demonstrated. Bonding to the surface apparently occurs as a hydrogen bond between the oxygen of the hydroxyl and an oxygen atom of the mineral surface.

Detailed studies have been undertaken with lead-sulfonate-quartz and lead-xanthate-quartz systems (13, 14, 15). The purpose of this study is to extend the scope of the investigation to include the system lead-oleate-quartz. Comparison of the three systems will yield a much fuller understanding of flotation phenomena.

## EXPERIMENTAL MATERIALS AND PROCEDURE

The following experimental materials were used:

### Quartz

Pegmatitic quartz was used in the investigation. This material was prepared by leaching the sized sample (48 x 150 mesh) with aqua regia, rinsing with distilled water, and releaching with concentrated hydrochloric acid until no colour could be detected in the leach liquor. This liquor was then tested with potassium ferrocyanide to detect the presence or absence of iron. The material was then washed with conductivity water until the liquor was at the pH of the water and dried.

### Water

Conductivity water was used in all of the experimental work. This water, made by passing distilled water through an ion exchange column, had an average measured conductivity of 1 micromho.

### Reagents

All the chemicals used in the experimental work were reagent grade in quality.

The potassium oleate was prepared with the following procedure (16):

**Synthesis:** A sample of pure oleic acid (11.1001 g) was added to 220.46 cc of a solution of absolute ethanol containing 10 mg per cc potassium hydroxide. Theoretically, 0.039298 mole of potassium oleate should be obtained after mixing, evaporating under reduced pressure at 50°C, washing with ether, filtering, drying, and desiccating under vacuum in the presence of sulfuric acid.

**Analysis:** Four 30.540-mg samples of this product were dissolved in 1 liter of conductivity water separately at an initial pH of 6.98. The normality of these solutions was theoretically  $9.527 \times 10^{-5}$  mole per liter and their theoretical values of pH were calculated to be 7.41. The measured values of pH were 7.38, 7.42, 7.61, and 7.45, showing a slight excess of base in the product. This difference was not thought to be significant.

### Micro-flotation cell

A small glass micro-flotation cell was used in the experimental work. The cell was constructed by removing the stem of a 150-cc Buchner funnel (fritted glass filter) and placing another stem parallel to the filter for gas introduction. A microscope slide is introduced into the cell to act as a baffle, while agitation is effected with a magnetic stirrer. See figure 1.

A photograph of the complete experimental arrangement is shown in figure 2. The gas used was nitrogen; it was purified by passing through a bottle containing Ascarite, for CO<sub>2</sub> removal. The burette used for collecting and measuring a constant volume of nitrogen can be noted in the center of the photograph, while the constant head vessel can be noted in the upper right portion.

This apparatus has two principal advantages:

1. System contamination is reduced to a minimum since no metallic components are involved.
2. Small charges of pure mineral may be used because of the small capacity of the cell.

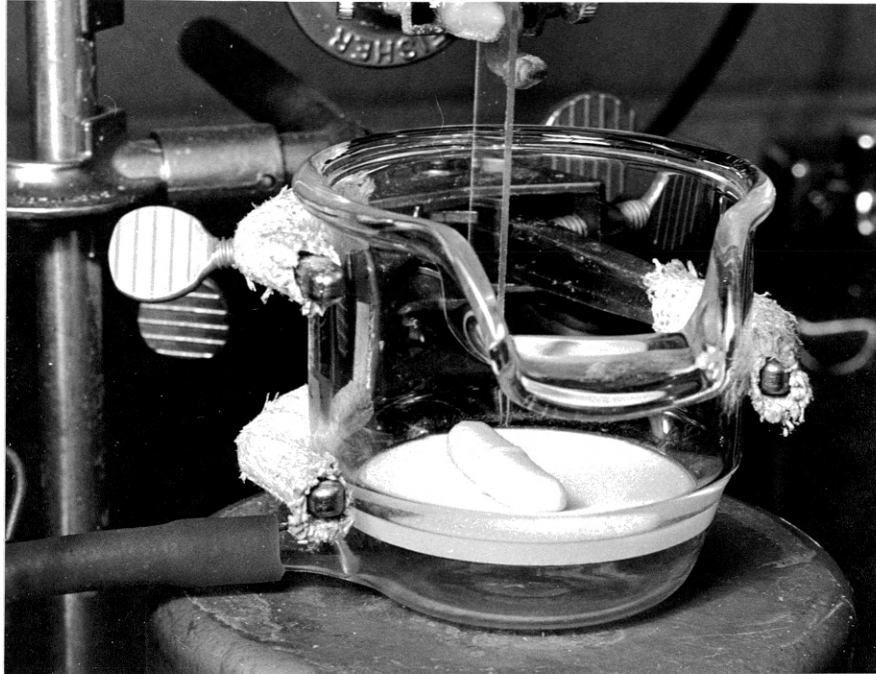


Figure 1 - Micro-flotation cell.

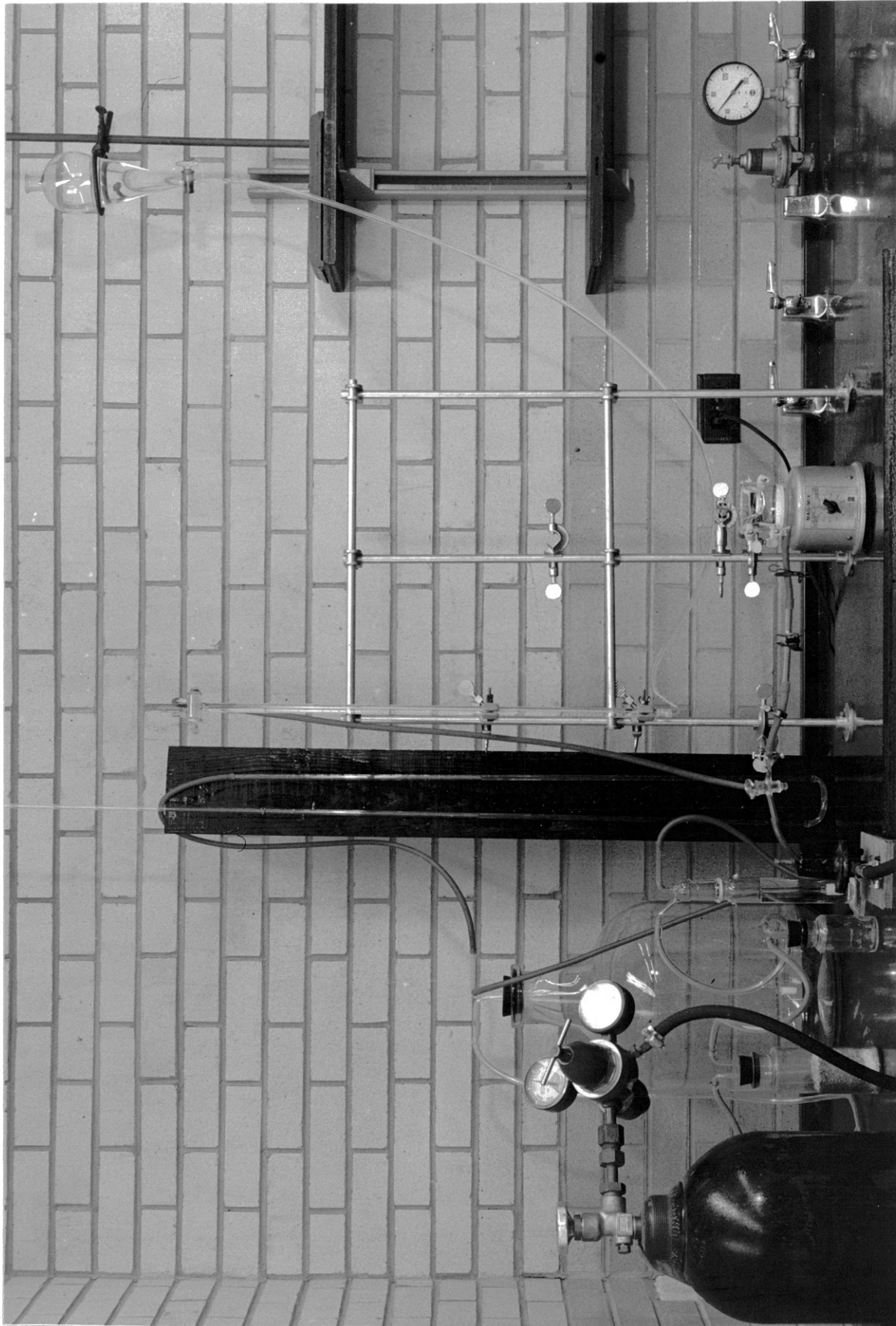


Figure 2 - Micro-flotation apparatus.



### Experimental Procedure

Experiments were conducted at room temperature with the following procedure:

1. Predetermined volumes of conductivity water and lead chloride were combined and the pH was adjusted to a desired value.
2. A given volume of potassium oleate solution was added so that the final volume was 100 cc.
3. One drop of iso-amyl alcohol was added as frother.
4. Five grams of quartz were added, and the pulp was conditioned for 3 minutes.
5. The pH of the pulp was measured, termed flotation pH.
6. A volume of 50 cc of purified nitrogen was passed through the pulp at constant pressure (3 feet of water) at which time the froth was collected.
7. The pH of the pulp was measured, termed final pH.

## EXPERIMENTAL RESULTS

The experimental results can be conveniently classified in five different categories relating the important parameters of this system:

1. Relationship between flotation recovery and pH at constant additions of oleate and lead chloride.
2. Relationship between oleate addition and hydroxyl ion concentration at constant additions of lead chloride and for a constant flotation recovery of 80 percent.
3. Relationship between lead addition and hydroxyl ion concentration at constant additions of oleate and for a constant recovery of 80 percent.
4. Relationship between flotation recovery and oleate addition at constant pH and constant additions of lead ions.
5. Relationship between flotation recovery and lead addition at constant pH and constant additions of oleate

### Flotation Recovery Versus Hydroxyl Concentration

In this series of experiments, the two parameters were oleate and lead additions. The results are presented according to the lead addition.

#### No lead addition

In the absence of lead ion, no flotation could be effected at any pH with three specific additions of oleate. See table 1.

Table 1 - Flotation pH and oleate additions with which zero recovery was obtained in the absence of lead ion.										
Oleate mole/liter	pH									
$5 \times 10^{-5}$	2.42	3.71	4.55	5.60	6.82	7.72	8.51	9.21	10.35	11.55
$1 \times 10^{-4}$	2.51	3.65	4.49	5.55	6.78	7.69	8.52	9.38	10.57	11.43
$2 \times 10^{-4}$	2.53	3.57	4.64	5.76	6.58	7.53	8.74	9.52	10.53	11.74

#### Addition of $1 \times 10^{-4}$ mole per liter $Pb^{++}$

As shown in figure 3, no flotation could be effected at pH 5.85 and below at constant oleate and lead additions of  $1 \times 10^{-4}$  mole per liter. A slight increase in flotation pH, i.e. to 6.00, resulted in a recovery of 14 percent, while complete flotation was effected at

pH 6.88. Complete flotation was possible in the range from pH 6.88 to 11.35. When the pH was increased to 12.0, recovery was only 39 percent, and finally complete depression resulted at pH 12.63 and above.

Increasing the oleate addition to  $2 \times 10^{-4}$  mole per liter at the same lead addition resulted in a shortening of the range in which complete flotation was possible, that is from pH 8.55 to 11.25. No flotation could be obtained below 6.95 and above pH 12.32.

Increasing the oleate addition to  $3 \times 10^{-4}$  mole per liter at the same lead addition required a pH of 10.40 to effect complete flotation.

When  $4 \times 10^{-4}$  mole per liter oleate was added, the maximum flotation recovery was reduced to an average of 83.5 percent. This recovery was obtained in a pH range from 11.52 to 12.11. See figure 4.

