

SOME CHEMICAL CONSIDERATIONS
OF COPPER OXIDE FLOTATION

By

R. S. Rickard

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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 malachite, cuprite, and chrysocolla were performed to determine the flotation characteristics of these minerals with high-molecular-weight sodium sulfonate and sodium oleate as collectors. Infrared analysis was used to determine the mode of collector adsorption and ultra-violet analysis was used to obtain a quantitative measure of the amount of sulfonate adsorbed under given conditions.

The experimental results indicate: 1) the pH range of copper-oxide floatability is limited, 2) the collector is chemisorbed, and 3) sodium sulfonate and sodium oleate function similarly in the system.

TABLE OF CONTENTS

INTRODUCTION.....	1
FLOTATION EXPERIMENTS.....	2
Materials.....	2
Minerals.....	2
Water.....	3
Reagents.....	4
Apparatus.....	4
Procedure.....	5
Flotation Results.....	6
Malachite.....	6
Cuprite.....	8
Chrysocolla.....	12
ADSORPTION MECHANISM EXPERIMENTS.....	16
Materials.....	16
Minerals.....	16
Reagents.....	17
Procedure.....	17
Infrared Adsorption Results.....	18
Oleate Adsorption.....	18
Sulfonate Adsorption.....	20

QUANTITATIVE COLLECTOR ADSORPTION EXPERIMENTS.....	29
Materials.....	29
Minerals.....	29
Apparatus.....	29
Procedure.....	30
Results of Adsorption Study.....	33
DISCUSSION OF RESULTS.....	36
Flotation.....	36
Adsorption Mechanism.....	40
Quantitative Collector Adsorption.....	42
SUMMARY AND CONCLUSIONS.....	43
BIBLIOGRAPHY.....	44

ILLUSTRATIONS

Figure	Page
1. Malachite Flotation Data, Recovery vs pH as a Function of Sulfonate Concentration.....	7
2. Malachite Flotation Data, Recovery vs pH with Potassium Oleate as the Collector.....	9
3. Malachite Flotation Data, Recovery vs pH as a Function of Ca^{++} Addition.....	10
4. Cuprite Flotation Data, Recovery vs pH as a Function of Sulfonate Concentration.....	11
5. Cuprite Flotation Data, Recovery vs pH with Potassium Oleate as Collector.....	13
6. Cuprite Flotation Data, Recovery vs pH as a Function of Ca^{++} Addition.....	14
7. Infrared Adsorption vs Frequency for Oleic Acid, and Sodium Oleate.....	19
8. Infrared Adsorption vs Frequency for Malachite Oleate System.	21
9. Infrared Adsorption vs Frequency for Cuprite Oleate System...	22

10. Infrared Adsorption vs Frequency for Chrysocolla Oleate System....	23
11. Infrared Adsorption vs Frequency for Sulfonic Acid, Sodium Sulfonate, and Cupric Sulfonate.....	25
12. Infrared Adsorption vs Frequency for the Malachite-Sulfonate System.....	26
13. Infrared Adsorption vs Frequency for the Cuprite-Sulfonate System.	27
14. Infrared Adsorption vs Frequency for Chrysocolla-Sulfonate System.	28
15. Percent Transmission vs Wavelength. Ultra-violet Spectra of Standard Sulfonate Solutions.....	31
16. Log (Percent Ultra-violet Adsorption at 236 mμ) vs Log (M/l Sodium Sulfonate).....	32
17. Percent Transmission vs Wavelength. Ultra-violet Spectra of Residual Solution from Mineral Contact.....	34

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INTRODUCTION

Oxide minerals have been floated by several means, but an explanation of the mechanism of collector adsorption has not been given. Flotation of the copper oxide minerals has been accomplished by using the following flotation schemes: a) sulfidizing the mineral and floating as a sulfide, b) floating with fatty acids, and c) floating with xanthates. All of these methods have definite disadvantages, such as the lack of selectivity when using fatty acids, reaction of xanthate with cupric ion in solution, and the cost of sulfidizing agent⁽¹⁾.

