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FLOTATION CHARACTERISTICS  
OF  
CERTAIN NATURAL MANGANESE OXIDES

by  
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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 conducted on several natural manganese oxides were used in conjunction with zero-point-of-charge determinations to determine the mechanism of collection for these minerals.

The experimental results indicate that several mechanisms are involved, i.e., coulombic attraction of the collector to the mineral surface, metal-ion activation, and chemisorption of a neutral molecule, e.g., oleic acid (aqueous) after hydroxylation of the surface.

## CONTENTS

	Page
Abstract.....	iii
Contents.....	iv
List of Figures .....	vi
List of Tables.....	ix
List of Appendices.....	x
Acknowledgments.....	xi
INTRODUCTION.....	1
MATERIALS and PROCEDURE. ....	4
Mineral Samples.....	4
Sample Preparation.....	5
Mineral Analysis.....	5
Water.....	6
Reagents.....	7
Micro-flotation Apparatus.....	7
Flotation Procedure.....	9
Zero-point-of-charge Determinations.....	10

Contents - (contd.)	Page
RESULTS.....	14
Flotation Results.....	14
Manganese Oxide (I).....	14
Manganese Oxide (II).....	16
Manganese Oxide (III).....	16
Activation Studies.....	25
Manganese Activation.....	25
Iron Activation.....	25
Calcium Activation.....	27
Zero-point-of-charge Determinations.....	27
Manganese Oxide (I).....	27
Manganese Oxide (II).....	27
Manganese Oxide (III).....	31
DISCUSSION OF RESULTS.....	33
CONCLUSIONS.....	41
APPENDIX.....	43
LITERATURE CITED.....	48

## LIST of FIGURES

Figure	Page
1. Schematic diagram of micro-flotation apparatus..	8
2. Schematic diagram of coagulation cell.....	11
3. Portion of a typical coagulation chart used in determination of zero-point-of-charge.....	13
4. Flotation recovery of $MnO_2(I)$ as a function of flotation pH. $7.4 \times 10^{-5}$ mole liter sulfonate, $23^\circ C$ $1.0 \times 10^{-4}$ mole per liter amine, $23^\circ C$ .....	15
5. Flotation recovery of $MnO_2(I)$ as a function of flotation pH, $1 \times 10^{-4}$ mole per liter oleate, $23^\circ C$ $1 \times 10^{-4}$ mole per liter oleate, $61^\circ C$ .....	17
6. Flotation recovery of $MnO_2(II)$ as a function of flotation pH. $1 \times 10^{-4}$ mole per liter sulfonate, $23^\circ C$ $1 \times 10^{-4}$ mole per liter amine, $23^\circ C$ .....	18
7. Flotation recovery of $MnO_2(II)$ as a function of flotation pH. $1 \times 10^{-4}$ mole per liter sulfonate, $61^\circ C$ $5 \times 10^{-4}$ mole per liter sulfonate, $63^\circ C$ ....	19

## List of Figures -(Cont'd)

Figure	Page
8. Flotation recovery of $MnO_2$ (II) as a function of flotation pH. 1 x 10 <sup>-4</sup> mole per liter oleate, 23°C.....	20
9. Flotation recovery of $MnO_2$ (III) as a function of flotation pH. 1 x 10 <sup>-4</sup> mole per liter sulfonate, 23°C... 1 x 10 <sup>-4</sup> mole per liter amine, 23°C.....	22
10. Flotation recovery of $MnO_2$ (III), as a function of flotation pH. 5 x 10 <sup>-4</sup> mole per liter sulfonate, 60°C 5 x 10 <sup>-4</sup> mole per liter sulfonate, 23°C 1 x 10 <sup>-4</sup> mole per liter sulfonate, 64°C 1 x 10 <sup>-4</sup> mole per liter amine, 60°C.....	23
11. Flotation recovery of $MnO_2$ (III) as a function of flotation pH. 1 x 10 <sup>-4</sup> mole per liter oleate, 23°C 1 x 10 <sup>-4</sup> mole per liter oleate, 60°C 1 x 10 <sup>-4</sup> mole per liter oleate, $Mn^{++}$ ; 23°C.	24
12. Flotation recovery of $MnO_2$ (II) as a function of flotation pH for a sulfonate addition of 1 x 10 <sup>-4</sup> mole per liter. 1 x 10 <sup>-4</sup> mole per liter $Mn^{++}$ .....	26
13. Flotation recovery of $MnO_2$ (II) as a function of flotation pH for a sulfonate addition of 1 x 10 <sup>-4</sup> mole per liter. 1 x 10 <sup>-4</sup> mole per liter $Fe^{+++}$ .....	28
14. Flotation recovery of $MnO_2$ (II) as a function of flotation pH for a sulfonate addition of 1 x 10 <sup>-4</sup> mole per liter. 1 x 10 <sup>-3</sup> mole per liter $Ca^{++}$ 1 x 10 <sup>-4</sup> mole per liter $Ca^{++}$ 1 x 10 <sup>-5</sup> mole per liter $Ca^{++}$ .....	29

## List of Figures - (Contd.)

Figure		Page
15.	Relative percent transmittance as a function of pH for $\text{MnO}_2(\text{I})$ and $\text{MnO}_2(\text{II})$ .....	30
16.	Relative percent transmittance as a function of pH for $\text{MnO}_2(\text{III})$ .....	32
17.	Proposed neutral molecule adsorption of oleic acid onto a manganese oxide surface..	37

LIST of TABLES

Table	Page
1. Concentration of various manganous ion species as a function of pH for a nominal addition of $1 \times 10^{-3}$ mole per liter manganous chloride to water.....	36

## LIST of APPENDICES

Appendix		Page
PART 1.	Experimental x-ray diffraction data	
	Manganese Oxide(I).....	44
	Manganese Oxide(II).....	44
	Manganese Oxide(III).....	45
PART 2.	A.S.T.M. card file reference data	
	Pyrolusite ( $\text{MnO}_2$ ).....	46
	Ramsdellite ( $\text{MnO}_2$ ).....	46
	Manganite ( $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ).....	47
	Alpha Quartz ( $\text{SiO}_2$ ).....	47

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## INTRODUCTION

Manganese, an element of strategic importance and twelfth most abundant element in the earth's crust, is found in relatively few high-grade ore deposits. Although the United States contains over 3,500 million tons of ore, over 90 percent of the domestic consumption is imported<sup>(1)</sup>. The bulk of the domestic supply comes from Butte, Montana, and the manganese occurs in the form of manganese carbonate<sup>(1)</sup>.

The domestic ores, however, occur much more abundantly in the form of oxides, among which are: pyrolusite, manganite, braunite, ramsdellite, hausmanite, and psilomelane. Pyrolusite,  $MnO_2$ , one of the most common manganese oxides, is a secondary mineral which forms in the highly oxidized zone of the ore body. It is often associated with other manganese oxides and with iron oxides such as hematite,  $Fe_2O_3$ , and limonite,  $Fe_2O_3 \cdot H_2O$ .

Froth flotation has been used for the recovery of manganese at many places with varying degrees of success. Many

studies have been conducted on practical separations of  $MnO_2$  from ore; some of these can be found in the following references (2,3,4,5).

Theoretical consideration of the collector-adsorption mechanisms involved in the flotation of manganese oxide has received little attention. Previous studies of collector adsorption on various metal oxides, though, have been presented in the case of alumina, hematite, rutile, cuprite, and zinc oxide. D. W. Fuerstenau and Modi<sup>(6)</sup> have shown that dodecyl sulfate, dodecylamine, and sodium laurate are adsorbed on corundum by coulombic attraction between the surface and collector ion.

Iwasaki, Cooke, and Choi<sup>(7)</sup> found that electrical phenomena are important when collectors of shorter chain length such as dodecyl sulfate and dodecylamine are used to float iron oxide. When the 18-carbon homologs of these collectors are used, neither surface charge nor sign of the collector ion assumes any significance in the system. They also demonstrated that fatty acids will float hematite at pH values much above the zero-point-of-charge (zpc).

Purcell and Sun<sup>(8)</sup> have shown that similar phenomena are also involved when rutile is floated with high molecular weight fatty acids. They found, however, that flotation could not be effected above the zpc with low additions of collector.

In a study with zinc oxide, Mular<sup>(9)</sup> has suggested that the flotation characteristics of this material with sodium oleate may be determined by surface charge.

M. C. Fuerstenau and R. S. Rickard<sup>(10)</sup> have found with infrared absorption techniques that both oleate and a high molecular weight sulfonate chemisorb on cuprite.

In an adsorption kinetics study, Marchandise<sup>(11)</sup> showed that cryptomelane ( $\text{KMn}_8\text{O}_{12}$ ) is floated over a narrow pH range (pH 5 to 6) with oleic acid. This study appears to be one of the few more theoretical treatments of manganese oxide flotation.

At the present time, there is little understanding of the mechanisms involved in collector adsorption in  $\text{MnO}_2$  systems. The purpose of this thesis is to obtain this information as well as to study the response of certain manganese oxides to flotation with high molecular weight collectors. Furthermore, the role of chemisorbed hydroxyl in oxide systems can be examined readily with  $\text{MnO}_2$  as opposed to those systems described previously. This fact is due to the narrow region in pH in which  $\text{Mn}^{++}$  ion hydrolyzes to  $\text{MnOH}^+$ .

## MATERIALS and PROCEDURE

The following experimental materials and methods were used in this investigation.

### Mineral Samples

The three different samples of natural manganese oxides chosen for this investigation are as follows:

(1) Manganese Oxide (I): a very pure pyrolusite, polianite, was purchased from a mineral supply. This highly crystalline sample was from Montana.

(2) Manganese Oxide (II): This pyrolusite sample, also from Montana, was essentially polianite, but contained some manganite.

(3) Manganese Oxide (III): This sample was essentially polianite, but contained some ramsdellite. The mineral was hand-picked from the Lake Valley mining district in New Mexico.

### Sample Preparation

Each of the above minerals was crushed to -6 mesh and hand-picked to remove as much of the gangue constituents as possible. They were then reduced to 100 x 200 mesh in a porcelain mortar. Because of the lack of sufficient manganese oxide (I), the 200 x 270-mesh fraction was used in some of the flotation work. These sized materials were cleaned magnetically, and samples were split for use in flotation and zero-point-of-charge studies and for chemical and x-ray analysis.

### Mineral Analysis

X-ray studies were twofold in character; both x-ray diffraction and fluorescent analyses were made. A Norelco diffractometer, with a copper target x-ray tube with a nickel filter, was operated at 50 kv and 30 ma. Scanning was done between  $2\theta = 12$  and 100 degrees. The powder data were compared with data in the A.S.T.M. Powder Data File to determine the crystalline constituents present in each mineral sample<sup>(12)</sup>.

Qualitative fluorescent x-ray analysis was undertaken to determine some of the major impurities present, as quantitative chemical analysis was thought to be unnecessary. Although the analytical limitations of this method are recognized, the more common elements such as calcium, barium, iron, zinc, silver, and lead are within the capabilities of the instrument.

The Norelco fluorescence unit was equipped with a tungsten tube which was operated at 50 kv and 30 ma. A NaCl crystal was used, and the scanning range was between  $2\theta = 10$  and 100 degrees. X-ray fluorescent spectrometer conversion tables were used to identify the elements present in the mineral samples<sup>(13)</sup>.

X-ray diffraction and fluorescent analysis showed the following crystalline components and impurities to be present in each of the minerals. (See appendix).

Manganese Oxide (I)-----Pyrolusite only.

Manganese Oxide (II)-----Pyrolusite and manganite.

Manganese Oxide (III)-----Pyrolusite and ramsdellite  
with a trace of quartz.  
Zinc and iron were present as impurities.

Chemical analysis was made only on the mineral sample that was shown by fluorescent analysis to contain impurities. Manganese oxides (I) and (II) were fine mineral specimens, highly crystallized, and showed no impurities upon fluorescent analysis. Analysis of manganese oxide (III), which was done by a private organization, showed zinc and iron to be present in the amounts of 0.21 and 4.32 percent, respectively.

### Water

Conductivity water, made by passing distilled water through a dual resin ion-exchange column, was used in all of the experimental work.

## Reagents

Sodium alkyl aryl sulfonate was supplied through the courtesy of Shell Oil Company<sup>(14)</sup>. This reagent had the following physical properties: sulfonate content 95 to 97 percent by weight; molecular weight 450 to 470; total carbon-atom content 25 to 27 atoms. The reagent is approximately 50 percent benzyl and 50 percent naphthyl sulfonate with side chains.