Increasing the oleate addition to  $6 \times 10^{-4}$  mole per liter also reduced the maximum recovery to 83.5 percent but in a pH range from 11.58 to 12.25.

#### Addition of $2 \times 10^{-4}$ mole per liter $Pb^{++}$

As shown in figure 5, no flotation was effected below pH 5.75 at constant oleate and lead additions of  $2 \times 10^{-4}$  mole per liter. Complete flotation was observed at pH 6.24 and above.

Flotation recovery (percent)

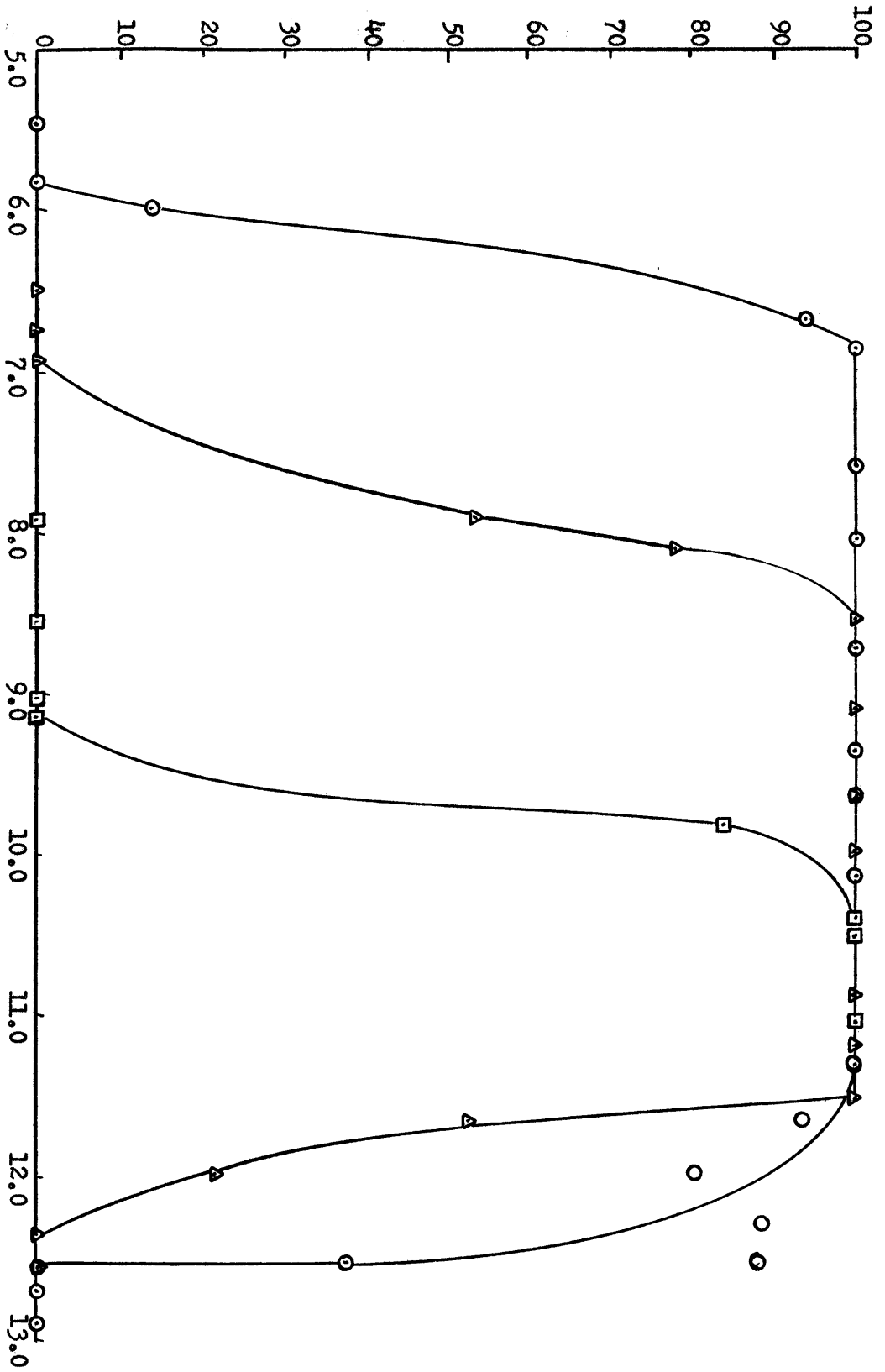


Fig. 3 - Relationship between recovery and pH at constant additions of oleate and lead ions in quartz flotation

○ 1 x 10<sup>-4</sup> mole/liter Oleate  
 △ 2 x 10<sup>-4</sup> mole/liter Oleate  
 □ 1 x 10<sup>-4</sup> mole/liter Pb<sup>++</sup>

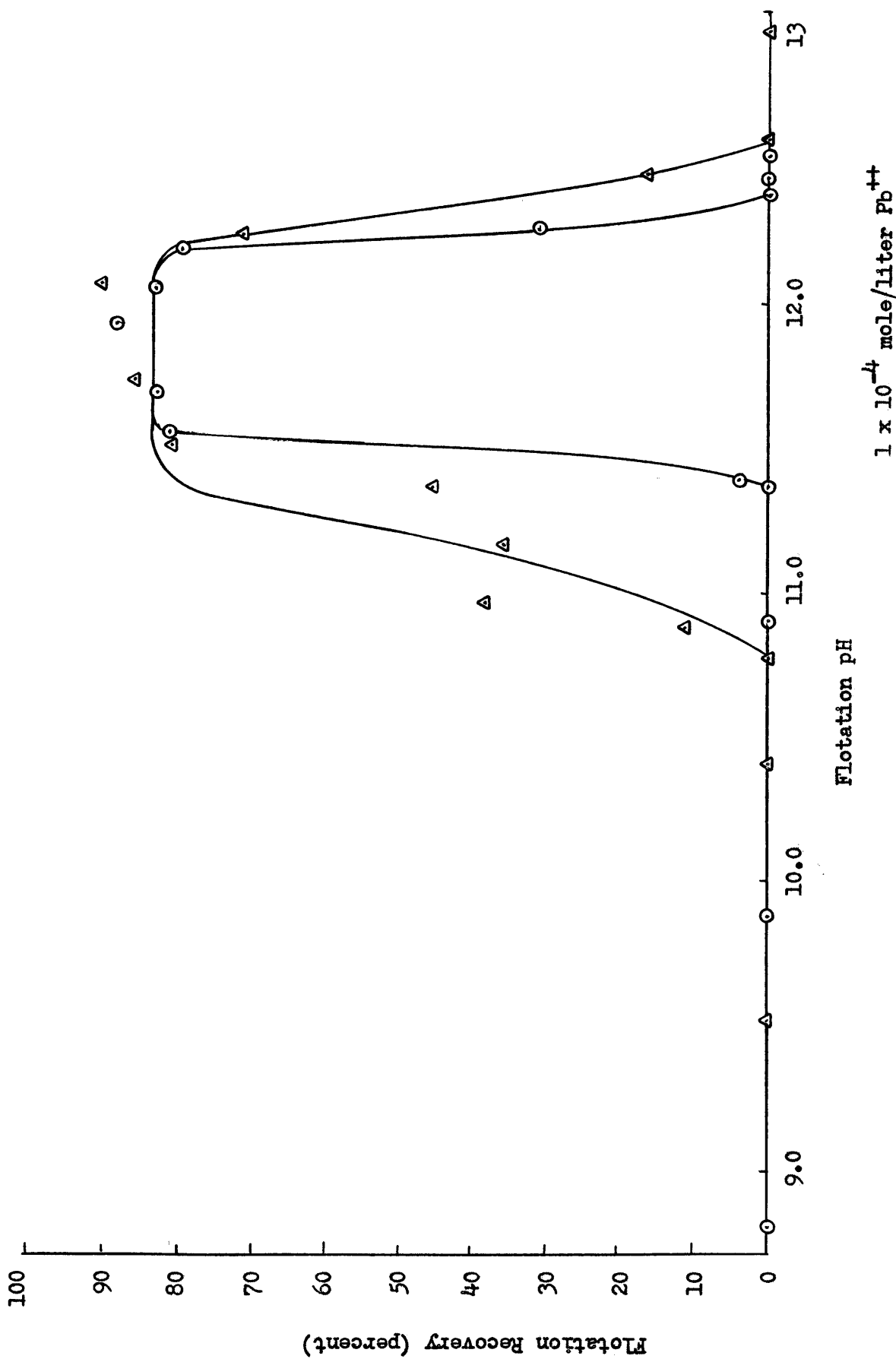


Fig. 4 - Relationship between recovery and pH at constant additions of oleate and lead ions in quartz flotation

When higher additions of oleate were made, higher values of the pH were required before total flotation occurred. For an oleate addition of  $3 \times 10^{-4}$  mole per liter, the pH had to be raised to 7.49. When  $4 \times 10^{-4}$  and  $6 \times 10^{-4}$  mole per liter oleate was added, the pH had to be raised to 11.40 to obtain a 95-percent recovery.

Addition of  $4 \times 10^{-4}$  mole per liter  $Pb^{++}$

Figure 6 shows the flotation response of quartz at a lead addition of  $4 \times 10^{-4}$  mole per liter. With an oleate addition of  $4 \times 10^{-4}$  mole per liter, no flotation could be effected at pH 7.95 and below, while a recovery of about 60 percent was obtained at pH 8.45. Increasing the pH resulted in an increase in recovery (84 percent at pH 9.95), and complete flotation was possible between pH 11.05 and 12.06. No flotation could be obtained at pH 12.45 and above.

When  $6 \times 10^{-4}$  mole per liter oleate was added, no flotation was obtained at pH 10.81 and below. Increasing the flotation pH to 10.95 resulted in a recovery of 27.5 percent, while a recovery of 51 percent was obtained at pH 11.28. A maximum recovery of 87.5 percent was obtained between pH 11.80 and 12.0.

Low additions of lead

Similar experiments were conducted with smaller additions of lead, namely  $5 \times 10^{-5}$  and  $2.5 \times 10^{-5}$  mole per liter. The data for these series of experiments are found in figures 7 and 8.

In all of the experiments described in this section, the bluish-white precipitated cloud, resulting from the addition of potassium oleate to lead chloride solutions, disappeared when the pH exceeded 12.25. The exact pH value varied slightly with the amounts of reagent added. Further, experiments showed that the flotation recovery was decreased when the pH exceeded 12 and was essentially zero above pH 12.63.