The use of high molecular weight sulfonates as collectors would seem to overcome most of these disadvantages, in that selectivity is possible, and sulfonate will not undergo oxidation when reacted with cupric ion.

The objective of this work was to determine: 1) the flotation characteristics of copper oxide minerals with a high molecular weight sulfonate and soap as collectors, 2) the mechanism of collector adsorption, and 3) amount of collector adsorbed per unit area of mineral surface.

FLOTATION EXPERIMENTS

All of the flotation work was performed using a standard technique of micro-flotation⁽²⁾. Some minor modifications of the procedure were needed due to such features as variable densities of the minerals.

Materials

Every precaution was taken to insure that the minerals and reagents used in this work were free of contamination, and that no contamination was introduced during the work.

Minerals: The copper oxide minerals used in this investigation were malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), cuprite (Cu_2O), and chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$). Chemical analysis of their copper content is compared with the theoretical composition in Table 1.

Table 1 - Copper Analysis of Minerals Used

<u>Mineral</u>	<u>Theoretical Analysis (percent Cu)</u>	<u>Actual Analysis (percent Cu)</u>
Malachite	57.4	54.7
Cuprite	88.3	89.6
Chrysocolla	35.8	20.8

X-ray examination of malachite and cuprite showed that the samples were well crystallized. The X-ray analysis of chrysocolla showed weak lines of crystallized silica. This chrysocolla sample was apparently amorphous, with quartz as the major impurity.

Mineral samples were hand-ground with a porcelain mortar and pestle to the required size. The minerals, because of their different specific gravities, were reduced to different sizes. The various sizes were determined by preliminary flotation experiments. The following sizes were found to give the desired results:

Malachite	-65 +150 mesh
Cuprite	-100 +150 mesh
Chrysocolla	-48 +100 mesh

The sized materials were wet-screened and deslimed by decanting with conductivity water.

Water: The water used in all of the flotation experiments was distilled and then passed through an ion exchange column.

Reagents: Two flotation reagents were used: potassium oleate, which was chemically pure, and sodium alkyl aryl sulfonate provided by the Shell Chemical Company. This sulfonate had the following characteristics⁽³⁾:

physical form	solid, finely ground
sulfonate content (wt %)	95 to 97
molecular weight	450 to 470

The pH was adjusted with reagent grade hydrochloric acid and potassium hydroxide.

Commercial nitrogen gas was used; it was scrubbed with concentrated caustic and passed through Ascarite. This treatment removed CO₂ and saturated the gas with water vapor.

Apparatus

A small glass micro-flotation cell, constructed to hold 100 ml of solution, was used in this study^(2,4). This cell had a fritted glass bottom for gas introduction. Agitation was provided by a magnetic stirrer. With this apparatus small charges of mineral (in this case, 2.5 grams) can be used.

Provisions for introduction of nitrogen into this cell include a monometer, constant head tank, a gas-measuring buret (water displacement), and a regulation valve.

Procedure

The flotation experiments were conducted at room temperature in the following manner:

1. The reagents were combined with water so that the final solution volume was 100 ml.
2. The pH of the solution was adjusted.
3. Two and one-half grams of the ground mineral were added to the solution and the pulp was conditioned for 3 minutes.
4. During this conditioning period, the pH was controlled because of the solubility of the mineral.
5. The pH was measured after conditioning which was just prior to flotation. This was considered the flotation pH.
6. Next, 30 ml (measured under 3 ft of water) of purified and saturated nitrogen was passed through the cell at the rate of 120 ml per min. The froth was collected during this time.
7. The pH of the solution remaining in the flotation cell was measured to insure that conditions during the test remained essentially constant.
8. The products (concentrate and tails) were dried and weighed, and the recovery was calculated.