Pure dodecyl amine was supplied through the courtesy of Armour Chemical Company.

High purity potassium oleate was prepared from chemically pure oleic acid.

Metal ions used in the activation studies were added as the chemically pure chloride salts.

## Micro-flotation Apparatus

A standard micro-flotation apparatus used in all of the flotation experiments<sup>(15)</sup> allowed for a constant volume of purified nitrogen under a nearly constant pressure head of three feet of water to be passed through a micro-flotation cell. The utility of this type of flotation cell is found in its ability to float small charges of pure mineral in a system free of metallic components. A schematic diagram of this apparatus is shown in Figure 1.

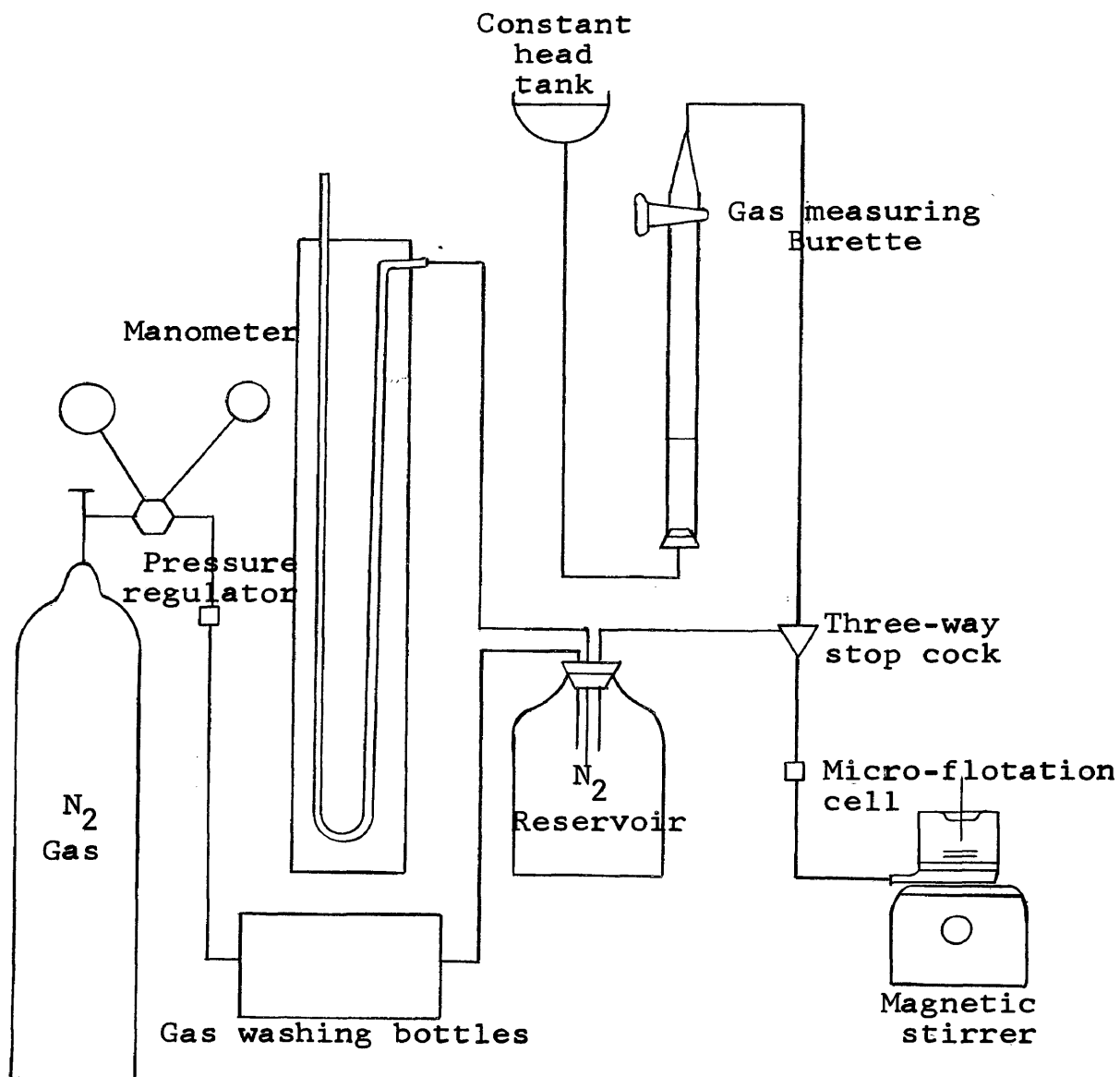


Figure 1. Schematic Diagram of Micro-flotation Apparatus.

### Flotation Procedure

Flotation experiments were conducted at ambient and elevated temperatures as follows:

1) A predetermined volume of conductivity water was combined with a given volume of solution containing the activating metal ion (if any).

2) A given volume of collector was added so that the total final volume was 150 cc.

3) The pH was adjusted to a predetermined value with KOH or HCl.

4) The solution was heated to the desired temperature (when elevated temperature was involved).

5) Two drops of a solution containing 1 part of n-amyl alcohol to 20 parts of water by volume were added as frother.

6) To the solution, 2.50 grams of mineral were added, and the pulp was conditioned for three minutes.

7) The pH of the pulp was measured, termed flotation pH.

8) The temperature of the pulp was measured, termed flotation temperature.

9) A volume of 100 cc of purified nitrogen was passed through the pulp for one minute, during which time the froth was collected.

10) The final pH and temperature were recorded to check against any excessive change in pH or temperature.

### Zero-Point-of-Charge Determinations

The zero-points-of-charge for the minerals were determined by a coagulation method, and the readers are referred to the article by D. W. Fuerstenau and Yopps<sup>(16)</sup>, which shows the excellent agreement between zero-points-of-charge determined with coagulation and those determined with electrophoretic techniques. Since pH is potential determining for oxides, the maximum degree of flocculation occurs at the zero-point-of-charge, where statistically half of the suspended material is negatively charged, and half is positively charged.

The transmission of light through a settling pulp of the finely divided minerals was followed with a chart recorder as a function of time. As the zero-point-of-charge of the mineral was approached, the subsequent flocculation and, hence, more rapid settling of particles allowed a greater percentage of light to be transmitted after a specified interval of time. A schematic diagram of this apparatus is shown in Figure 2.

When percent of transmittance (in arbitrary units) was charted after a given interval of time as a function of pH, the zero-point-of-charge could be determined as that pH at which maximum light transmittance was observed.

The procedure for the zero-point-of-charge determinations was as follows:

- 1) The mineral was ground to a fine powder for four hours in an automatic mullite mortar.

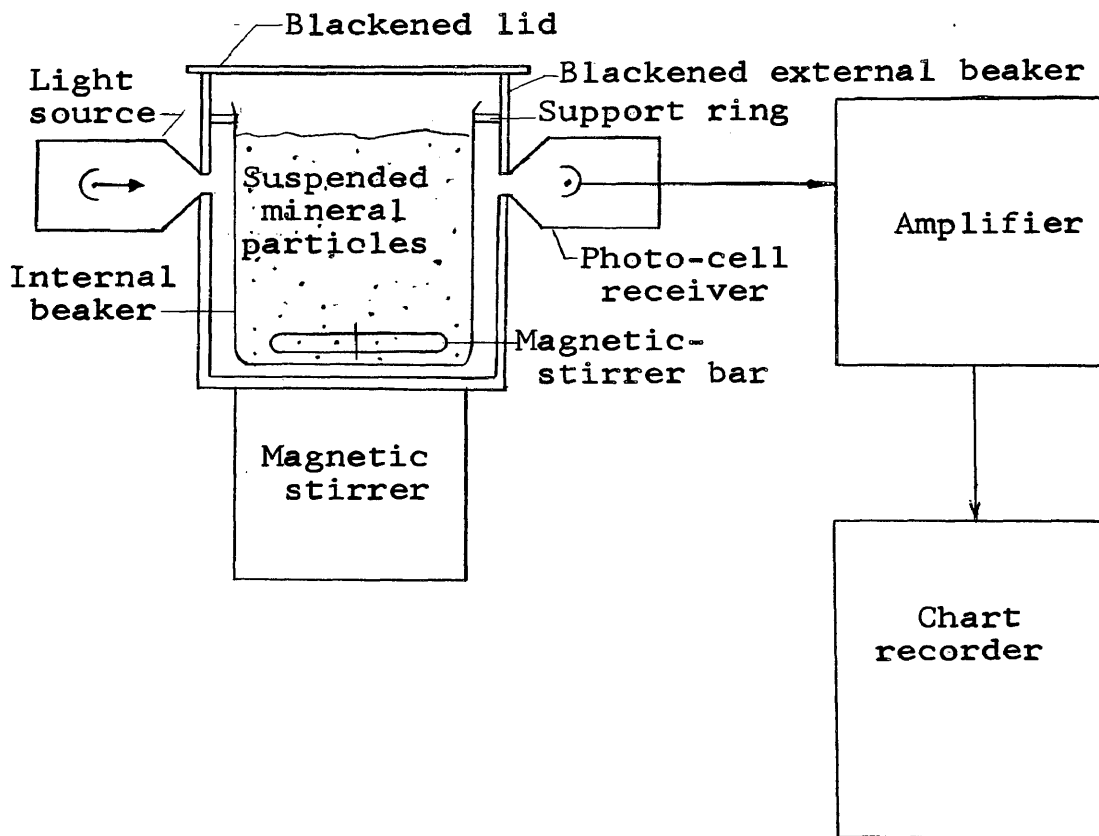


Figure 2. Schematic Diagram of Coagulation Cell.

2) Five grams of this powder was agitated in 150 cc of conductivity water for five minutes at the desired pH.

3) Agitation was stopped, and the rate of flocculation and sedimentation was followed with the chart recorder. A typical chart is shown in Figure 3.

4) The pH was measured after the recording of the settling rate to ensure that no significant change in pH had occurred during the run.

5) After recordings had been made at all desired values of pH, the shortest interval of time required to reach 50 percent transmittance (arbitrary units) was taken as the time interval for that particular zero-point-of-charge determination.

6) The relative percent transmittance for the chosen interval of time was then charted as a function of the experimental pH.

7) The pH of maximum transmittance, representing maximum flocculation and rate of settling, was taken as the zero-point-of-charge for the mineral.

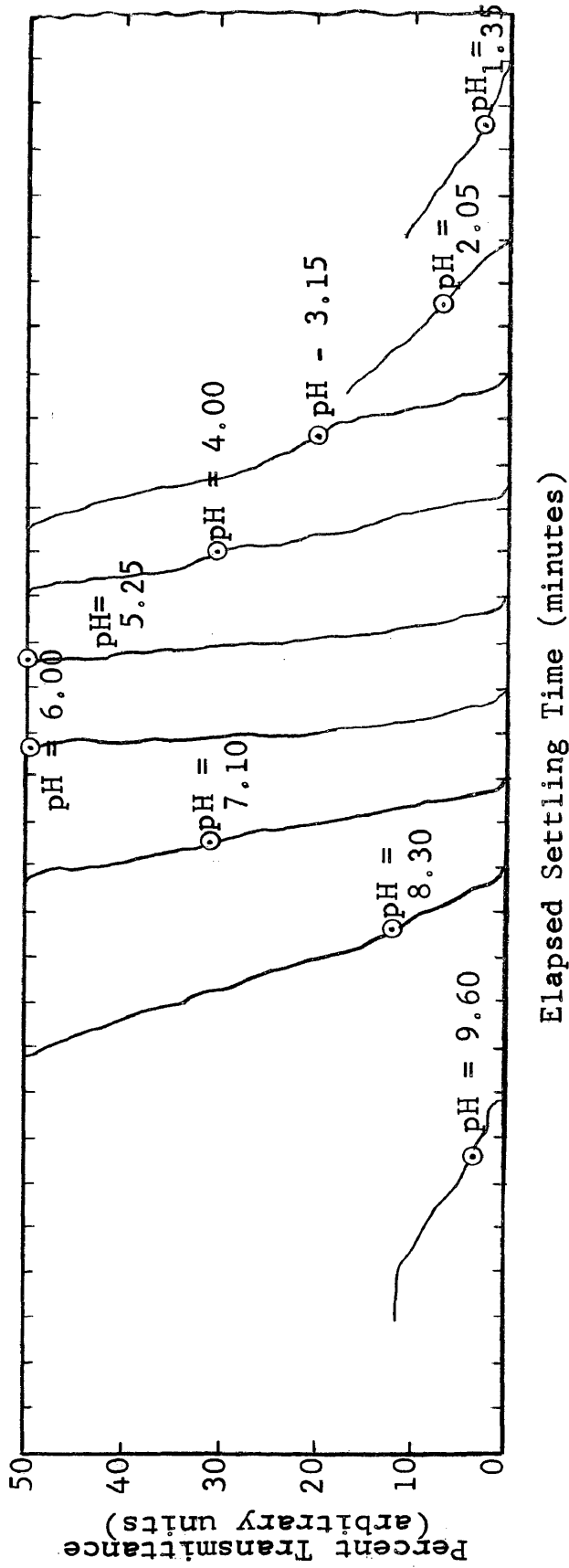


Figure 3. Portion of a Typical Coagulation Chart Used in Determination of Zero-Point-of-Charge.