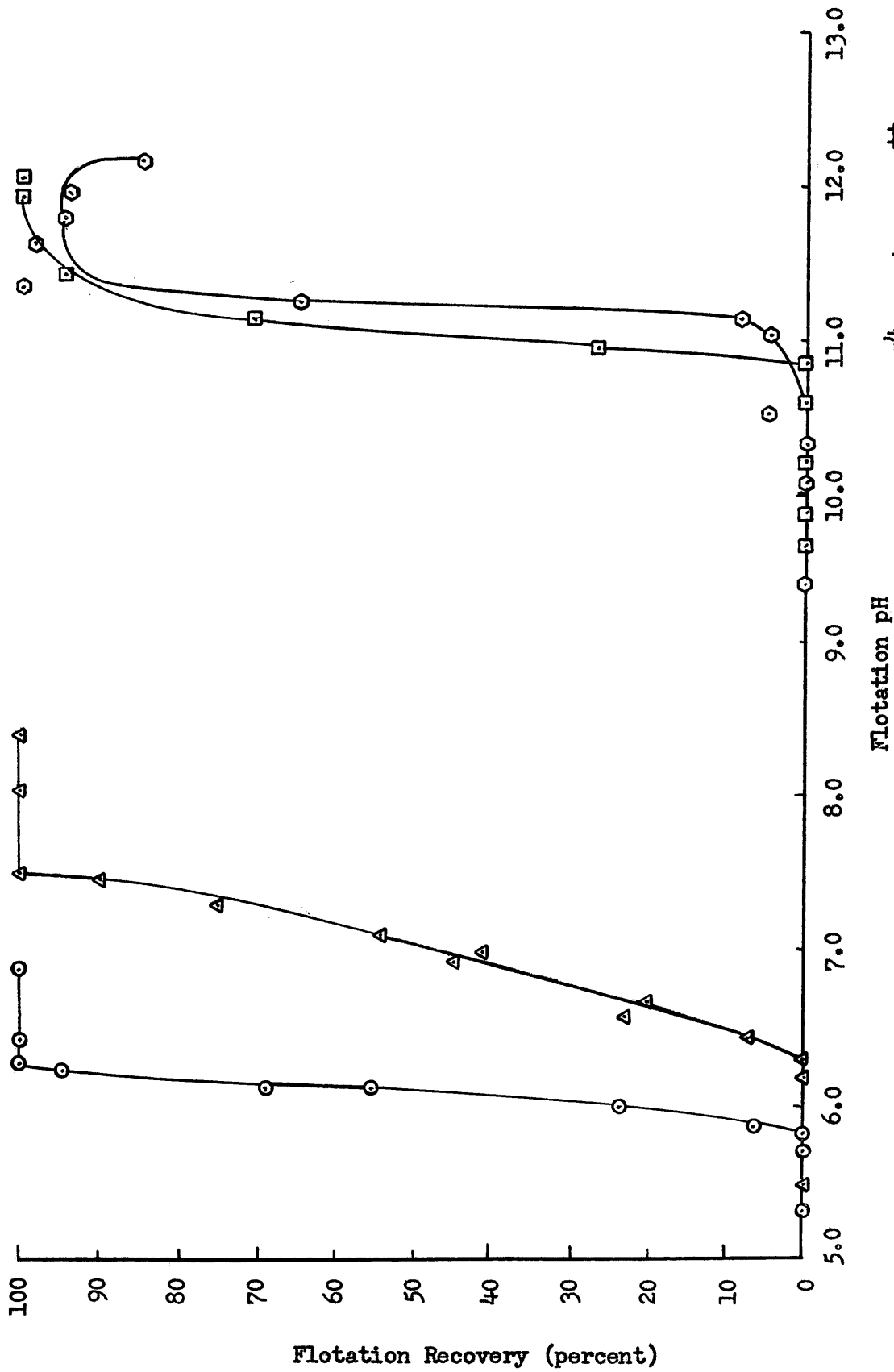


Figure 5 - Relationship between recovery and pH at constant additions of oleate and lead ions in quartz flotation.

2 x 10<sup>-4</sup> mole/liter Pb<sup>++</sup>  
 2 x 10<sup>-4</sup> mole/liter Oleate  
 3 x 10<sup>-4</sup> mole/liter Oleate  
 4 x 10<sup>-4</sup> mole/liter Oleate  
 6 x 10<sup>-4</sup> mole/liter Oleate

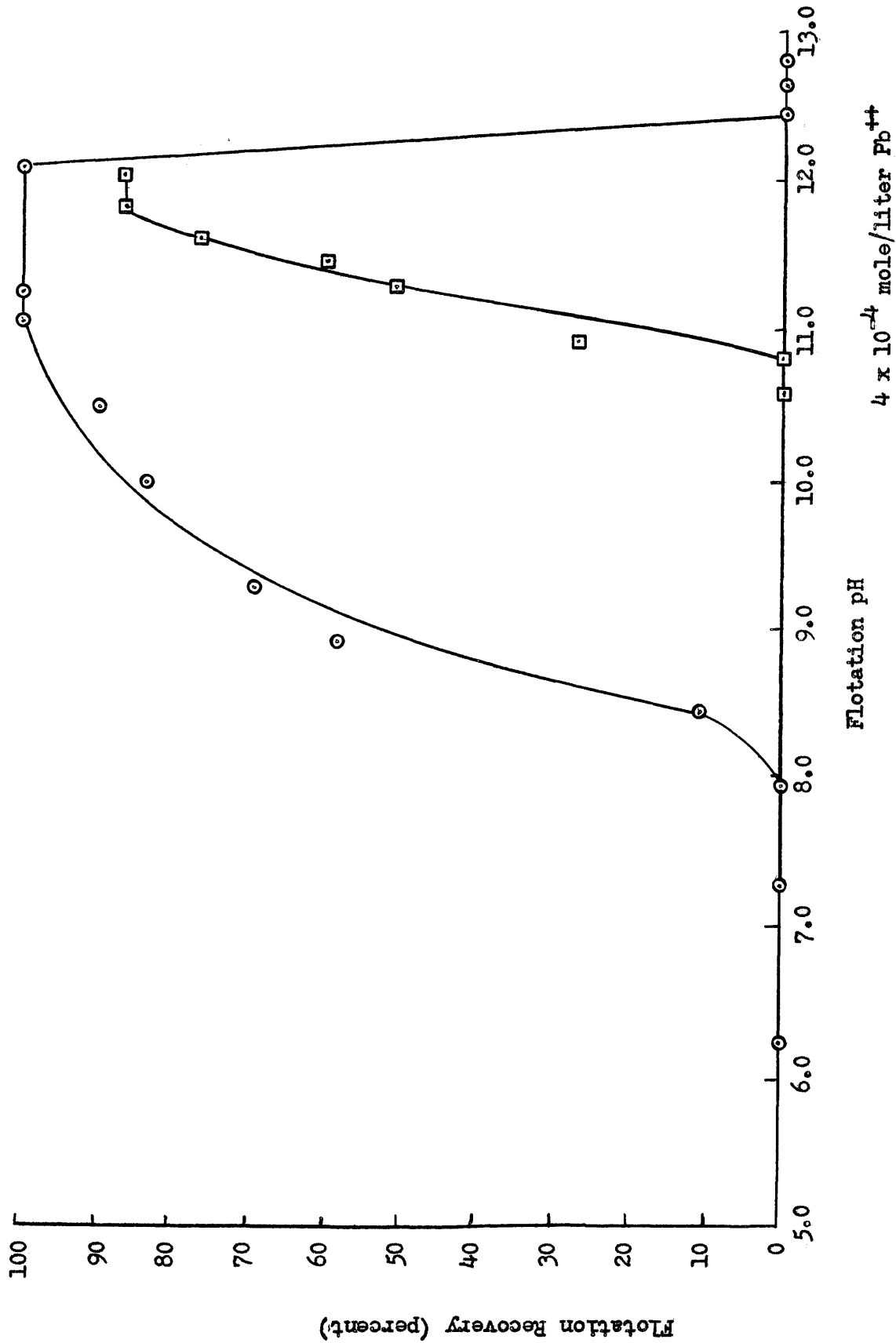


Fig. 6 - Relationship between recovery and pH at constant additions of oleate and lead ions

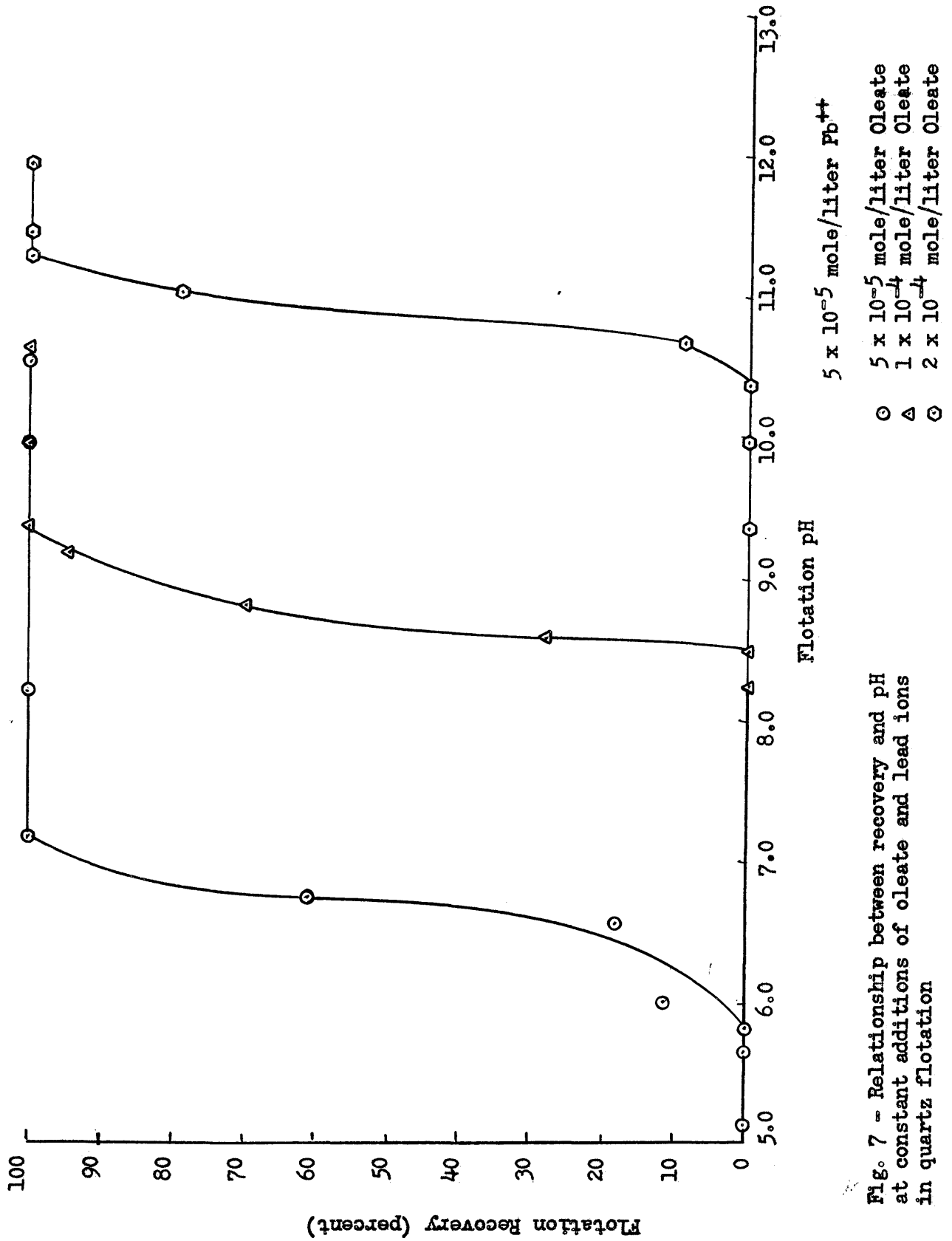


Fig. 7 - Relationship between recovery and pH at constant additions of oleate and lead ions in quartz flotation