Flotation Results

Several series of experiments were performed using the three minerals. These were:

1. the effect of pH on flotation recovery as a function of sulfonate addition,
2. the effect of pH on flotation recovery when oleate was used as collector,
3. the effect of pH on flotation recovery as a function of Ca^{++} addition with sulfonate as collector.

Malachite: The effect of pH on flotation recovery is very pronounced as is the amount of collector present⁽⁵⁾. There should be a point where the pH and reagent addition produce an optimum recovery. A series of experiments were conducted in which the pH was varied at several concentrations of sulfonate. As shown in Figure 1, optimum recovery is obtained at pH 5.2. Further, the sulfonate concentration greatly affects the recovery but does not affect the optimum pH, until a sufficient quantity was present to produce the broad plateau (1×10^{-5} M/l, Figure 1).

These data also show that malachite flotation recovery is zero at values of pH above 11.2. Recovery is also decreased at the low values of pH, i.e., below 4.

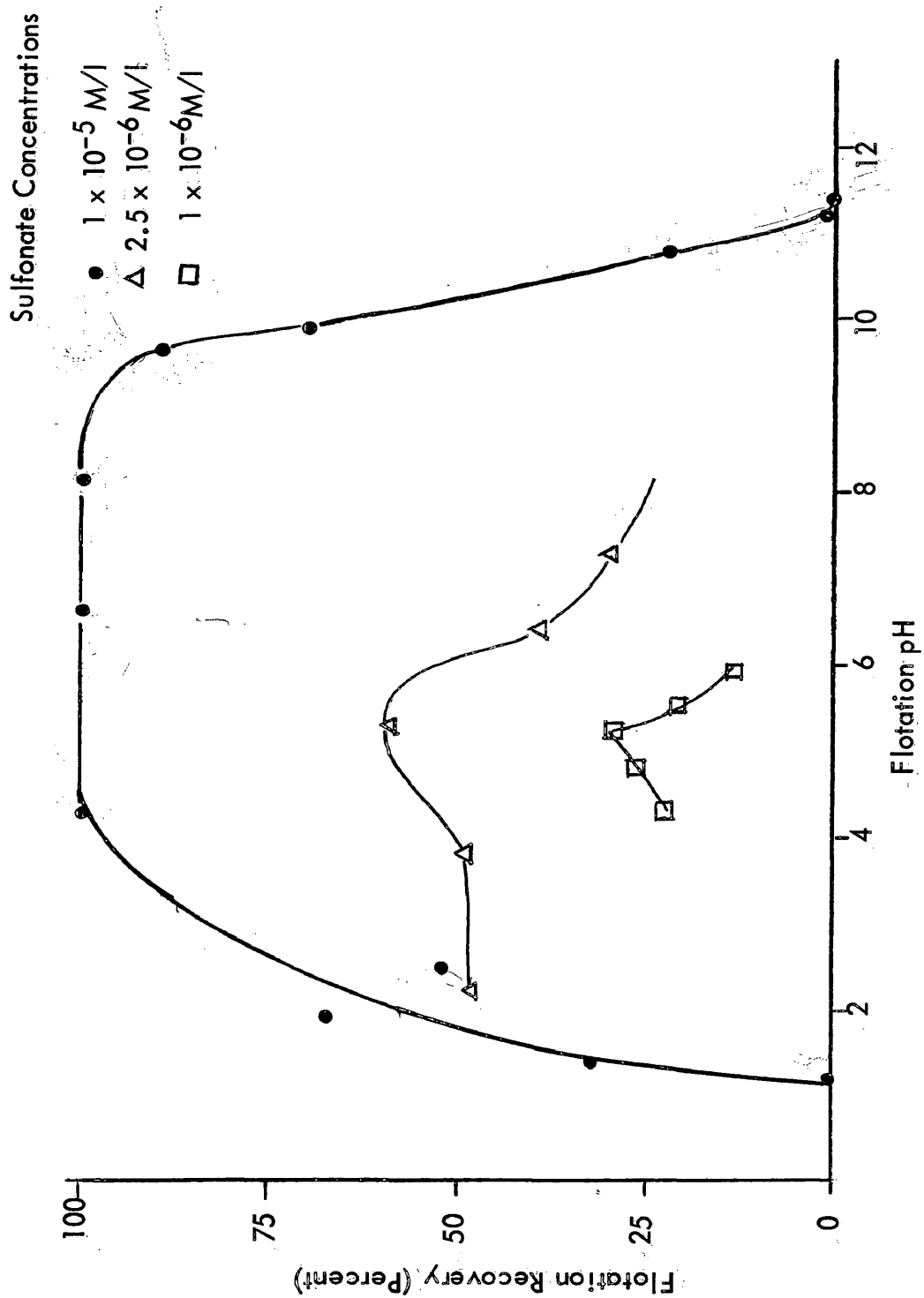


Figure 1: Malachite Flotation Data, Recovery vs pH as a Function of Sulfonate Concentration