## RESULTS

The experimental work has been divided into three main categories: flotation studies involving sulfonate, amine, and oleate as collector; metal-ion activation studies using sulfonate collector; and zero-point-of-charge determinations.

### Flotation Results

Flotation studies were conducted with each of the three mineral samples. Most of the experiments were conducted at room temperature, but several of them were carried out at about 60°C to establish whether one of the hypotheses made in this thesis is correct or not.

Manganese Oxide (I): When manganese oxide (I) was floated with  $7.4 \times 10^{-5}$  mole per liter sulfonate,  $\text{RSO}_3^-$ , good flotation was obtained from pH 1 to 8 (Figure 4). System depression was noted at pH 10. Figure 4 also shows data determined with  $1 \times 10^{-4}$  mole per liter dodecylamine,  $\text{RNH}_3^+$ , where maximal recovery was obtained at pH 11.5.

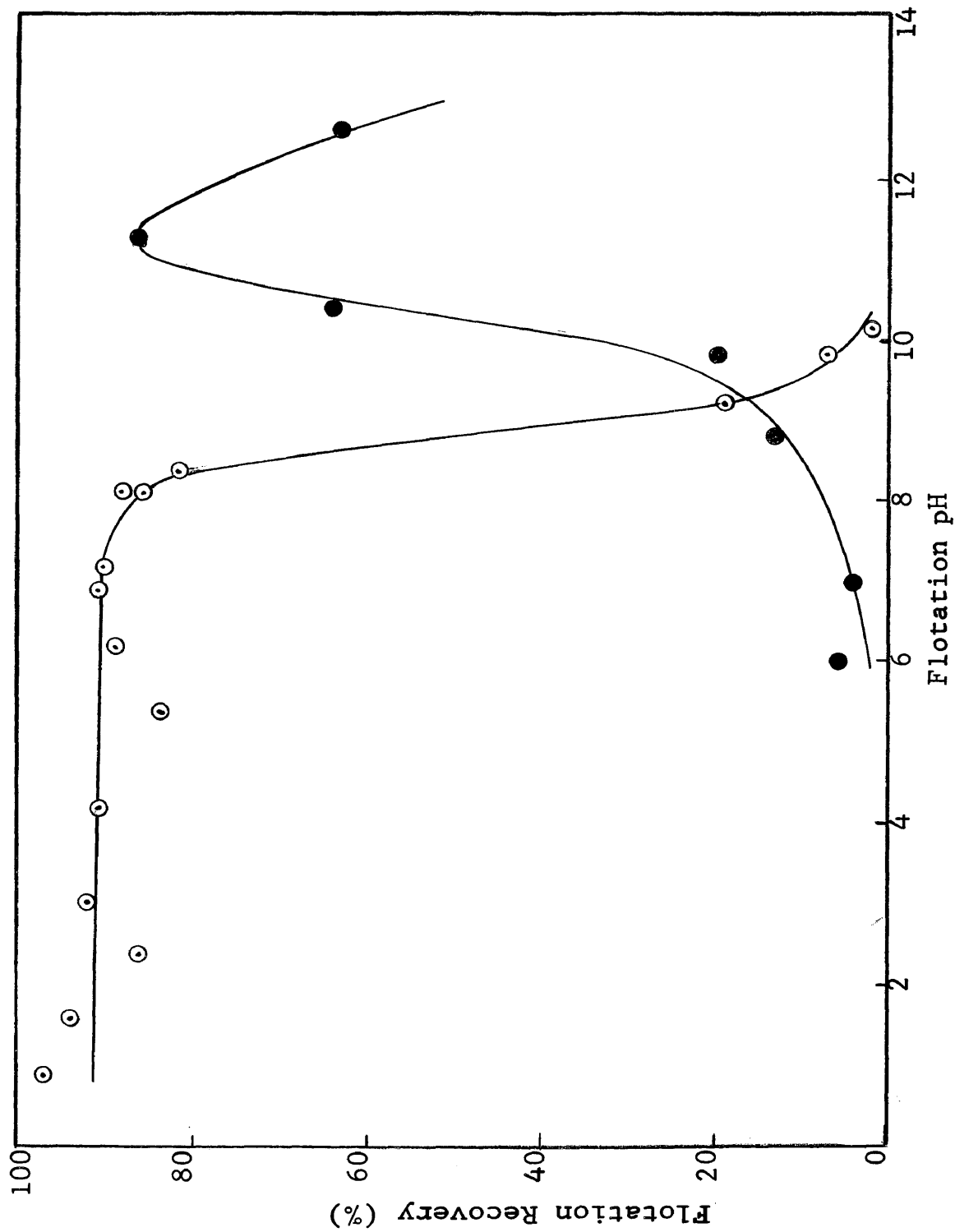


Figure 4. Flotation Recovery of  $\text{MnO}_2(\text{I})$  as a Function of Flotation pH  
 $\circ 7.4 \times 10^{-5} \text{ M RSO}_3^-$ ,  $23^\circ\text{C}$ .       $\bullet 1 \times 10^{-4} \text{ M RNH}_2$ ,  $23^\circ\text{C}$ .

The use of potassium oleate, K01, as collector at ambient and elevated temperatures revealed a number of interesting phenomena (Figure 5). First, good flotation was achieved only from pH 4 to 7 at ambient temperature. When the pulp temperature was increased to 61°C, essentially complete flotation was obtained at pH 8.5, as compared with a recovery of 7 percent that was obtained at this pH at ambient temperature.

Manganese Oxide (II): Figures 6, 7, and 8 show data determined for manganese oxide (II) with the same three collectors. As observed with manganese oxide (I), the pH range in which a favorable flotation response was obtained with sulfonate is the same range in which essentially no flotation was possible with dodecylamine and vice versa. Increasing the temperature to 61°C, at  $1 \times 10^{-4}$  mole per liter sulfonate, had little effect on flotation recovery. When the sulfonate addition was increased five-fold, maximal recovery was increased, but flotation recovery decreased markedly above pH 7.5 (Figure 7).

When potassium oleate was used as collector, two pH ranges were noted in which a favorable flotation response was obtained (Figure 8). Contrasted to manganese oxide (I), essentially complete flotation was obtained at pH 8.5 at ambient temperature.

Manganese Oxide (III): A third manganese oxide was floated under similar conditions, and the same phenomena observed with oxides (I) and (II) were observed for oxide (III),

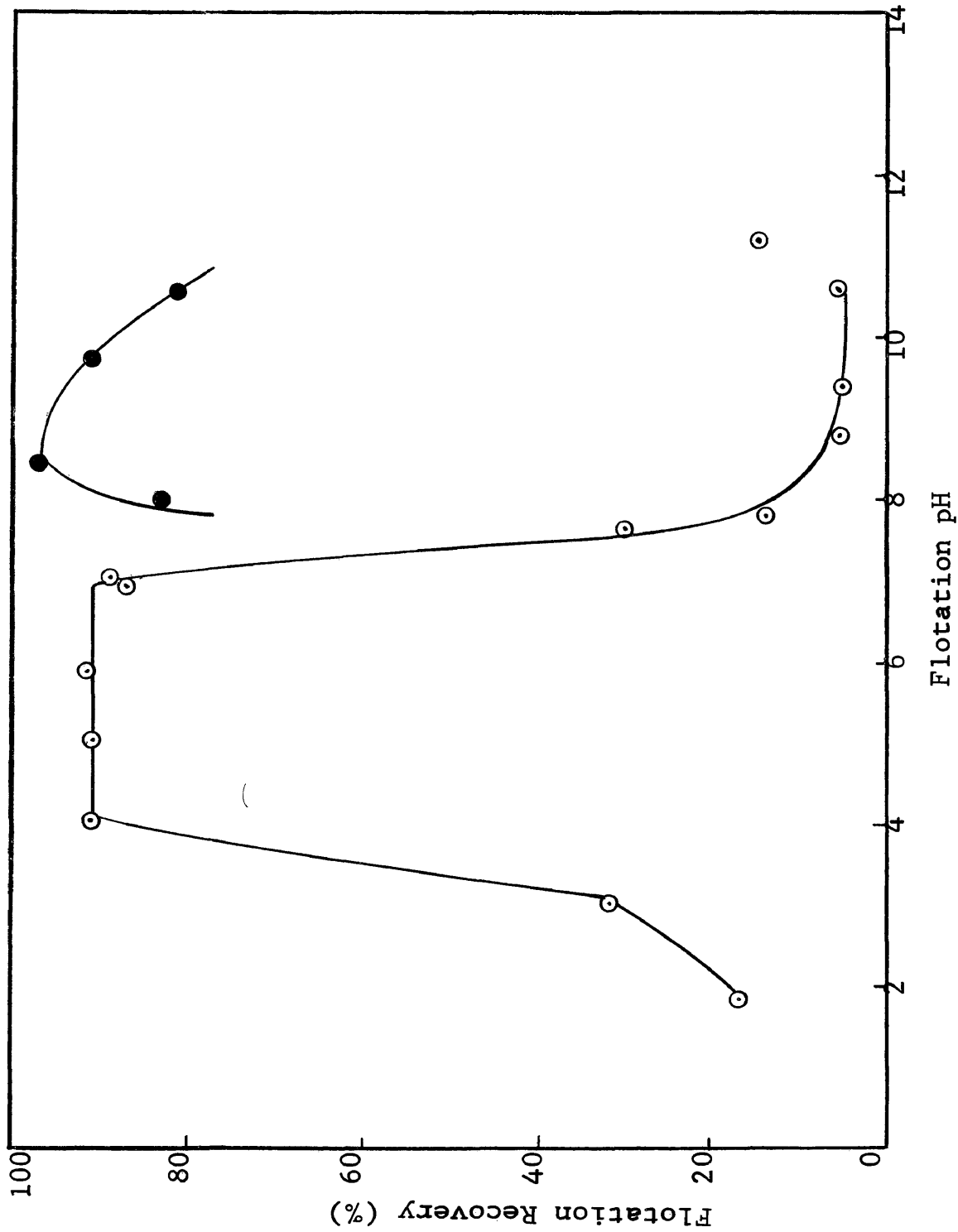
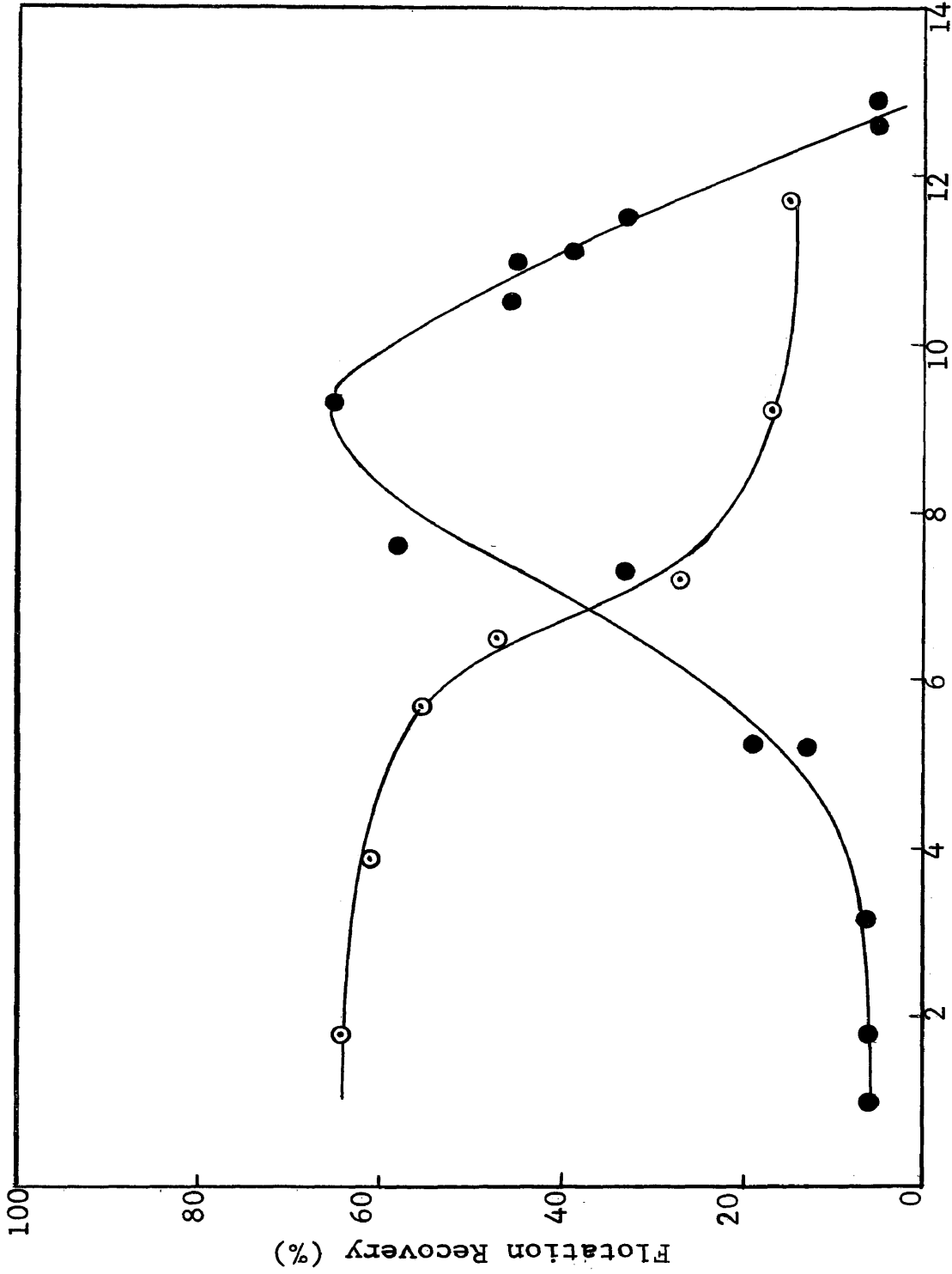