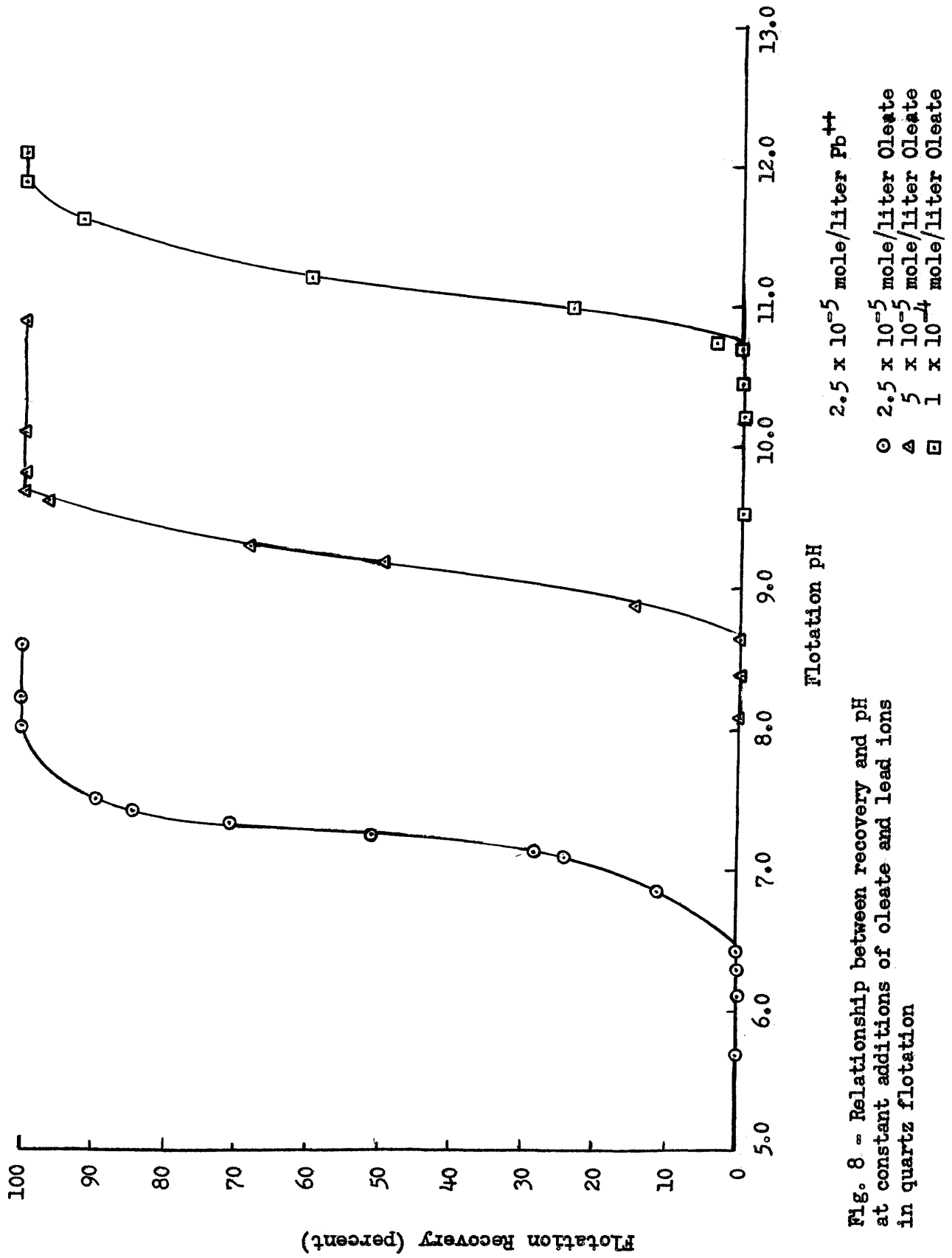


Fig. 8 - Relationship between recovery and pH at constant additions of oleate and lead ions in quartz flotation

Flotation pH

○  $2.5 \times 10^{-5}$  mole/liter Pb<sup>++</sup>  
 △  $2.5 \times 10^{-5}$  mole/liter Oleate  
 ◻  $5 \times 10^{-5}$  mole/liter Oleate  
 ◻  $1 \times 10^{-4}$  mole/liter Oleate

### Oleate Addition Versus Hydroxyl Concentration

The curves of recovery as a function of pH obtained in the preceding section showed that, at constant addition of lead, flotation recovery is strongly dependent on the amount of oleate added. To determine what relationship if any exists between these parameters, logarithmic plots were made of the lowest value of pH at which complete flotation occurred as a function of oleate addition. These plots were made at constant additions of lead. Complete flotation was taken as 80-percent recovery. Figure 9 shows the results graphically. The data are also listed in table 1-A in the appendix. The logarithm of the hydroxyl ion concentration for an 80-percent recovery appears to be a linear function of the logarithm of the oleate additions.

As shown in table 2, the slopes of these straight lines are almost constant for oleate additions less than  $3 \times 10^{-4}$  mole per liter. They have an average value of 6.99. For oleate additions greater than  $3 \times 10^{-4}$  mole per liter, the slope is practically doubled, i.e. 13.66. The changes in slope are shown in figure 9 by the angle between the continuous and dashed lines.

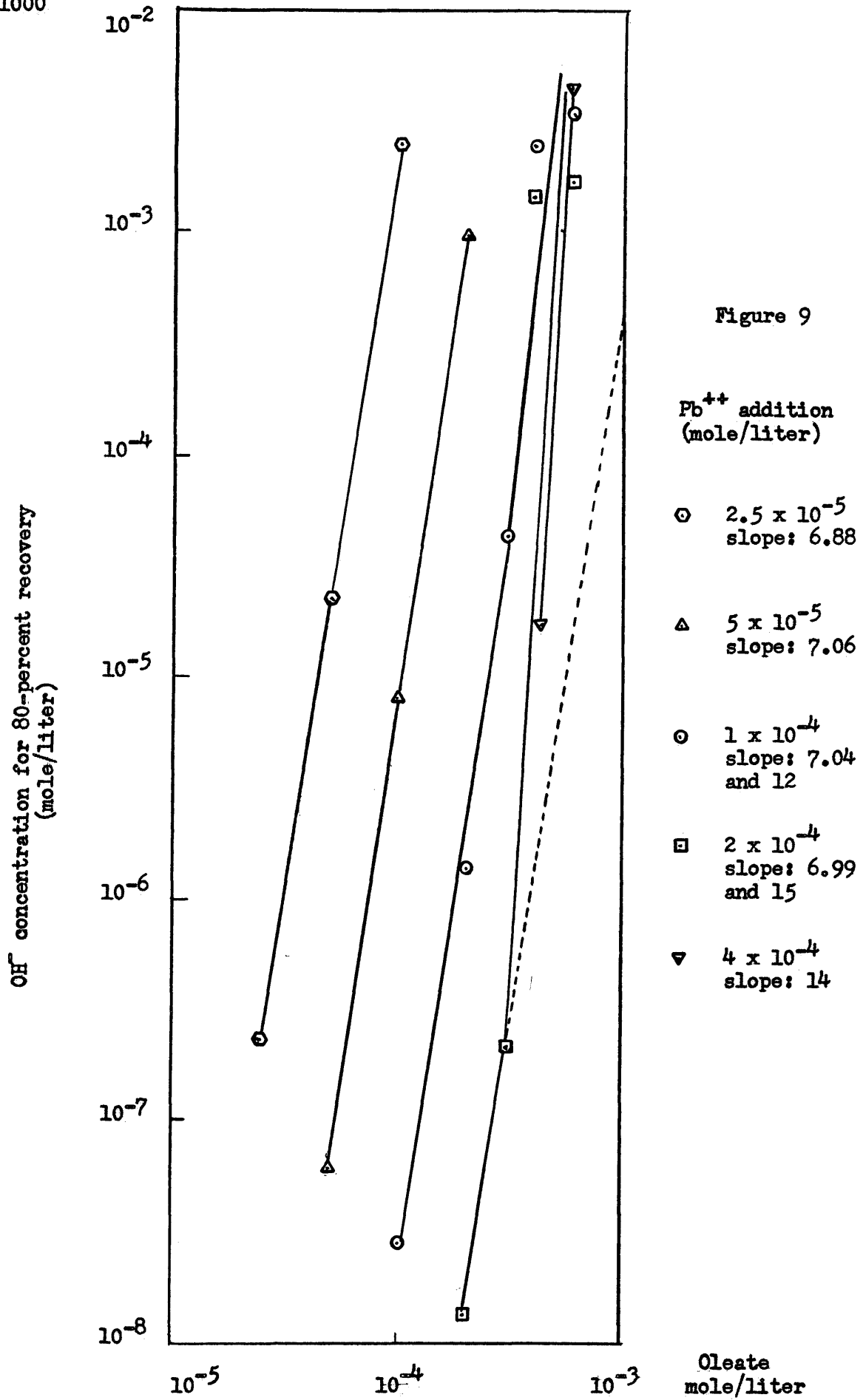


Table 2 - Slopes of the lines,  $\log (\text{OH}^-)$  versus  $\log$  oleate, at constant lead addition (from figure 9)

Oleate additions less than  $3 \times 10^{-4}$  mole per liter

Pb <sup>++</sup> addition (mole/liter)	Slope
$2.5 \times 10^{-5}$	6.88
$5 \times 10^{-5}$	7.06
$1 \times 10^{-4}$	7.04
$2 \times 10^{-4}$	6.99

Oleate additions greater than  $3 \times 10^{-4}$  mole per liter

Pb <sup>++</sup> addition (mole/liter)	Slope
$1 \times 10^{-4}$	12
$2 \times 10^{-4}$	15
$3 \times 10^{-4}$	14

### Lead Addition Versus Hydroxyl Concentration

To illustrate the effect of lead addition on flotation recovery, the lowest value of pH for 80-percent recovery was plotted as a function of lead addition. These plots were made at constant additions of oleate. The results are shown in figure 10 and listed in table 2-A in the appendix. This study was limited to oleate additions less than  $3 \times 10^{-4}$  mole per liter.

The logarithm of the hydroxyl ion concentration appears to be a linear function of the logarithm of the lead additions. The slopes of these lines are listed in table 3. They were noted to decrease slightly as the oleate additions increased, and they averaged 8.08.

Table 3 - Slopes of the lines,  $\log (\text{OH}^-)$  versus  $\log$  lead, at constant oleate addition (from figure 10)

Oleate addition (mole/liter)	Slopes
$5 \times 10^{-5}$	- 8.60
$1 \times 10^{-4}$	- 8.25
$2 \times 10^{-4}$	- 7.75
$3 \times 10^{-4}$	- 7.72



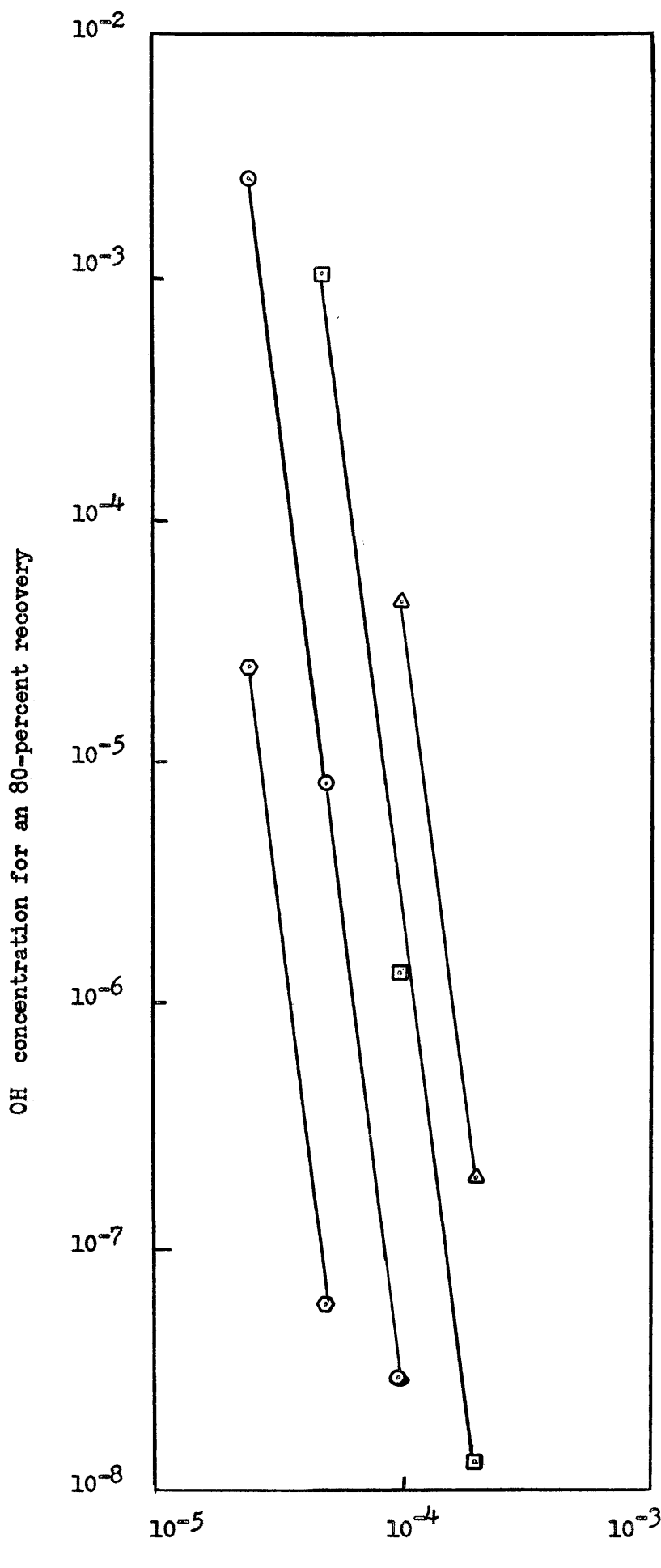


Figure 10

Oleate addition  
mole/liter

- ⊙ 5 x 10<sup>-5</sup>
- 1 x 10<sup>-4</sup>
- 2 x 10<sup>-4</sup>
- △ 3 x 10<sup>-4</sup>