Similar experiments were also conducted with potassium oleate as collector. See Figure 2. When 1×10^{-5} M/l oleate was present, recoveries similar to those obtained with 1×10^{-5} M/l sulfonate were achieved. Experiments were not conducted in moderately acid systems because of the hydrolysis of oleate⁽⁴⁾.

The effects of metal ions in solution have a pronounced effect on flotation response^(5,6). To determine if these phenomena are applicable in this copper carbonate system, calcium ions were added to the flotation system. These data are presented in Figure 3. Note here the suppression of recovery in the pH range 5 to 8. At pH 9 the recovery is greatly depressed, and then as the pH is increased, the recovery is increased. At pH 9.8 complete flotation was achieved, while recovery was reduced above pH 11.9. Complete depression was noted at pH 12.3.

Cuprite: Experiments, similar to those conducted with malachite were performed with cuprite.

First, the effect of pH as a function of the sulfonate concentration was examined. See Figure 4. These data show an optimum pH as did malachite. This optimum is at pH 6.9 when 1×10^{-6} M/l sulfonate was present. There are several other similarities between these data and those obtained with malachite. That is, both systems show a decrease in recovery with a decrease in sulfonate concentration and depression at high values of pH. With cuprite and 1×10^{-5} M/l sulfonate, complete depression occurred at pH 11.1, while complete depression