Figure 5. Flotation Recovery of  $MnO_2(I)$  as a Function of Flotation pH  
⊙  $1 \times 10^{-4}$  M KOL, 23°C      ●  $1 \times 10^{-4}$  M KOL, 61°C



Flotation pH  
Figure 6. Flotation Recovery of  $\text{MnO}_2(\text{II})$  as a Function of Flotation pH  
 $\odot 1 \times 10^{-4} \text{ M RSO}_3^-$ ,  $23^\circ\text{C}$        $\bullet 1 \times 10^{-4} \text{ M RNH}_2^-$ ,  $23^\circ\text{C}$

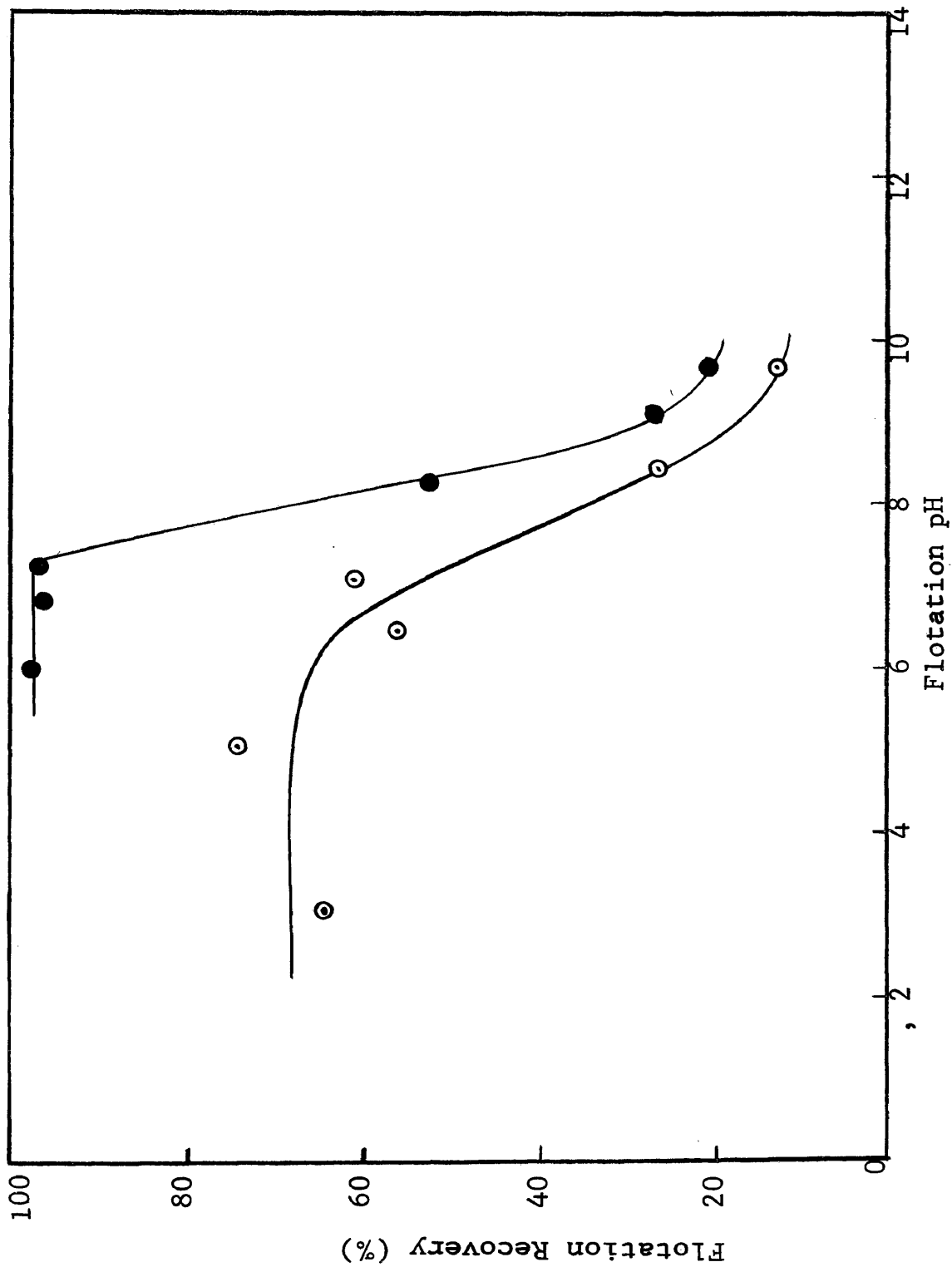


Figure 7. Flotation Recovery of  $MnO_2(II)$  as a Function of Flotation pH  
 O  $1 \times 10^{-4} M RSO_3^-$ ,  $61^\circ C$       ●  $5 \times 10^{-4} M RSO_3^-$ ,  $63^\circ C$

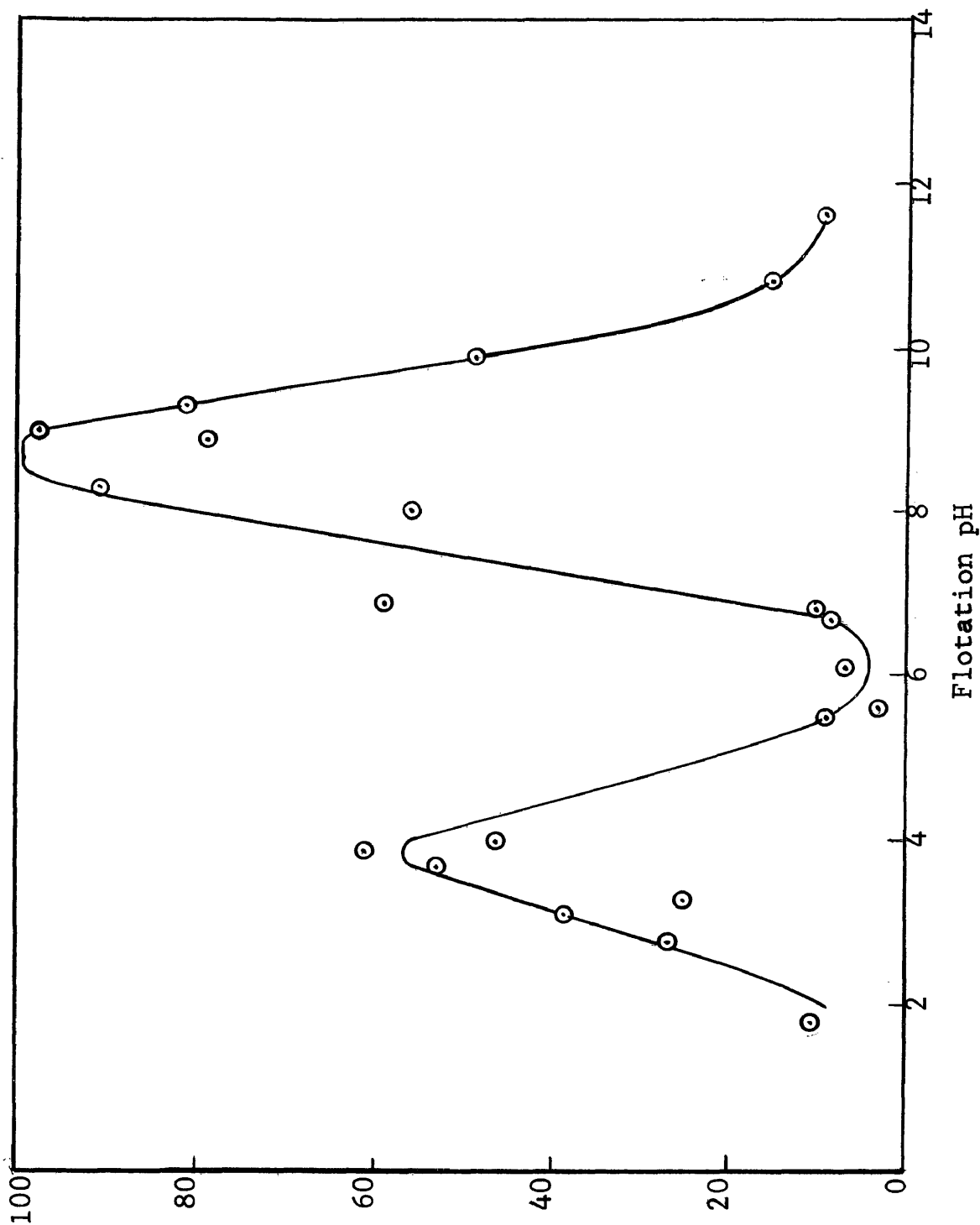


Figure 8. Flotation Recovery of  $MnO_2(II)$  as a Function of Flotation pH.  
 $\odot 1 \times 10^{-4}$  KOI,  $23^\circ C$ .

i.e., the mineral responded to amine flotation in the region where there was essentially no response to sulfonate flotation, and vice versa (Figure 9).

The anomaly in the recovery curve for amine at pH 10 is as yet unexplained (Figure 9). In this region the froth became unstable, and although the mineral particles appeared to respond to the collector, the unstable froth prevented a higher recovery. The recovery curve was thus drawn as a broken line through this region.

Figure 10 shows that a temperature increase to about 60°C at  $1 \times 10^{-4}$  mole per liter sulfonate addition had little effect on the flotation response in the pH range of 8 to 10, while the flotation recovery was shifted about one pH unit to the right with the amine present. Also, an increase in sulfonate addition to  $5 \times 10^{-4}$  mole per liter at ambient temperature produced no change in recovery at pH 9. At elevated temperature and increased sulfonate addition, however, essentially complete flotation was effected at pH 7, and good response was obtained till pH 9. Above pH 10, at this temperature and concentration, recovery was negligible.

Figure 11 shows data determined with potassium oleate, and it can be noted that a recovery of about 40 percent was obtained at pH 10 at ambient temperature. When the temperature was increased to 60°C, essentially complete flotation was obtained at pH 8.7 at the same level of collector addition.