Pb<sup>++</sup> addition  
mole/liter

Flotation Recovery Versus Oleate Addition

As shown previously, high additions of oleate depress these systems at moderate values of the flotation pH. The effect of oleate addition at constant lead addition and at three values of pH is shown in figure 11 and results are listed in table 4.

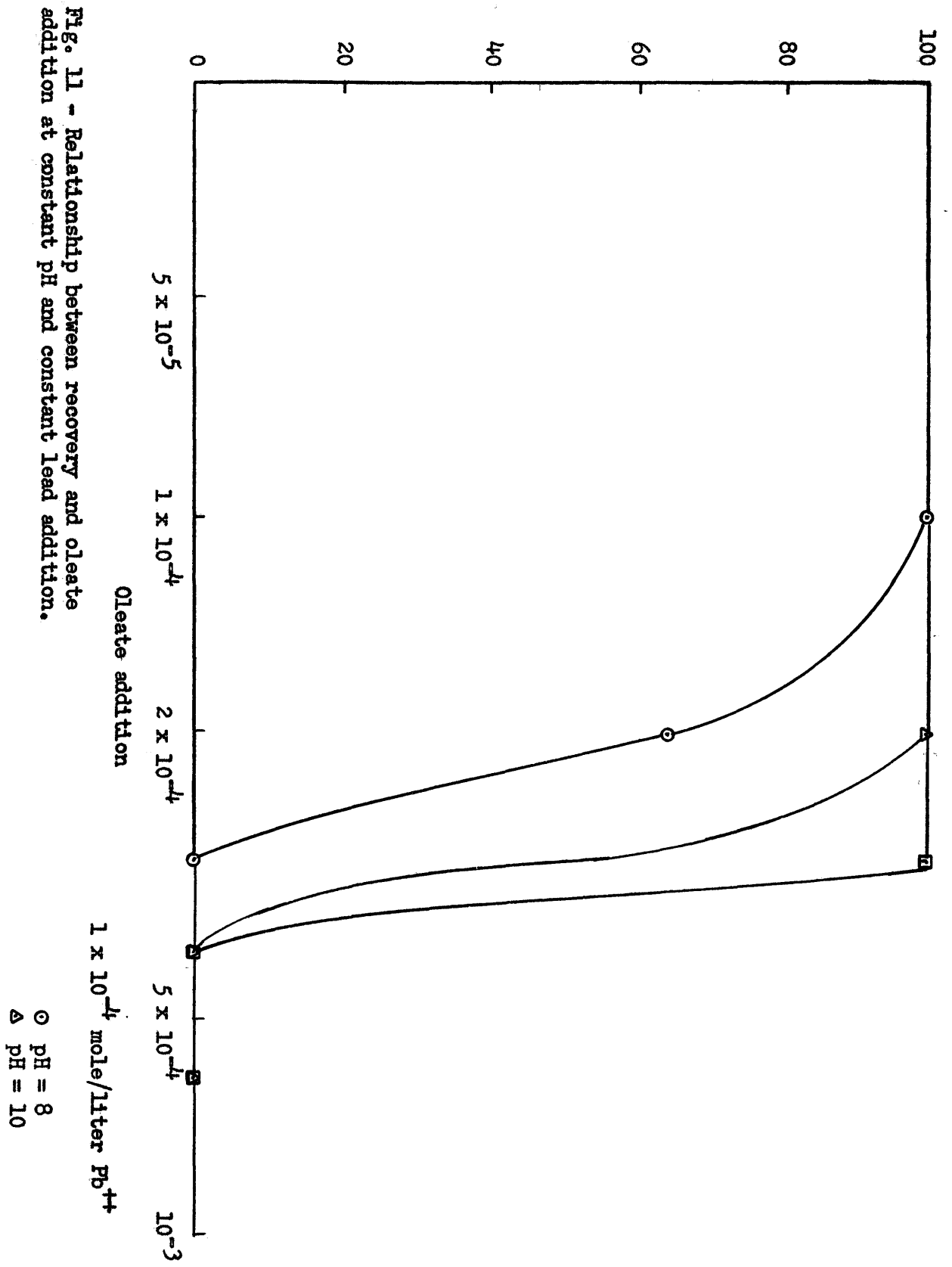
Table 4 - Oleate addition necessary for complete depression of quartz, for a lead addition of  $1 \times 10^{-4}$  mole per liter.

Flotation pH	Oleate addition (mole/liter)
$8.00 \pm 0.17$	$3 \times 10^{-4}$
$10.00 \pm 0.11$	$4 \times 10^{-4}$
$11.00 \pm 0.09$	$5 \times 10^{-4}$

It was found that no flotation could be effected with  $1 \times 10^{-6}$  mole per liter oleate, while complete flotation was obtained with  $3 \times 10^{-6}$  mole per liter oleate with  $1 \times 10^{-4}$  mole per liter lead at three values of pH.

Further, complete depression occurred at pH 8 when  $3 \times 10^{-4}$  mole per liter oleate was added and at pH 11 when  $4 \times 10^{-4}$  mole per liter oleate was added.

Flotation Recovery (percent)



Flotation Recovery Versus Lead Addition

Flotation recovery was studied as a function of lead addition at constant pH and constant oleate addition. See figure 12 and table 5.

Table 5 - Lead addition necessary for complete flotation of quartz<sub>A</sub> for an oleate addition of  $1 \times 10^{-4}$  mole per liter

Flotation pH	Minimum Pb <sup>++</sup> addition (mole/liter)	Maximum Pb <sup>++</sup> addition (mole/liter)
8.00 ± 0.13	$8.5 \times 10^{-5}$	$6 \times 10^{-4}$
10.00 ± 0.09	$5 \times 10^{-5}$	$6 \times 10^{-4}$
11.00 ± 0.08	$3 \times 10^{-5}$	$6 \times 10^{-4}$

It was found that no flotation could be effected with  $1 \times 10^{-5}$  mole per liter lead, while complete flotation was effected at  $2.5 \times 10^{-5}$  mole per liter with  $1 \times 10^{-4}$  mole per liter oleate at pH 11. At pH 10 complete flotation occurred with  $5 \times 10^{-5}$  mole per liter lead, whereas  $1 \times 10^{-4}$  mole per liter lead was necessary at pH 8.

Further, excess lead was found to depress quartz. At  $1 \times 10^{-3}$  mole per liter lead, the flotation recovery is only 70 percent at the three values of pH indicated, and total depression occurred with  $2.5 \times 10^{-3}$  mole per liter Pb<sup>++</sup>.

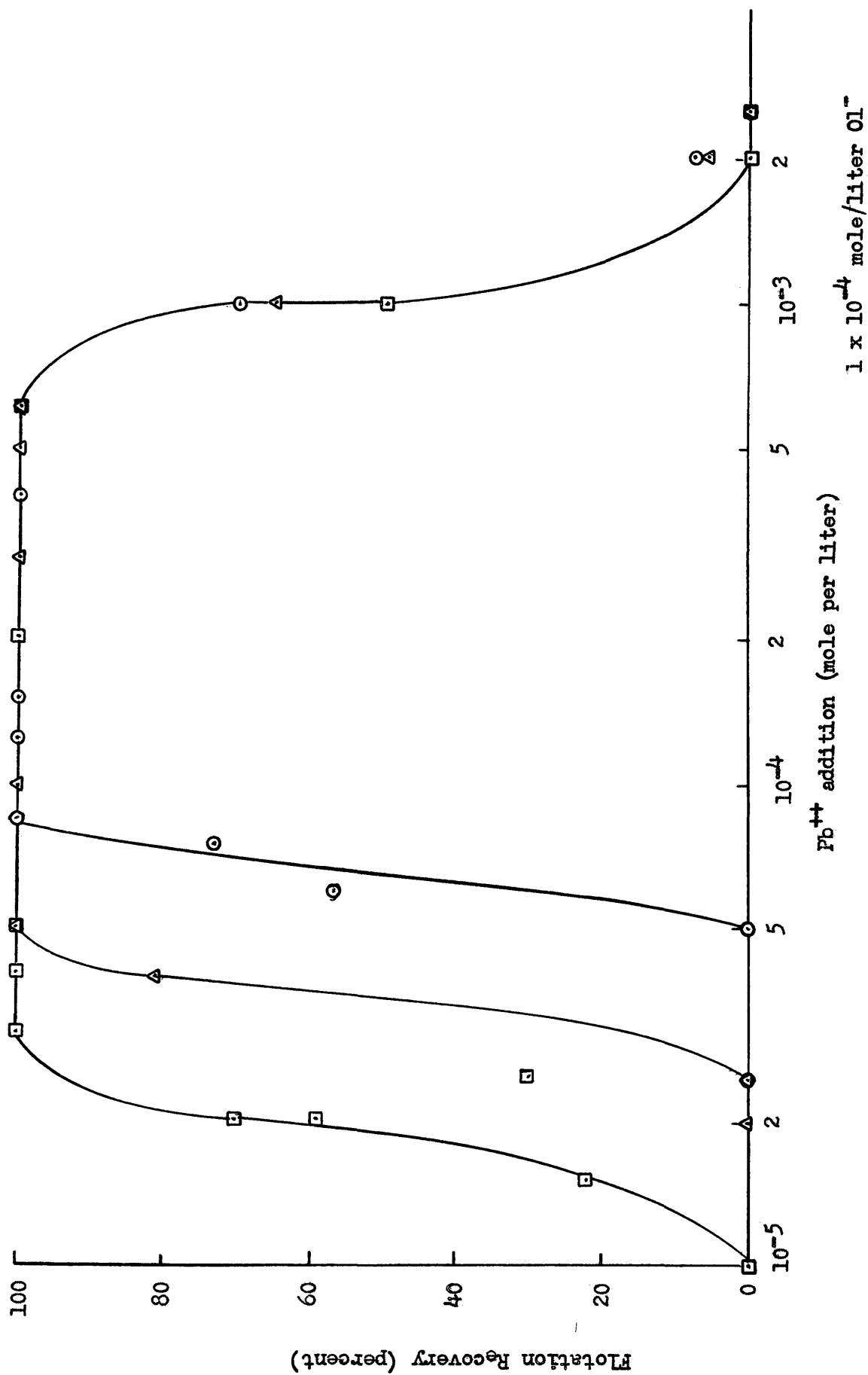


Fig. 12 - Relationship between recovery and lead addition at constant pH and constant oleate addition

○ pH = 8  
 △ pH = 10  
 □ pH = 11

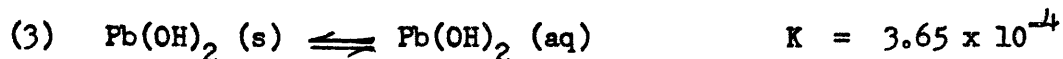
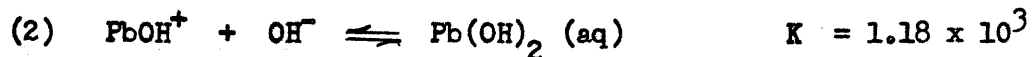
## DISCUSSION OF RESULTS

The experimental results revealed that pure quartz could not be floated with oleate alone but responded well to flotation in the presence of lead ion at specific values of pH and collector additions.