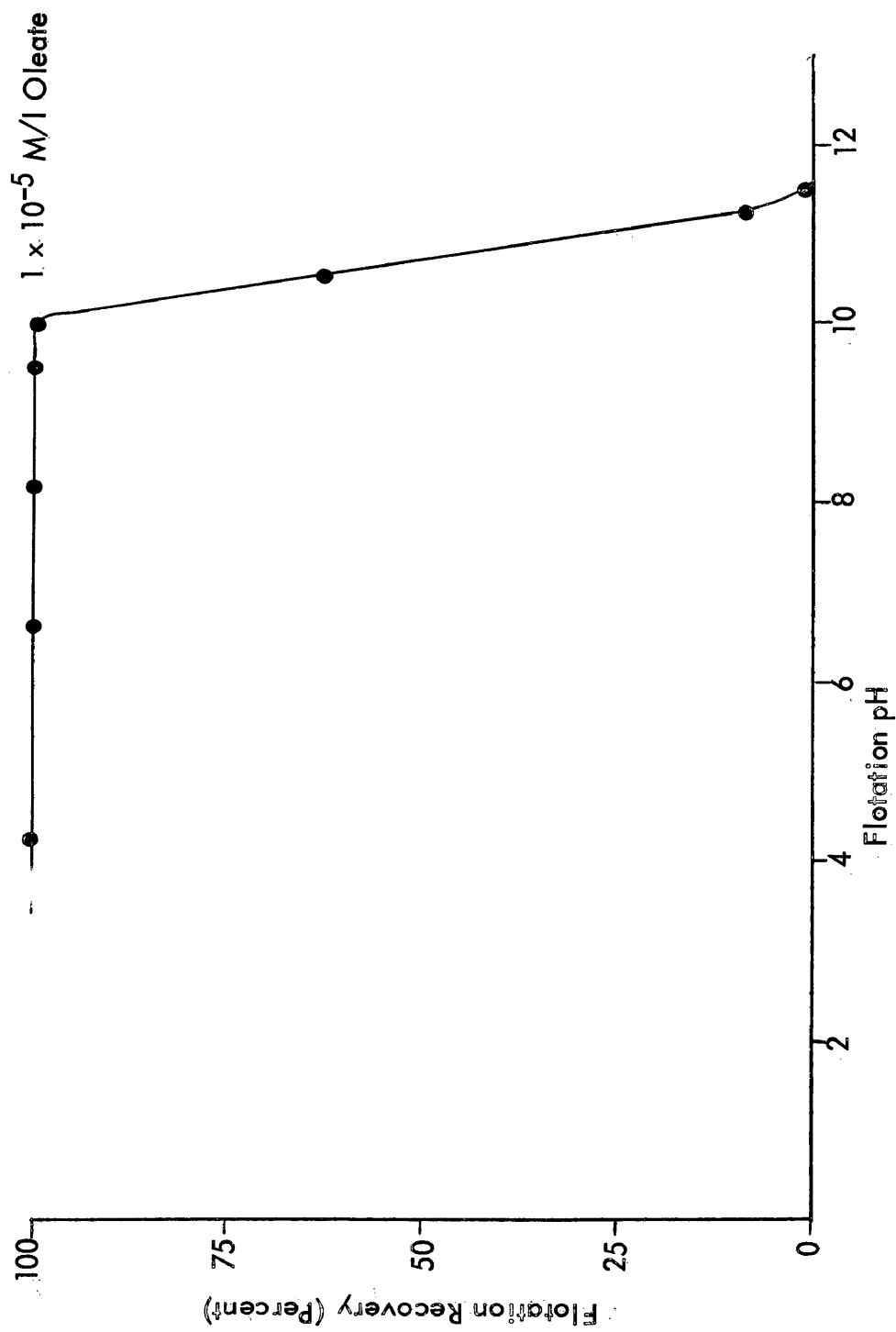


Figure 2: Malachite Flotation Data, Recovery vs pH with Potassium Oleate as the Collector