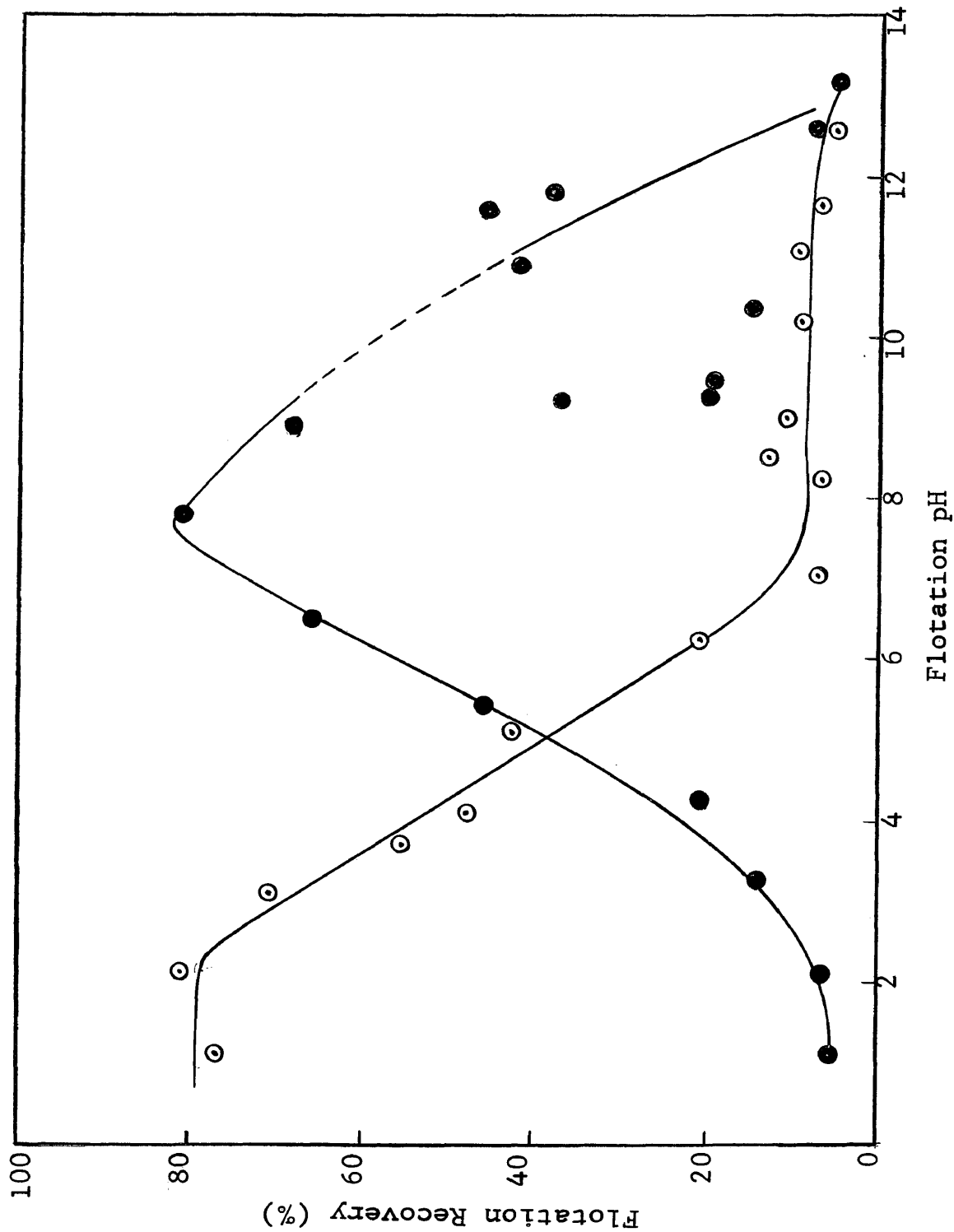


Figure 9. Flotation Recovery of  $\text{MnO}_2(\text{III})$  as a Function of Flotation pH.  
 ○  $1 \times 10^{-4} \text{ M RSO}_3^-$ ,  $23^\circ\text{C}$ .      ●  $1 \times 10^{-4} \text{ M RNH}_2$ ,  $23^\circ\text{C}$ .

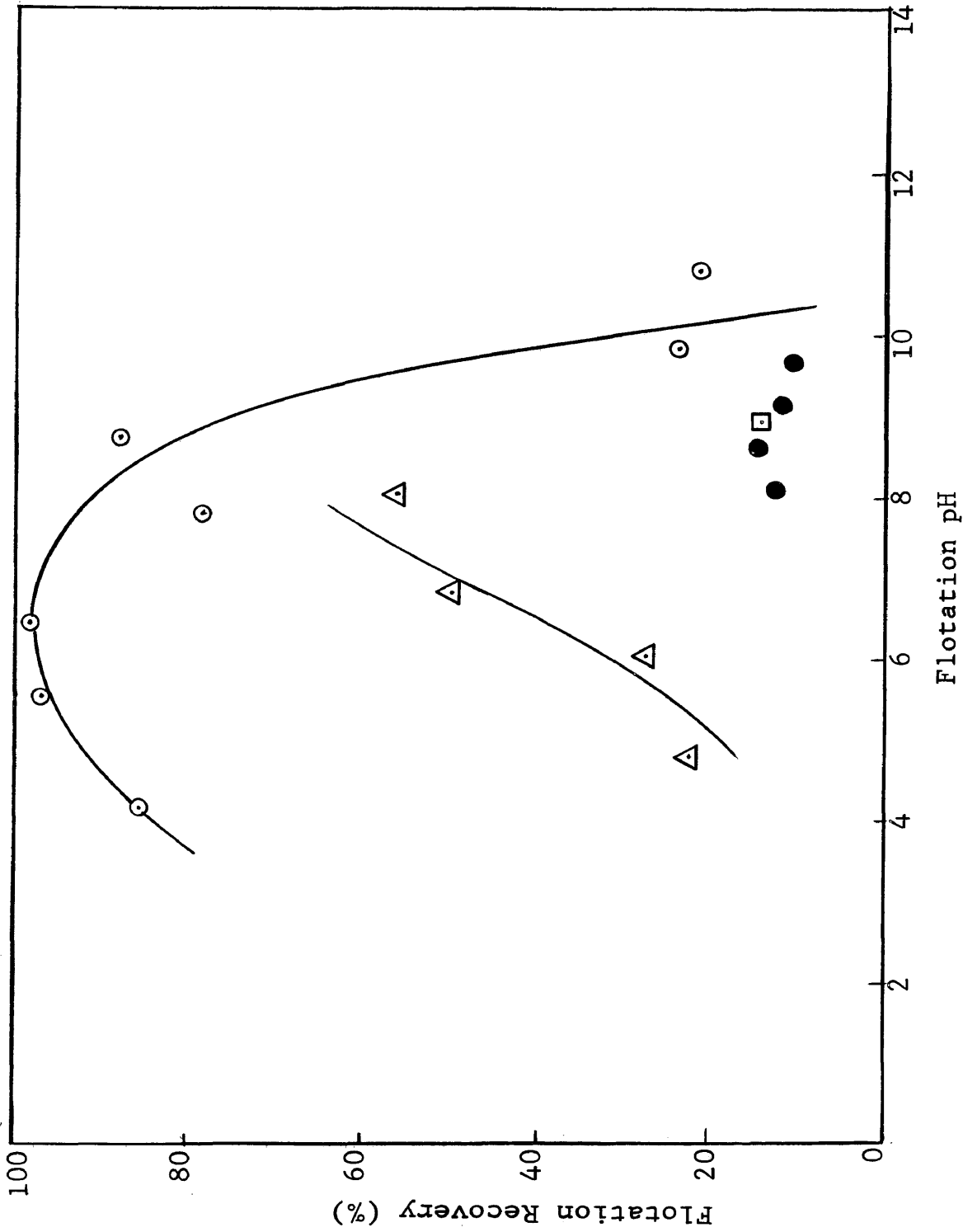


Figure 10. Flotation Recovery of  $\text{MnO}_2(\text{III})$  as a Function of Flotation pH

- $5 \times 10^{-4} \text{ M RSO}_3^-$ ,  $60^\circ\text{C}$
- $5 \times 10^{-4} \text{ M RSO}_3^-$ ,  $23^\circ\text{C}$
- $1 \times 10^{-4} \text{ M RSO}_3^-$ ,  $64^\circ\text{C}$ .
- △  $1 \times 10^{-4} \text{ M RNH}_2$ ,  $60^\circ\text{C}$ .

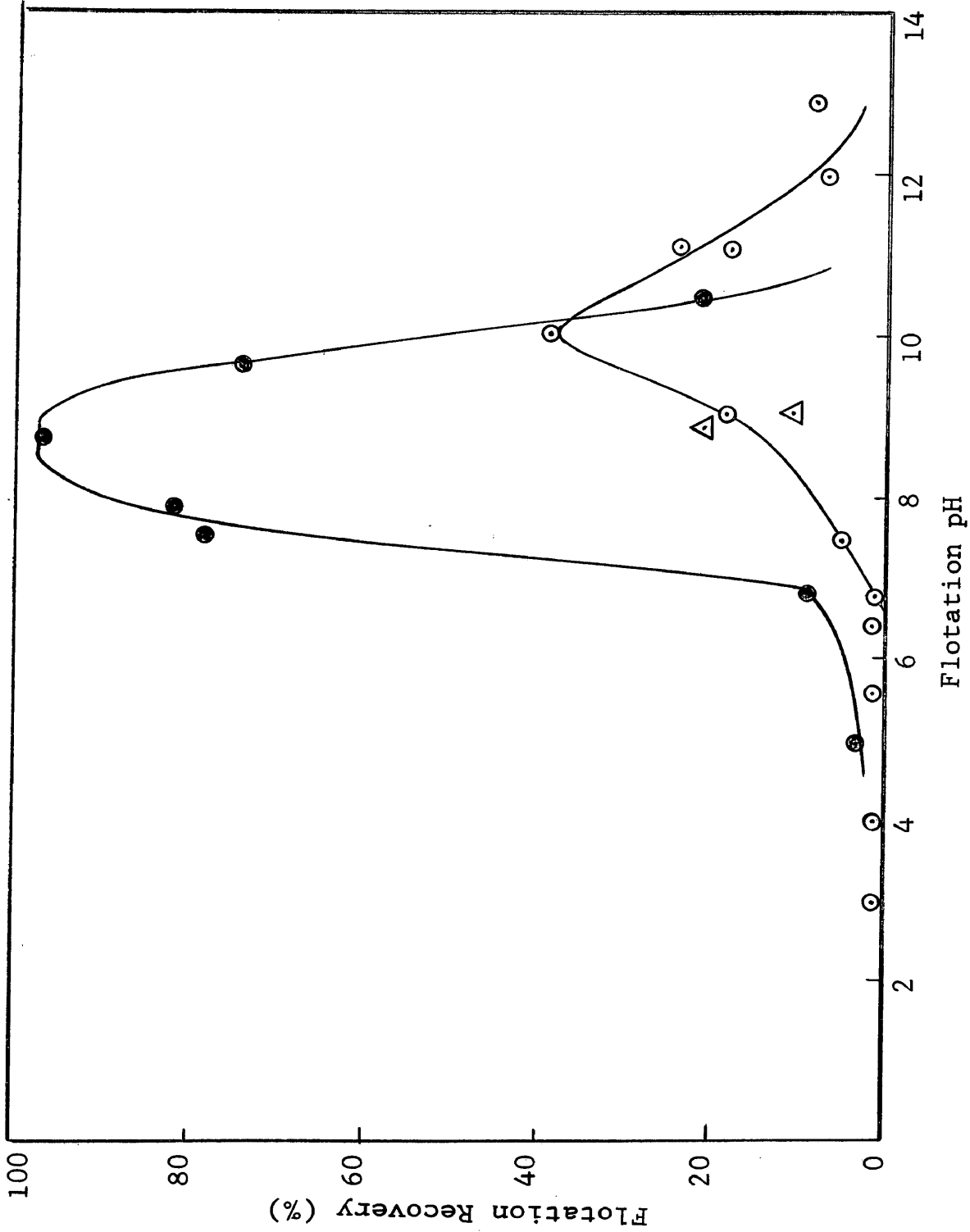


Figure 11. Flotation Recovery of MnO<sub>2</sub>(III) as a Function of Flotation pH

○ 1 x 10<sup>-4</sup> M KOL, 23°C      ● 1 x 10<sup>-4</sup> M KOL, 60°C

△ 1 x 10<sup>-4</sup> M KOL, 23°C; 1 x 10<sup>-4</sup> M Mn<sup>++</sup>

Two flotation experiments were run at pH 9 with the same collector addition of  $1 \times 10^{-4}$  mole per liter oleate and with  $1 \times 10^{-4}$  mole per liter manganous ion as an activator. The experiments, conducted at ambient temperature, showed about the same flotation response as with the metal ion absent, other parameters being the same. (Figure 11).