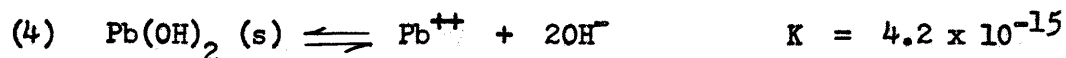
The data suggest strongly that lead ion hydrolysis is one of the basic phenomena responsible for flotation collection in this system. Therefore a review of the hydrolysis of lead ion as a function of pH will be helpful.

Theoretical Considerations

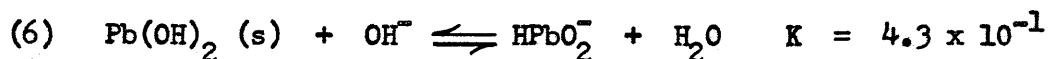
Lead ion hydrolysis involves two hydroxide complexes between hydrated lead ion and insoluble lead hydroxide. This may be represented by the following equations:



When the system is saturated with respect to lead hydroxide, the following equilibria will be present:



Further, lead hydroxide is amphoteric (17). As a result, lead hydroxide will dissolve in strong alkali solutions and form plumbite ion. The form of this ion has been given as  $\text{Pb(OH)}_3^-$  or  $\text{HPbO}_2^-$ . The latter form is used in this discussion. In equation form,



An additional equilibrium is involved between  $\text{Pb(OH)}_2 (aq)$  and  $\text{HPbO}_2^-$ :



The relative concentrations of the various species of lead, i.e.  $\text{Pb}^{++}$ ,  $\text{PbOH}^+$ ,  $\text{Pb(OH)}_2 (aq)$ , and  $\text{HPbO}_2^-$ , are shown as a function of pH for an initial lead chloride concentration of  $1 \times 10^{-4}$  mole per liter in figure 13. It should be noted that this system is not saturated with respect to lead hydroxide and that only equations 1, 2, and 7 and a mass balance on lead are involved in the calculations.

In figure 14, the relative equilibrium concentrations of oleic acid and oleate ion are shown as a function of pH, for an addition of  $1 \times 10^{-5}$  mole per liter of potassium oleate. A dissociation constant of  $1.5 \times 10^{-5}$  for oleic acid was used in the calculations (18, 19).

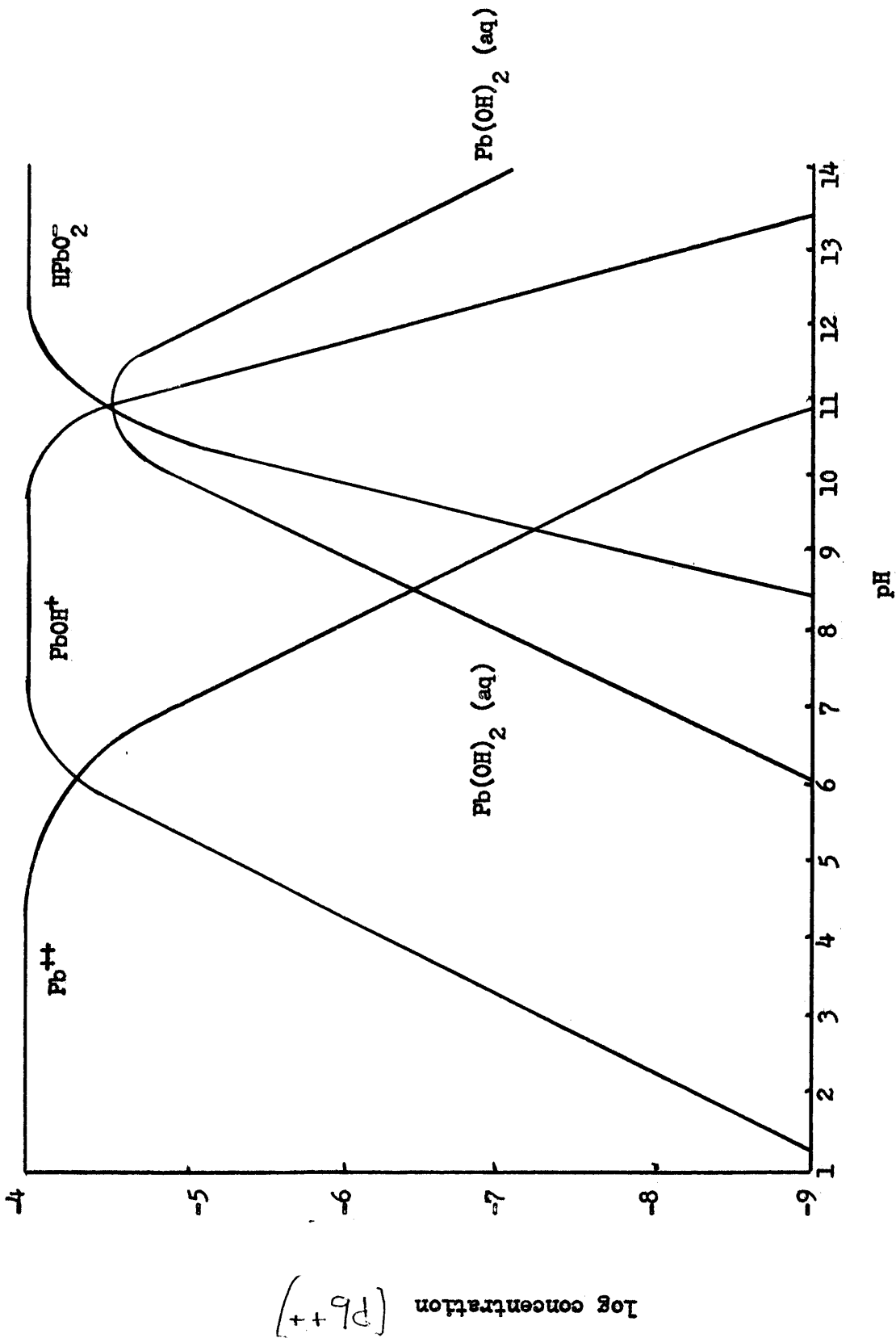


Fig. 13 - Logarithmic concentration diagram for  $1 \times 10^{-4}$  molar  $Pb^{++}$ .



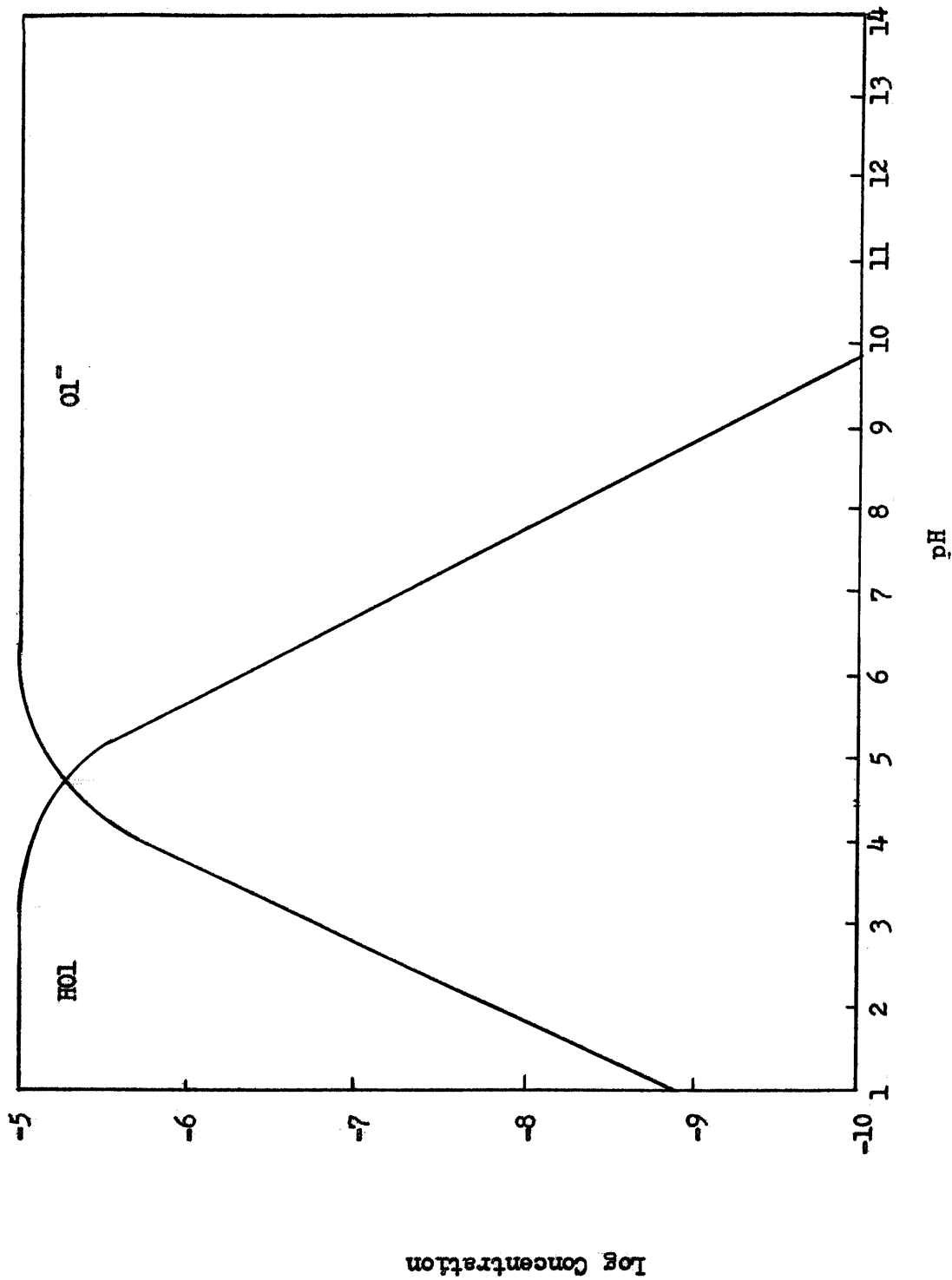


Fig. 14 - Logarithmic concentration diagram for 1 x 10<sup>-5</sup> molar oleic acid.

### Interpretation of Data

The configuration of any lead compound, such as its oleate salts, is dependent on the extent of hydrolysis of lead ion which is in turn determined by pH. The extent of dissociation of oleic acid is also determined by pH.

The influences of flotation pH and of lead and oleate additions are discussed successively.