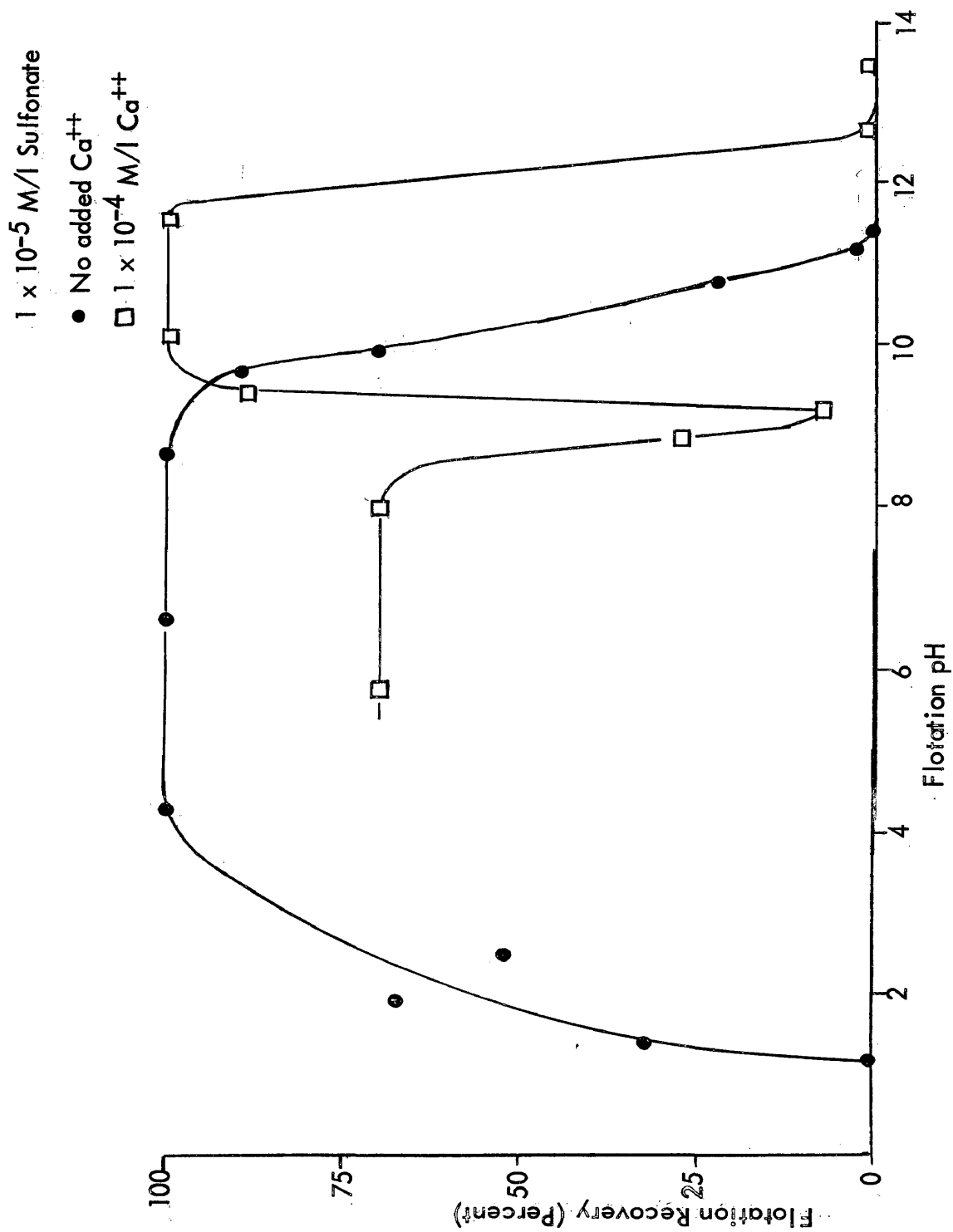


Figure 3: Malachite Flotation Data, Recovery vs pH as a Function of Ca⁺⁺ Addition