### Activation Studies

Conditions for activation were conducted on rather pure manganese oxide (II) to determine the effect that some of the more common cations might have upon flotation results. The metal salts used in this study were those of  $Mn^{++}$ ,  $Fe^{+++}$ , and  $Ca^{++}$ . The collector addition used in all of the activation studies was  $1 \times 10^{-4}$  mole per liter sulfonate.

Manganese Activation: When  $1 \times 10^{-4}$  mole per liter  $Mn^{++}$  was added to the flotation system, the response obtained under these conditions was similar to that obtained in the absence of added  $Mn^{++}$  ion. A maximal recovery of 68 percent was obtained from pH 1 to pH 5.5. Above pH 5.5, recovery fell off slowly to about 20 percent at pH 9.5 (Figure 12).

Iron Activation: Ferric ion was also added to these systems and markedly changed the flotation characteristics of manganese oxide. Flotation response was 70 percent at pH 2 but dropped rapidly to zero between pH 2.3 and 3.5. From pH 3.5 to 4.5, recovery was nil. Increasing the pH from 4.5 to 7.0 increased the recovery to 19 percent. Above this pH,

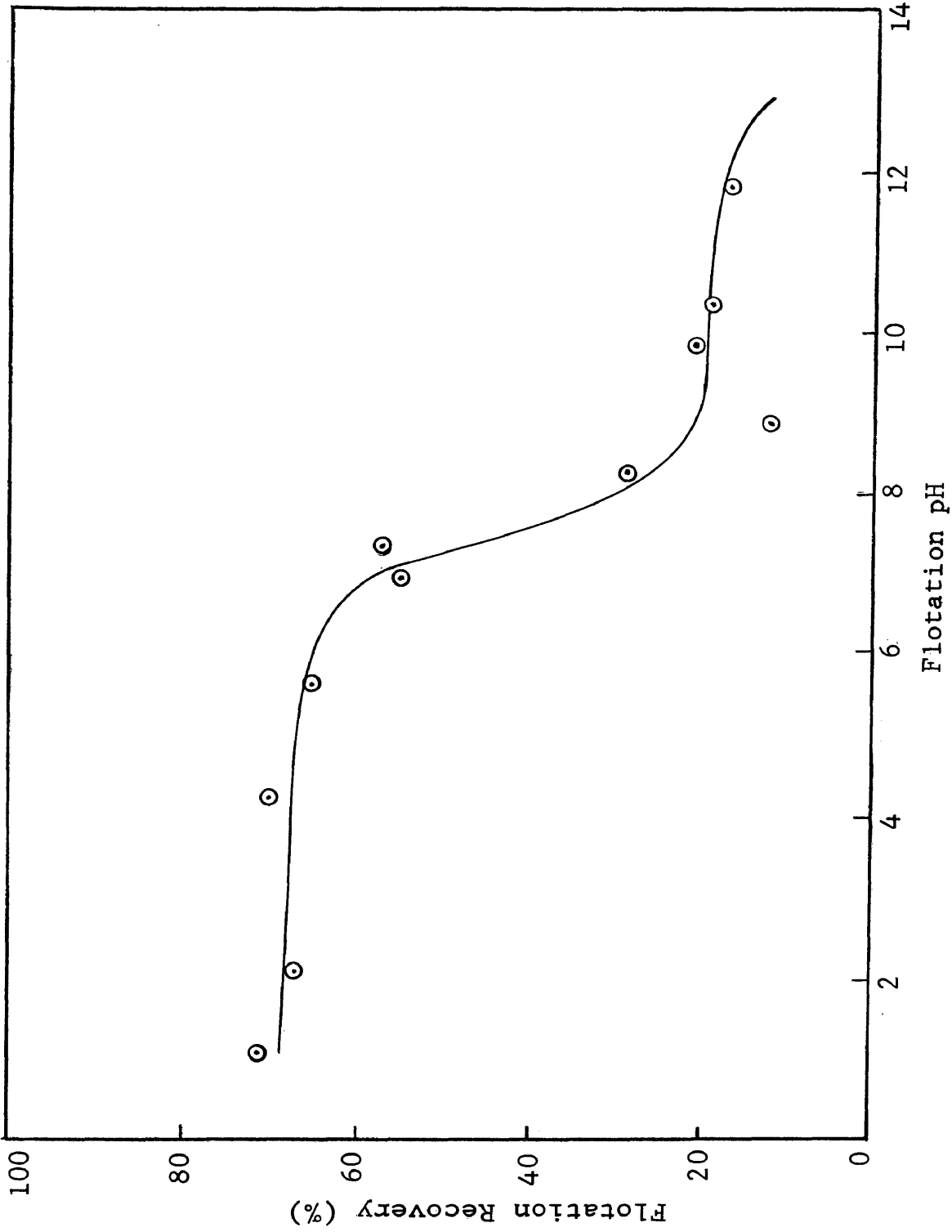


Figure 12. Flotation Recovery of  $MnO_2$  (II) as a Function of Flotation pH for a Sulfonate Addition of  $1 \times 10^{-4}$  Mole per Liter.

⊙  $1 \times 10^{-4}$  M  $Mn^{++}$

recovery again diminished (Figure 13).

Calcium Activation: Calcium activation was studied at three different levels of addition, i.e., at  $1 \times 10^{-3}$ ,  $1 \times 10^{-4}$ , and  $1 \times 10^{-5}$  molar. (Figure 14).

When  $1 \times 10^{-3}$  mole per liter calcium was added to the system, recovery was about 70 percent below pH 4.5. From pH 4.5 to 8.0, recovery declined to a minimal value of 9 percent at pH 8.0. Above this pH recovery increased and was 38 percent at pH 10.6 and 60 percent at pH 12.1.

An addition of  $1 \times 10^{-4}$  molar  $\text{Ca}^{++}$  exhibited no effect on flotation response below pH 8. Flotation response was enhanced above this pH, and recoveries of 30 to 50 percent were obtained at pH 10.1 and 12.9, respectively.

#### Zero-Point-of-Charge Determinations

Zero-point-of-charge determinations were made with each of the samples used in the investigation. In this study the relative amount of light transmittance after a specified time interval is charted as a function of pH.

Manganese Oxide (I): Figure 15 shows the percentage transmittance after 1.6 minutes for manganese oxide (I). Transmittance was 50 percent between pH 7.0 and 8.0 and declined rapidly on both sides of this range.

Manganese Oxide (II): Figure 15 also shows these data for manganese oxide (II). The percent transmittance after a

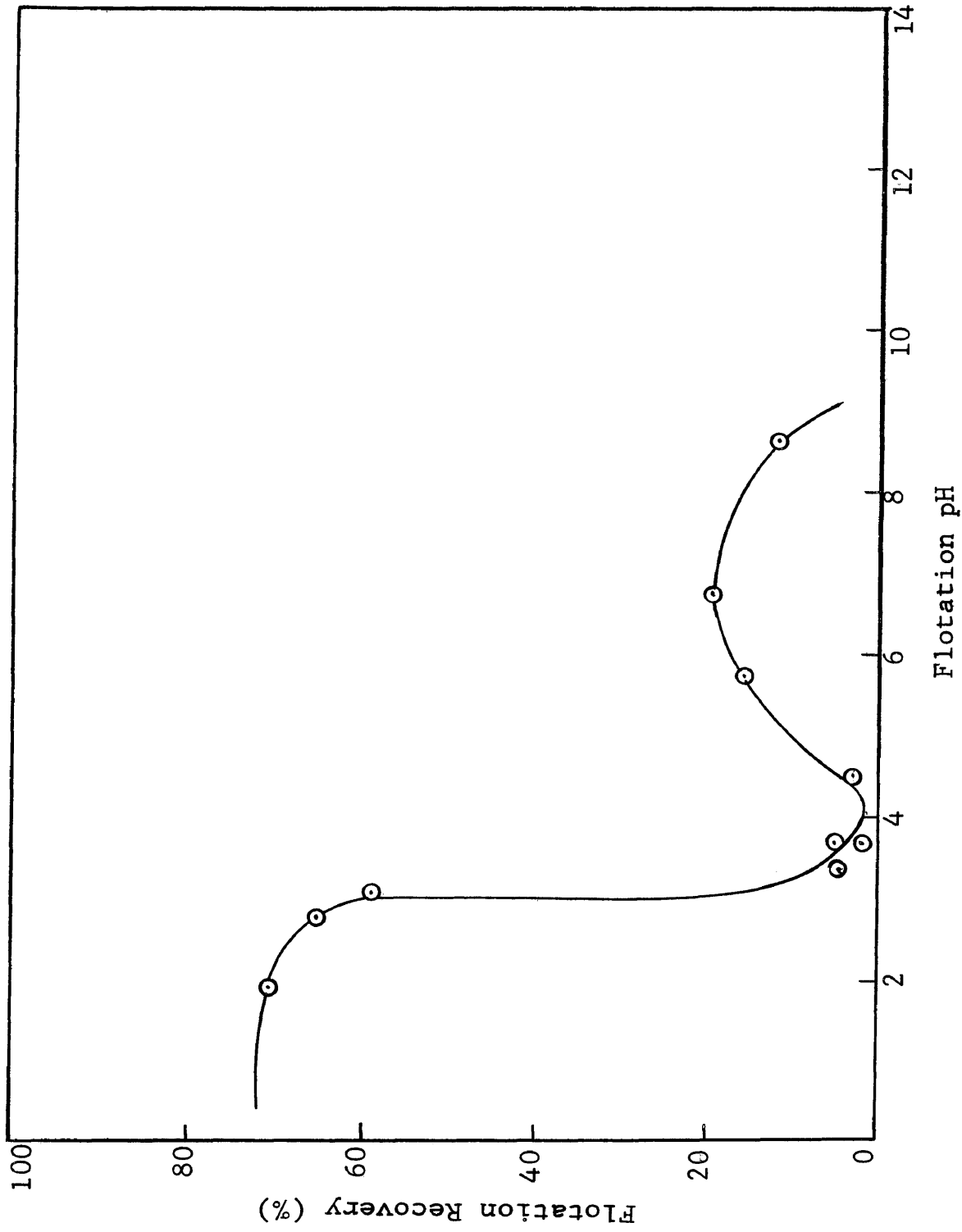


Figure 13. Flotation Recovery of  $MnO_2$  (II) as a Function of Flotation pH for a Sulfonate Addition of  $1 \times 10^{-4}$  Mole per Liter.