#### Influence of flotation pH

Experiments showed that colloidal precipitates resulting from the combination of oleate and lead solutions had to be present in order to obtain flotation. The minimum additions of lead and oleate for minimum flotation (20-percent recovery) at the lowest pH possible were determined to be:

$Pb^{++}$	$1.25 \times 10^{-5}$	mole per liter
$Ol^{-}$	$2.0 \times 10^{-6}$	mole per liter
$OH^{-}$	$1.0 \times 10^{-8}$	mole per liter

where  $Ol^{-}$  symbolizes the oleate ion.

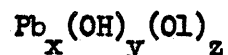
Assuming two moles of oleate are consumed with one mole of lead in the precipitation of lead oleate, this represents an activity product of:

$$(1.25 \times 10^{-5}) (2 \times 10^{-6})^2 = 5 \times 10^{-17}$$

The reported solubility product of lead oleate is (20):

$$K = 1.6 \times 10^{-17}$$

From figure 13 it can be seen, however, that at pH 6 ( $10^{-8}$  mole per liter  $\text{OH}^-$ ), 40 percent of the added lead will have hydrolyzed to  $\text{PbOH}^+$ . Under these conditions and in presence of oleate, some of the valences of lead will be occupied by hydroxyl and the rest by oleate. The compound lead oleate then will be actually lead-hydroxy-oleate; a general formula for this compound might be:



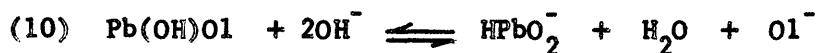
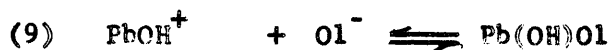
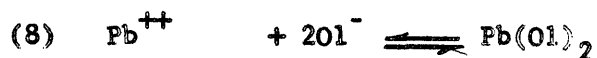
where x, y, and z represent positive whole numbers.

If lead-hydroxy-oleate is the collector in these systems, then there should be a specific range in pH in which flotation is possible. This will be true because there is a specific range in pH in which lead will be in a favorable state of hydrolysis, i.e.  $\text{PbOH}^+$ .

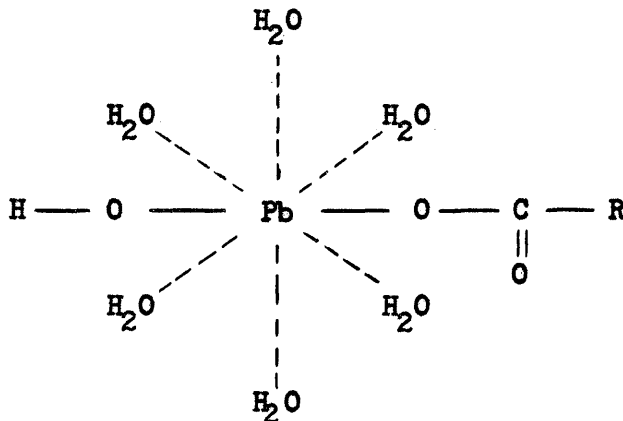
The range in pH in which  $\text{PbOH}^+$  is present in significant quantity in an unsaturated lead hydroxide solution is from about pH 6 to pH 12 (figure 13). Below pH 6, lead will be present predominantly as  $\text{Pb}^{++}$  and above pH 12,  $\text{HPbO}_2^-$  is the stable species. These values of pH are essentially the limits between which flotation occurred in this system. See the curves determined with  $1 \times 10^{-4}$  mole per liter oleate and lead in figure 3.

As a matter of fact, the precipitate of lead-hydroxy-oleate was noted to disappear or redissolve at pH 12.25, denoting that  $\text{HPbO}_2^-$  is more stable than lead-hydroxy-oleate under these conditions.

Assuming that x, y, and z are unity in the compound  $\text{Pb}_x(\text{OH})_y(\text{Ol})_z$ , the following equilibria can be represented:



As an analogy with the model of ferric-hydroxy-sulfonate presented by Fuerstenau, Martin, and Bhappu (12), the configuration of the compound lead-hydroxy-oleate might be represented as follows:



This representation is constructed assuming a coordination number of lead of 8 and also that one lead, one hydroxyl, and one oleate ion are involved in the compound. Sufficient data is not available to state that this is the exact configuration of the compound. This model is presented only for the purpose of visualizing the form that the compound might have.

Bonding to the surface could occur as a hydrogen bond between the oxygen of the hydroxyl contained in the compound and an oxygen of the surface. The quartz-solution interface might then look as follows:

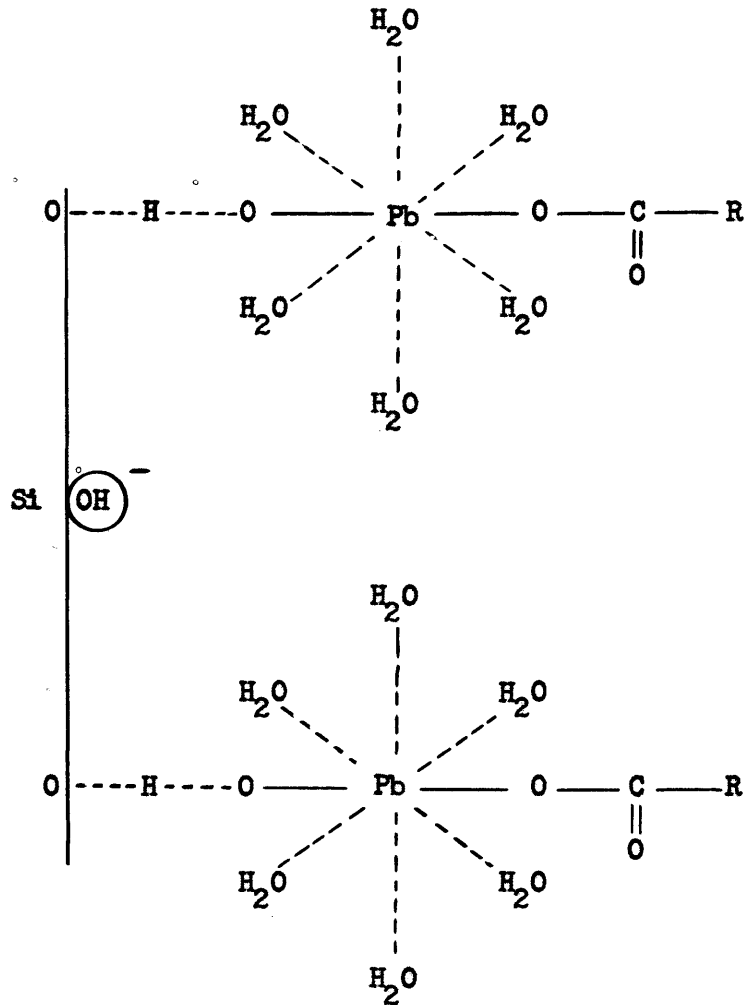


Figure 15 - Schematic representation of the quartz-solution interface showing the bonding between the collector and the mineral surface

For the sake of simplicity, potassium and chloride ions were not represented. At moderate concentrations they should not affect the flotation response. They remain in solution and may adsorb to the surface of the quartz.

Illustrations depicting the quartz-solution interfaces in pH regions of non-flotation and also flotation are given in figures 16, 17, and 18.

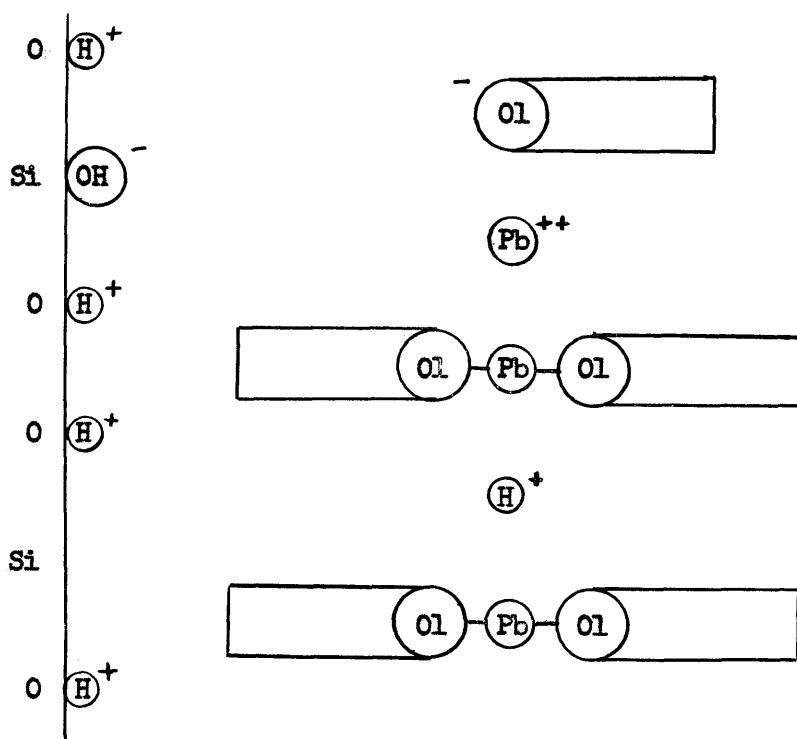


Figure 16 - Quartz-solution interface below pH 6.

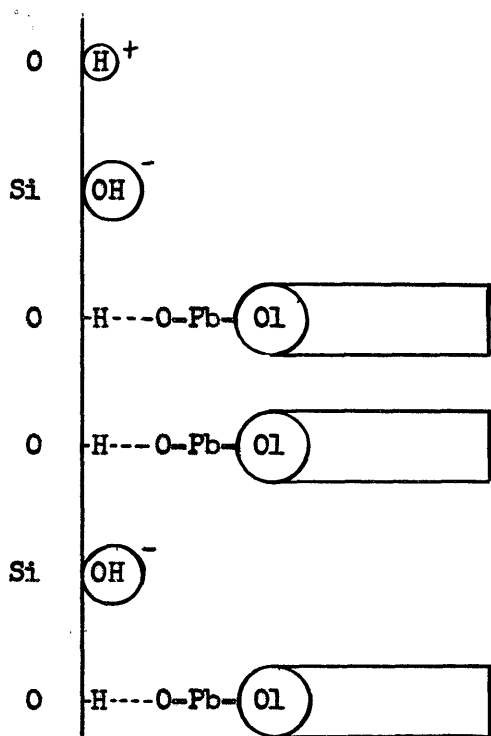


Figure 17 - Quartz-solution interface between pH 6 and 12.

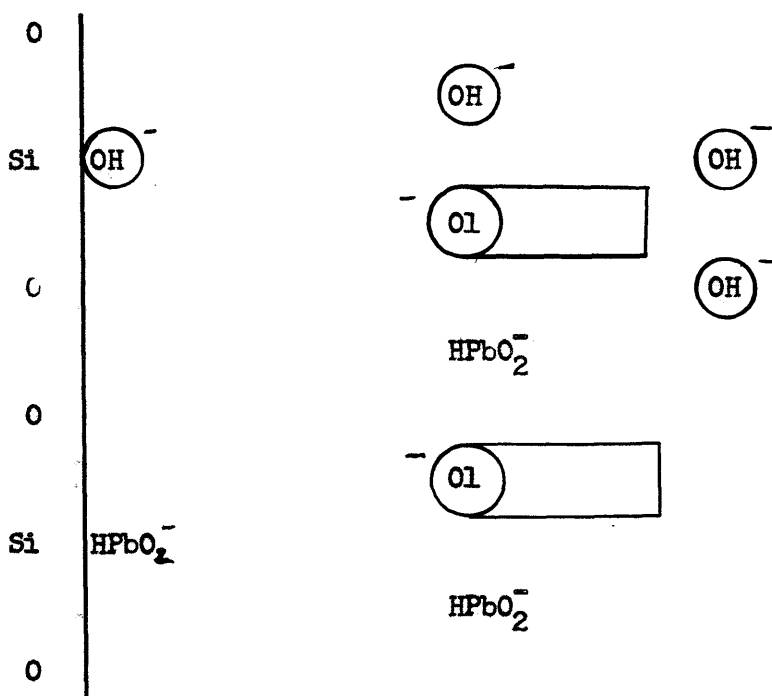
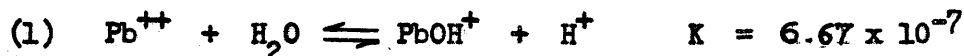


Figure 18 - Quartz-solution interface above pH 12.