⊙  $1 \times 10^{-4} M Mn^{++}$

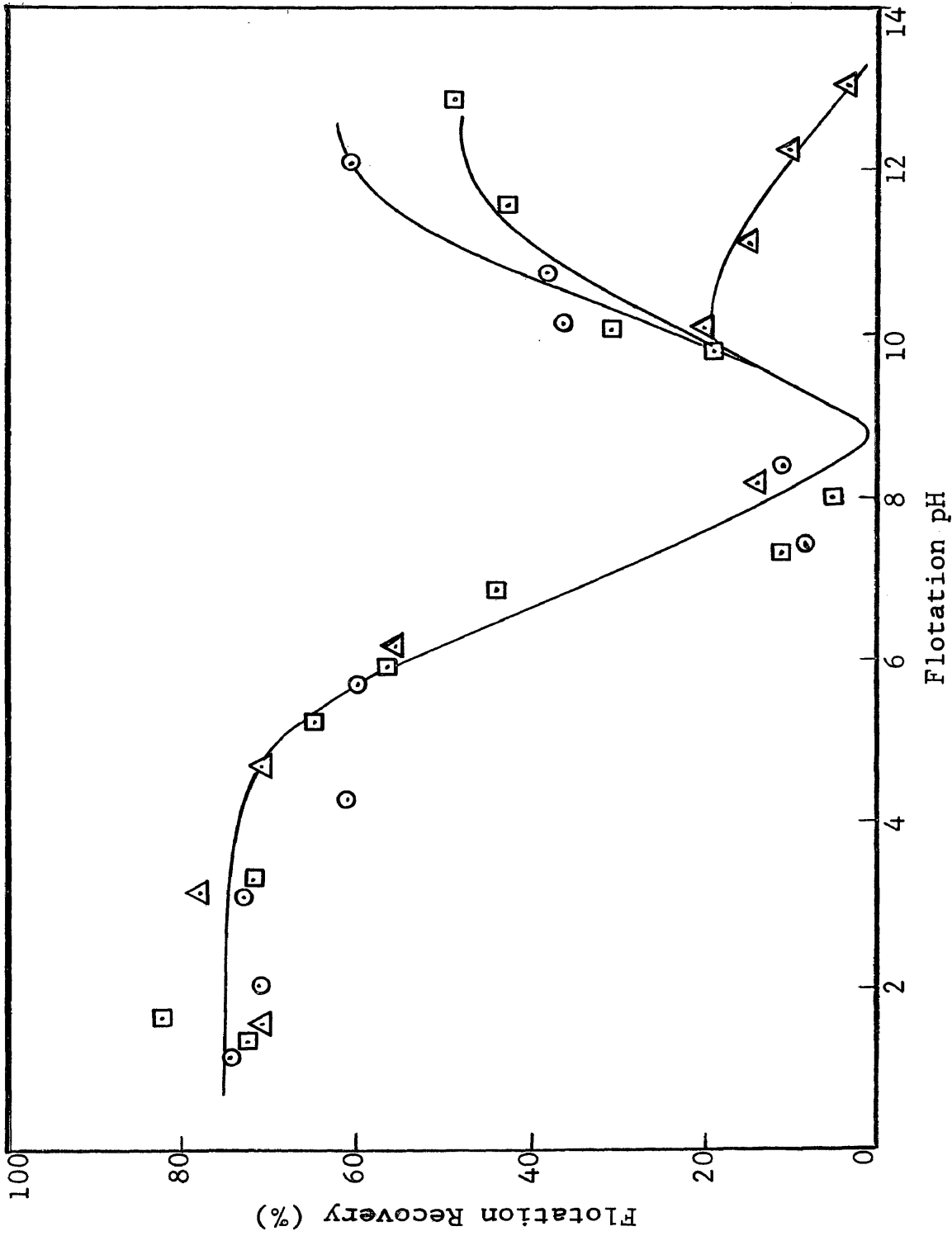


Figure 14. Flotation Recovery of MnO<sub>2</sub> (II) as a Function of Flotation pH for a Sulfonate Addition of 1 x 10<sup>-4</sup> Mole per Liter.

○ 1 x 10<sup>-3</sup> M Ca<sup>++</sup>      □ 1 x 10<sup>-4</sup> M Ca<sup>++</sup>  
△ 1 x 10<sup>-5</sup> M Ca<sup>++</sup>

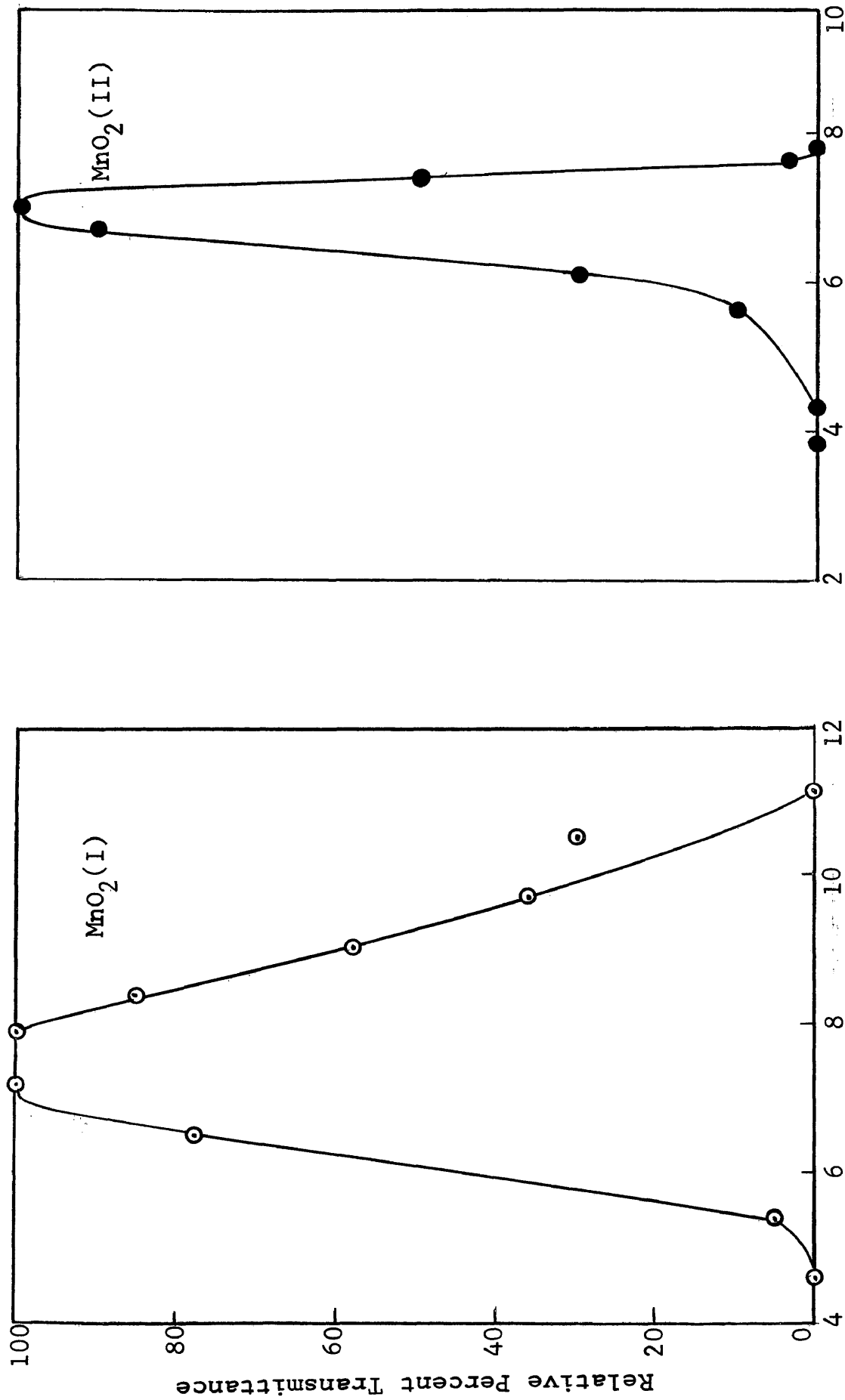


Figure 15. Relative Percent Transmittance as a Function of pH

time interval of 1.2 minutes was a maximal 50 percent at pH 7.0. Above and below this pH, recovery decreased sharply to zero.

Manganese Oxide (III): Transmittance data for manganese oxide (III) after a time interval of 1.4 minutes are presented in Figure 16. Transmittance was a maximum between pH 5.0 and 6.0.

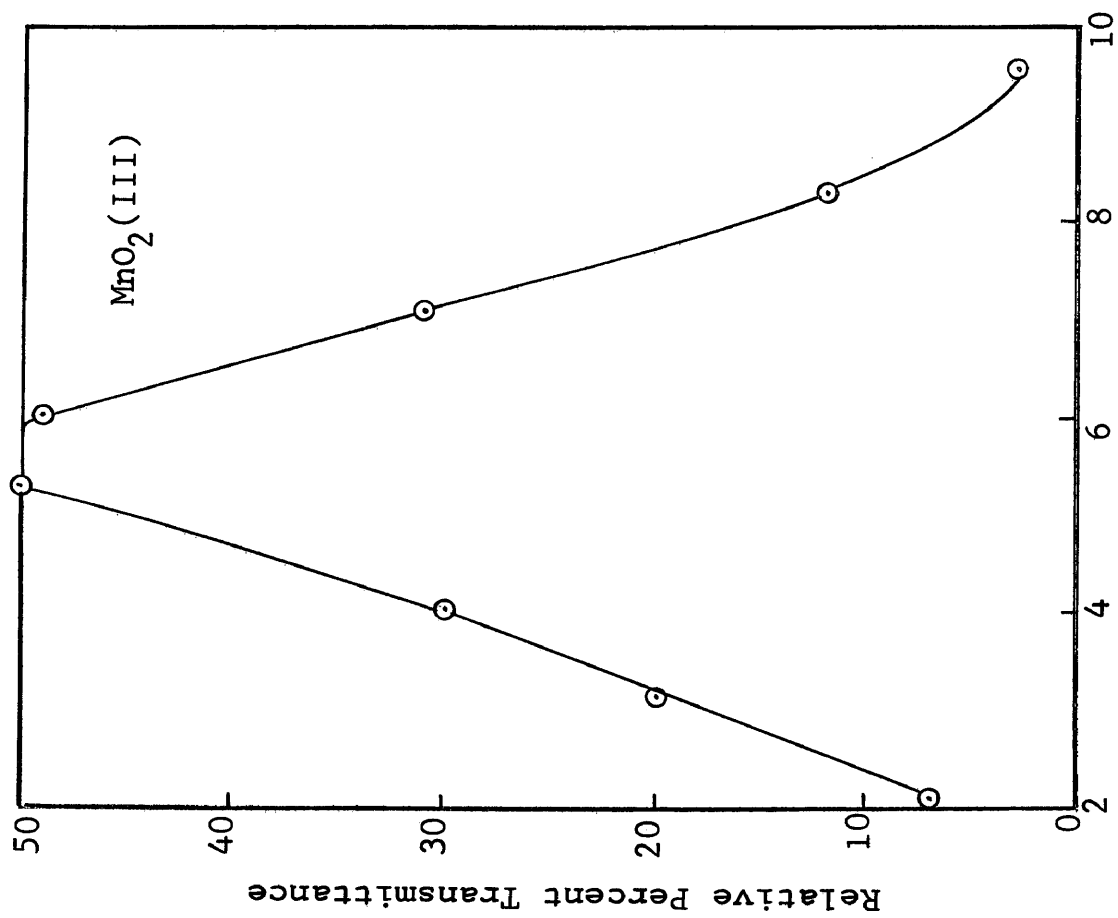


Figure 16. Relative Percent Transmittance as a Function of pH.

## DISCUSSION of RESULTS

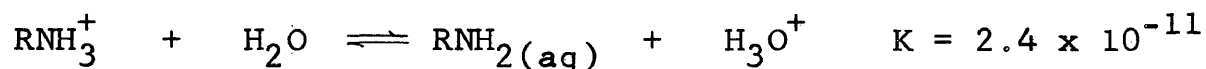
Zero-points-of-charge of pH 7.6, 7.0, and 5.6 were measured for manganese oxides (I), (II), and (III), respectively.

Comparison of the flotation data determined at ambient and elevated temperature with zero-point-of-charge determinations shows that adsorption of sulfonate and amine is apparently controlled by coulombic effects. That is, when the mineral surface is positively charged due to  $H^+$  adsorption, aminium ions,  $RNH_3^+$ , will be repelled from the surface, while sulfonate ions,  $RSO_3^-$ , will physically adsorb.

Similarly, above the zpc where the mineral is negatively charged, sulfonate ions will be repelled, and  $RNH_3^+$  will be adsorbed. The agreement between measured zpc and flotation response with amine and sulfonate is striking in the case of manganese oxides (II) and (III) (Figures 6,9). The data in Figure 4, however, indicate that the zpc for oxide (I) may be about pH 9.5, rather than the measured zpc of 7.6.

The decrease in flotation recovery at high values of pH

with amine is probably due to the following equilibrium reaction<sup>(17)</sup>:



above pH 11 the collector is predominately in the form of precipitated  $\text{RNH}_2$ , and  $\text{RNH}_3^+$  is no longer in sufficient quantity to effect flotation.

Figure 10 shows that good flotation of manganese oxide (III) is achieved at high sulfonate additions and elevated temperature four units in pH above the zpc. A similar response was noted with manganese oxide (II). This phenomenon is probably due to hydrocarbon chain association<sup>(7)</sup>, but the possibility of chemisorption of collector should not be overlooked. This mechanism can be established with infrared techniques and is to be the subject of another investigation.

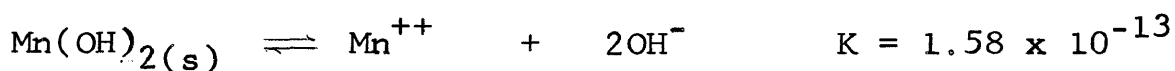
The oleate flotation study has proved to be the most interesting and informative portion of this investigation. If the zpc is sufficiently high, oleate ion also appears to adsorb coulombically at the surface, as illustrated in Figures 5, 8, and 11. Manganese oxide (II) shows a maximal recovery of 60 percent at pH 4 (Figure 8). Depression below pH 4 can probably be attributed to the formation of oleic acid (aqueous) from oleate ion.