Influence of lead and oleate additions

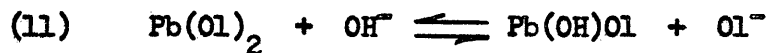
The relative ratio of  $\text{PbOH}^+$  to  $\text{Pb}^{++}$  is dependent on pH in an unsaturated system. For example, from the following equation:



it can be seen that to have the same quantity of  $\text{PbOH}^+$  at pH 7 as at pH 8, a tenfold increase in lead addition must be made. Figure 12 illustrates this phenomenon, that the higher the pH, the lower the addition of lead necessary to effect complete flotation. A minimum amount of lead,  $1.25 \times 10^{-5}$  mole per liter, is necessary to obtain minimum flotation at pH 11 but  $5 \times 10^{-5}$  mole per liter was required at pH 8. Figure 12 also demonstrates that  $\text{PbOH}^+$  is not the only complex ion involved because an increase in hydroxyl ion concentration of two orders of magnitude (from pH 8 to pH 10) resulted in a decrease of required lead of only a factor of about 2 instead of 100.

Increasing the lead addition to  $2 \times 10^{-3}$  molar resulted in complete depression at three different values of pH (figure 12). At this condition, the system was very turbid and had a different physical appearance from the systems at lower lead addition. Precipitated lead hydroxide is probably formed in preference to lead-dihydroxy-oleate with this high lead addition.

Experiments with other systems (13) (lead-sulfonate-quartz) have revealed that the relative ratio of collector to metal ion is exceedingly important. As a matter of fact, it is this ratio that determines whether any flotation is possible at a specific value of pH. This same phenomenon was observed in this system. For example, when the system was floated at constant lead addition of  $1 \times 10^{-4}$  mole per liter, 80-percent recovery was obtained at pH 6.45, 9.65, and 11.55, when  $1 \times 10^{-4}$ ,  $3 \times 10^{-4}$ , and  $6 \times 10^{-4}$  mole per liter oleate was added, respectively. It would seem that the following equilibrium is involved:

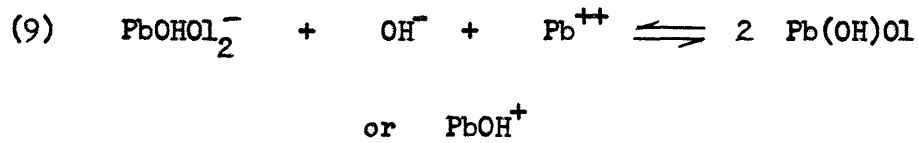


When the oleate addition is increased at constant pH and constant lead addition, the equilibrium is shifted to the left, which results in the formation of  $\text{Pb(OL)}_2$  and  $\text{OH}^-$ .  $\text{Pb(OL)}_2$  is not a collector, and as a result, the system is depressed. For flotation to be effected under these conditions, the pH must be raised, or the  $\text{OH}^-$  concentration increased, to drive the equilibrium to the right to form the collector  $\text{Pb(OH)OL}$ .

With reference to figure 9 it can be seen that some quantification of this phenomenon can be made. For example, with the curves



and the following equilibrium could be involved:



As a matter of fact, it was found that, for oleate additions exceeding  $3 \times 10^{-4}$  mole per liter, flotation could be effected by increasing the amounts of lead and hydroxyl ions in solution. See the critical curves of flotation, in figure 9.

The quartz-solution interface might then look as follows:

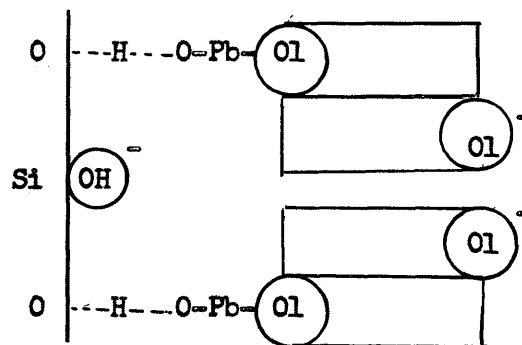


Figure 19 - Suggested model of the quartz-solution interface for oleate additions exceeding  $3 \times 10^{-4}$  mole per liter.

The outside layer would then be negatively charged and hence hydrophilic. As a result the mineral would not attach to a nitrogen bubble.

In essence, hemi-micelles may be forming at the quartz-solution interface. To verify these hypotheses, additional experimental work of a rather sophisticated nature would have to be undertaken. For example, a radiometric technique would seem to lend itself to determining the residual concentrations of lead and oleate ions in equilibrium with precipitated lead-hydroxy-oleate. This would enable the determination of the solubility product and the formula of the various compounds. Such measurements were not made in this investigation because they require special equipment which was not available.

## CONCLUSIONS

A micro-flotation technique was used to determine the mechanisms of lead activation in oleate flotation of quartz. The results of this investigation lead to the following conclusions:

- 1 - Pure quartz cannot be floated with oleate alone.
- 2 - Quartz responds well to flotation with oleate as collector and lead ion as activator. This observation is important practically, as clean concentrates have been difficult to obtain with fatty acids.
- 3 - Optimum oleate additions range from  $5 \times 10^{-6}$  to  $2 \times 10^{-4}$  mole per liter. An oleate addition greater than  $3 \times 10^{-4}$  mole per liter results in complex formation at the quartz-solution interface, with consequent reduction in recovery.

4 - Optimum lead additions range from  $5 \times 10^{-5}$  to  $6 \times 10^{-4}$  mole per liter. The lower limit decreases with increasing pH. Excess lead results in decreasing the recovery; essentially no flotation occurs with lead additions in excess of  $2.5 \times 10^{-3}$  mole per liter.

5.- The optimum ratio of lead to oleate additions is 1 to 1. At neutral pH, the optimum additions range from  $5 \times 10^{-5}$  to  $2 \times 10^{-4}$  mole per liter of each.

6.- Quartz responds well to oleate flotation in the presence of lead ions from pH 6 to 11.65 under optimum conditions. Above pH 11.65, the flotation recovery is decreased and is essentially zero at pH 12.5 because of plumbite formation.

7 - The mechanism of flotation collection involves the hydrolysis of lead ion. In the absence of metal ions, no flotation occurs. In the presence of added lead, flotation occurs when the conditions are such that the lead ions are able to hydrolyze. They form hydroxide complexes which react with oleate ions to form an insoluble lead-hydroxy-oleate. It is suggested that the hydrogen atom of the hydroxyl contained in the lead-hydroxy-oleate provides a means of bonding between an oxygen of the mineral surface and the collector.

8 - A flotation constant  $k$  determined by the lead ion addition can be calculated from the equation:

$$A_{OH^-} = k (Ol^-)^{7.0}$$

for lead additions of  $2.5 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$  and  $2 \times 10^{-4}$  mole per liter below  $3 \times 10^{-4}$  mole per liter oleate. When the ratio of  $A_{OH^-}$  to  $(Ol^-)^{7.0}$  equals or exceeds  $k$ , flotation occurs.

9 - In view of the fact that insoluble lead oleate was noted to be present both in the regions of flotation and non-flotation, the prime criterion for activation seems to be the presence of a hydroxyl in a precipitated lead-hydroxy-oleate. The data appear to de-emphasize the importance of surface charge in this system. The hydrolysis of the lead ions is apparently the only necessary condition for activation.



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**APPENDIX**

Table 1-A - Relationship between oleate addition and hydroxyl ion concentration at constant lead addition and flotation recovery

$Pb^{++}$ (mole/liter)	Oleate (mole/liter)	Recovery (percent)	pH	$OH^-$ (mole/liter)
$2.5 \times 10^{-5}$	$2.5 \times 10^{-5}$	80	7.38	$2.40 \times 10^{-7}$
$2.5 \times 10^{-5}$	$5 \times 10^{-5}$	80	9.37	$2.34 \times 10^{-5}$
$2.5 \times 10^{-5}$	$1 \times 10^{-4}$	80	11.40	$2.55 \times 10^{-3}$
$5 \times 10^{-5}$	$5 \times 10^{-5}$	80	6.80	$6.30 \times 10^{-8}$
$5 \times 10^{-5}$	$1 \times 10^{-4}$	80	8.90	$7.95 \times 10^{-6}$
$5 \times 10^{-5}$	$2 \times 10^{-4}$	80	11.00	$1.00 \times 10^{-3}$
$1 \times 10^{-4}$	$1 \times 10^{-4}$	80	6.45	$2.82 \times 10^{-8}$
$1 \times 10^{-4}$	$2 \times 10^{-4}$	80	8.15	$1.42 \times 10^{-6}$
$1 \times 10^{-4}$	$3 \times 10^{-4}$	80	9.65	$4.46 \times 10^{-5}$
$1 \times 10^{-4}$	$4 \times 10^{-4}$	80	11.40	$2.55 \times 10^{-3}$
$1 \times 10^{-4}$	$6 \times 10^{-4}$	80	11.55	$3.55 \times 10^{-3}$
$2 \times 10^{-4}$	$2 \times 10^{-4}$	80	6.14	$1.38 \times 10^{-8}$
$2 \times 10^{-4}$	$3 \times 10^{-4}$	80	7.35	$2.24 \times 10^{-7}$
$2 \times 10^{-4}$	$4 \times 10^{-4}$	80	11.18	$1.51 \times 10^{-3}$
$2 \times 10^{-4}$	$6 \times 10^{-4}$	80	11.25	$1.78 \times 10^{-3}$
$4 \times 10^{-4}$	$4 \times 10^{-4}$	80	9.70	$5.00 \times 10^{-5}$
$4 \times 10^{-4}$	$6 \times 10^{-4}$	80	11.64	$4.35 \times 10^{-3}$

Note: The data listed in this table were determined according to the curves of recovery versus pH

Table 2-A - Relationship between lead addition and hydroxyl ion concentration at constant oleate addition and flotation recovery

Pb <sup>++</sup> (mole/liter)	Oleate (mole/liter)	Recovery (percent)	pH	OH <sup>-</sup> (mole/liter)
$5 \times 10^{-5}$	$2.5 \times 10^{-5}$	80	9.37	$2.34 \times 10^{-5}$
$5 \times 10^{-5}$	$5 \times 10^{-5}$	80	6.80	$6.30 \times 10^{-8}$
$1 \times 10^{-4}$	$2.5 \times 10^{-5}$	80	11.40	$2.55 \times 10^{-3}$
$1 \times 10^{-4}$	$5 \times 10^{-5}$	80	8.90	$7.95 \times 10^{-6}$
$1 \times 10^{-4}$	$1 \times 10^{-4}$	80	6.45	$2.82 \times 10^{-8}$
$2 \times 10^{-4}$	$5 \times 10^{-5}$	80	11.00	$1.00 \times 10^{-3}$
$2 \times 10^{-4}$	$1 \times 10^{-4}$	80	8.15	$1.42 \times 10^{-6}$
$2 \times 10^{-4}$	$2 \times 10^{-4}$	80	6.14	$1.38 \times 10^{-8}$
$3 \times 10^{-4}$	$1 \times 10^{-4}$	80	9.65	$4.46 \times 10^{-5}$
$3 \times 10^{-4}$	$2 \times 10^{-4}$	80	7.35	$2.24 \times 10^{-7}$

Note: The data listed in this table were determined according to the curves of recovery versus pH