Depression at pH 6 is not clear if the zpc of this oxide is pH 7. It would seem that good flotation should still have

been obtained until about pH 6, as was obtained with sulfonate (Figure 6).

Figures 5, 8, and 11 indicate that flotation of manganese oxides with potassium oleate in the basic pH range is due to the formation of insoluble manganous oleate at the surface.\* The pH range in which this compound forms is apparently that range in which  $Mn^{++}$  hydrolyzes to  $MnOH^+$ . This fact can be seen from the calculations listed in Table 1, which shows that the  $MnOH^+$  concentration is a maximum at about pH 9, for a nominal addition of  $1 \times 10^{-3}$  mole per liter manganous chloride to water.

These calculations were made by using the following equilibria<sup>(18)</sup>:



Note that concentrations were used instead of activities in order to simplify calculation.

By analogy, it seems logical to assume that some of the surface  $Mn^{++}$  ions have also hydrolyzed to  $MnOH^+$  at pH 8, and to  $Mn(OH)_2(s)$  at pH 9.2 and above. Stated in other words, hydroxyl ion is assumed to have chemisorbed at the surface

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\*The surface of  $MnO_2$  is assumed to be manganous oxide because of the instability of manganic ion in water solution.

TABLE 1. Concentration of various manganous ion species as a function of pH for a nominal addition of  $1 \times 10^{-3}$  molar manganous chloride to water.

pH	Species		
	$\text{Mn}^{++}$	$\text{MnOH}^+$	$\text{Mn}(\text{OH})_2(\text{s})$
7.0	$1.0 \times 10^{-3}$	$2.5 \times 10^{-7}$	0
7.2	$1.0 \times 10^{-3}$	$4.0 \times 10^{-7}$	0
7.4	$1.0 \times 10^{-3}$	$6.3 \times 10^{-7}$	0
7.6	$1.0 \times 10^{-3}$	$9.9 \times 10^{-7}$	0
7.8	$1.0 \times 10^{-3}$	$1.6 \times 10^{-6}$	0
8.0	$1.0 \times 10^{-3}$	$2.5 \times 10^{-6}$	0
8.2	$1.0 \times 10^{-3}$	$3.9 \times 10^{-6}$	0
8.4	$1.0 \times 10^{-3}$	$6.2 \times 10^{-6}$	0
8.6	$1.0 \times 10^{-3}$	$9.8 \times 10^{-6}$	0
8.8	$9.8 \times 10^{-4}$	$1.6 \times 10^{-5}$	0
9.0	$9.7 \times 10^{-4}$	$2.4 \times 10^{-5}$	0
9.2	$6.3 \times 10^{-4}$	$2.5 \times 10^{-5}$	$3.4 \times 10^{-4}$
9.4	$2.5 \times 10^{-4}$	$1.6 \times 10^{-5}$	$7.3 \times 10^{-4}$
9.6	$9.9 \times 10^{-5}$	$9.9 \times 10^{-6}$	$9.0 \times 10^{-4}$
9.8	$4.0 \times 10^{-5}$	$6.3 \times 10^{-6}$	$1.0 \times 10^{-3}$
10.0	$1.6 \times 10^{-5}$	$3.9 \times 10^{-6}$	$1.0 \times 10^{-3}$

above about pH 8. If dissolved but undissociated oleic acid is functioning as the collector, then adsorption could occur as shown in Figure 17.

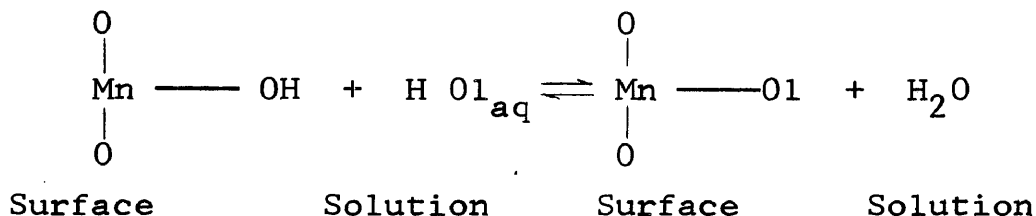


Figure 17. Proposed Neutral Molecule Adsorption of Oleic Acid on Manganese Oxide Surface.

By this mechanism water would be split out, and manganese oleate would be formed at the surface. If oleate ion is chemisorbing at the interface, then the reason for the necessity of hydroxylating the surface is not so obvious.

Sulfonate would not be expected to function in this manner because of the fact that sulfonic acid is a strong acid, and there would be an insufficient amount of  $\text{HRSO}_3(\text{aq})$  at pH 8. Oleic acid, on the other hand, is a weak acid and has a dissociation constant of about  $1 \times 10^{-5}$ .

The effect of temperature in this system is probably due to thermodynamic considerations rather than to adsorption kinetics. That is, if the hydrolysis reaction of  $\text{Mn}^{++}$  to  $\text{MnOH}^+$  is endothermic, then the addition of heat to the system will favor the formation of  $\text{MnOH}^+$ .

Another mechanism of adsorption of oleate in this pH range can be suggested. If the adsorption of oleate between pH 8 and 9 involves  $\text{MnOH}^+$  activation, similar to that which happens with quartz\*<sup>(19)</sup>, dissolved manganese ion will have to be obtained from the mineral. The beneficial effect of elevated temperature might then be due to the increased solubility of  $\text{MnO}_2$  under these conditions. If this were the case, however, then manganese activation should have occurred when the mineral was floated with  $1 \times 10^{-4}$  mole per liter manganous ion. Figure 11 shows that no difference in flotation response was obtained with the metal ion present. Manganese activation, therefore, is probably not the mechanism occurring in this pH range. At present, it is not understood why manganous ion will not activate the mineral while calcium ion does, in its own region of hydrolysis.

Activation studies were undertaken to determine the effect that various metal ions may have upon the flotation characteristics of the manganese oxides when a high molecular weight sulfonate is used as a collector.

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\*In metal-ion activation systems, flotation has been suggested to involve the combination of the first hydroxy complex of a metal ion, e.g.,  $\text{MnOH}^+$ , and sulfonate or oleate in solution to form either an aqueous complex  $\text{Mn}(\text{OH})(\text{RSO}_3)_{(\text{aq})}$  or a basic metal-collector salt  $\text{Mn}(\text{OH})(\text{RSO}_3)_{(\text{s})}$  either of which could function as a collector.

Manganese ion was the first metal ion considered. Figure 12 shows that the addition of  $1 \times 10^{-4}$  mole per liter manganous chloride has only a minor effect on flotation recovery, as compared with the data in Figure 6. The curve of recovery as a function of pH in the presence of  $Mn^{++}$  does fall off about one pH unit higher than does the one obtained in the absence of added manganous chloride, however. This phenomenon may be due to the fact that  $Mn^{++}$  is potential determining for  $MnO_2$  and will tend to make the surface positive.

When  $1 \times 10^{-4}$  mole per liter  $Fe^{+++}$  ion was added to the system, flotation recovery decreased above pH 3.0 (Figure 13). This decrease might be explained as follows: below about pH 7.0, the mineral is positively charged and should respond to sulfonate flotation below neutral pH. Flotation apparently occurs by this mechanism up to about pH 3, at which pH ferric ion undergoes hydrolysis to ferric hydroxide. Finely divided  $Fe(OH)_3(s)$  is a colloid with extremely high surface area. As the zpc of ferric hydroxide is known to be about pH 6.7, extensive adsorption of sulfonate ions will occur below this pH, with the result that few of the collector ions will be available for the manganese oxide surface.

Calcite is often associated with manganese oxides, and the effect of  $Ca^{++}$  ions was also examined. Calcium has little effect on the acid side of the pH range, but recovery increases proportionally with concentration above about pH 10. Calcium

ion forms its first hydroxy complex,  $\text{Ca}(\text{OH})^+$ , the activation species at about pH 10.5 (19, 20), where sufficient  $\text{CaOH}^+$  is present to effect activation. (See Figure 14).

## CONCLUSIONS

The zpc of the manganese oxides examined were found to range from pH 5.5 to pH 7.5. The experimental data suggest that flotation of manganese oxides with high molecular weight sulfonate and amine collectors is controlled by coulombic effects. That is, flotation is achieved only when the surface charge is opposite to that of the collector.

At elevated temperature, sulfonate is seen to adsorb a number of pH units above the zpc; this phenomenon may be due to hydrocarbon chain association or perhaps to chemisorption.

Oleate flotation may also be coulombic if the mineral zpc is sufficiently high, i.e., above pH 7.

Oleate flotation is also dependent upon hydroxylation of the mineral surface in the pH region 8 to 9. Two methods of collector adsorption may be possible in this range. One mechanism of adsorption might be  $\text{MnOH}^+$  activation in which the dissolved manganese ions are obtained from the mineral, but the possibility of this phenomenon occurring is doubtful

in view of previous work. The second mechanism might involve chemisorption of the neutral molecule,  $\text{HOl}_{(\text{aq})}$ , on the hydroxylated mineral surface. If this mechanism is occurring, surface manganous oleate and water will be formed. Flotation recovery in this pH range may be markedly increased by an increase in the temperature of the flotation pulp.

Activation studies showed that manganous ion has little effect upon changing flotation recovery when a sulfonate collector is used; whereas iron and calcium ions produce marked effects in their respective regions of hydrolysis.

APPENDIX  
X-RAY DIFFRACTOMETER DATA  
Parts 1 and 2

Part 1 of this appendix gives the d spacings (A.U.) and the relative intensities for the minerals used in the experimental work. Part 2 of this appendix gives data obtained from the A.S.T.M. card file for the minerals and their impurities in order that a comparison may be made with the experimental data.

Appendix - PART 1. Experimental X-ray Diffraction Data

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<u>Manganese Oxide (I)</u>		<u>Manganese Oxide (II)</u>	
<u>d spacing</u>	<u>Rel. Intensity</u>	<u>d spacing</u>	<u>Rel. Intensity</u>
3.13	100	3.42	20
2.41	8	3.13	100
2.21	20	2.65	20
2.11	4	2.42	24
1.97	6	2.21	6
1.63	18	2.12	4
1.53	20	1.63	20
1.36	4	1.56	16
		1.40	6
		1.31	12

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Appendix - PART I. Experimental X-ray Diffraction Data (cont).

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Manganese Oxide (III)

<u>d spacing</u>	<u>Rel. Intensity</u>
4.27	5
4.05	80
3.34	25
3.25	7
3.11	100
2.89	55
2.55	62
2.44	5
2.41	7
2.32	12
2.20	5
2.14	5
2.07	7
1.90	12
1.83	5
1.66	10
1.62	30
1.56	15
1.52	5

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## Appendix - PART 2. A.S.T.M. Card File Reference Data

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<u>Pyrolusite (MnO<sub>2</sub>)</u>		<u>Ramsdellite (MnO<sub>2</sub>)</u>	
<u>d spacing</u>	<u>Rel. Intensity</u>	<u>d spacing</u>	<u>Rel. Intensity</u>
3.48	10	4.04	100
3.14	100	2.54	80
2.41	50	2.43	60
2.21	10	2.33	60
2.13	25	2.13	70
1.98	15	2.05	20
1.81	5	1.90	60
1.68	1 ?	1.65	70
1.63	50	1.61	70
1.56	25		
1.43	15		
1.40	15		
1.31	20		
1.25	5		
1.20	5		
1.16	5		
1.125	5		
1.10	5		
1.057	15		
1.04	10		
1.0	1		

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 Appendix - PART 2. A.S.T.M. Card File Reference Data (cont.)
 

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<u>Manganite (Mn<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O)</u>		<u>Alpha Quartz (SiO<sub>2</sub>)</u>	
<u>d spacing</u>	<u>Rel. Intensity</u>	<u>d spacing</u>	<u>Rel. Intensity</u>
3.40	100	4.26	35
2.64	60	3.343	100
2.53	5	2.458	12
2.41	20	2.282	12
2.28	50	2.237	6
2.23	5 N	2.128	9
2.20	5	1.980	6
1.783	20	1.817	17
1.708	40	1.801	1
1.672	30	1.672	7
1.636	40	1.659	3
1.502	20	1.608	1
1.437	30	1.541	15
1.326	10	1.453	3
1.297	10	1.418	1
1.256	5	1.382	7
1.24	20 S	1.375	11
1.21	20 S	1.372	9
1.183	10	1.288	3
1.162	10	1.256	4
*		1.228	2

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\*More d spacings are given in the A.S.T.M. card file, but since their relative intensities are so small, they are of little value in this thesis.

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