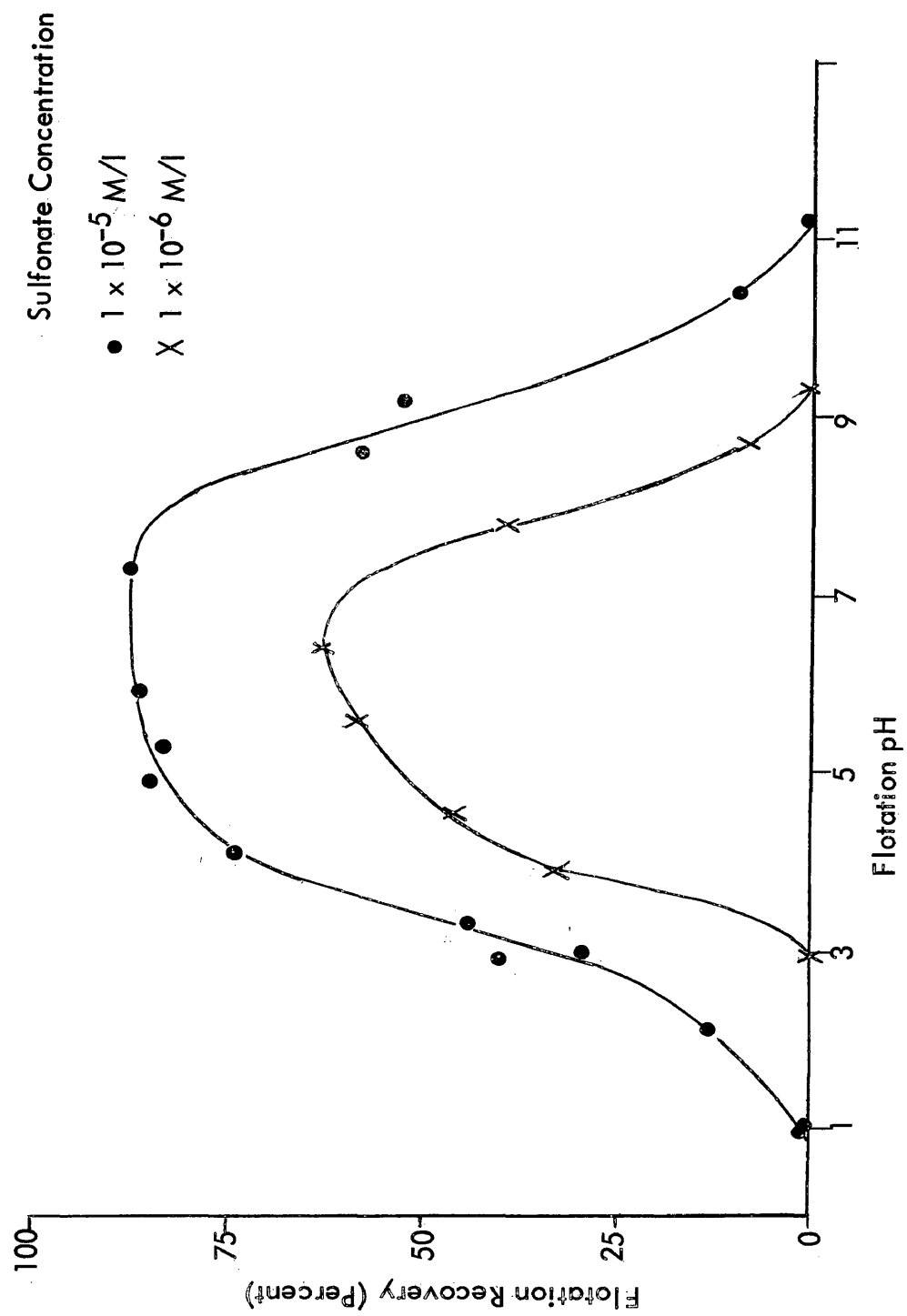


Figure 4: Cuprite Flotation Data, Recovery vs pH as a Function of Sulfonate Concentration

occurred at pH 9.3 with 1×10^{-6} M/l sulfonate present. Recovery was also reduced in the low pH range, i.e., less than pH 4, with a concentration of 1×10^{-5} M/l sulfonate. Zero recovery was obtained at pH 1.

The effect of pH on flotation response with potassium oleate as collector was examined next. These data show a striking similarity with the equivalent sulfonate concentration; as shown in Figure 5, complete depression was noted to occur at pH 11.4. Again, data were not obtained for low values of pH due to hydrolysis of the oleate.

The important role that metal ion hydrolysis displayed in these systems is demonstrated with this mineral and Ca^{++} ion (Figure 6). As shown, recovery was reduced when 1×10^{-4} M/l Ca^{++} was added as compared with recovery obtained in the absence of added calcium. This was also observed with malachite. The pattern continues through a deep depression and subsequent increase in recovery. Finally, the recovery drops to zero at pH 12.6.

Chrysocolla: Experiments performed with this mineral were similar to those performed with the previous minerals.

The effect of pH and sulfonate concentration was investigated first. In this series of experiments, no flotation recovery was produced over the entire pH range (pH 2 to 11) with 1×10^{-5} M/l sulfonate. An increase in the sulfonate concentration by twenty-fold (2×10^{-4} M/l) still did not result in any flotation.

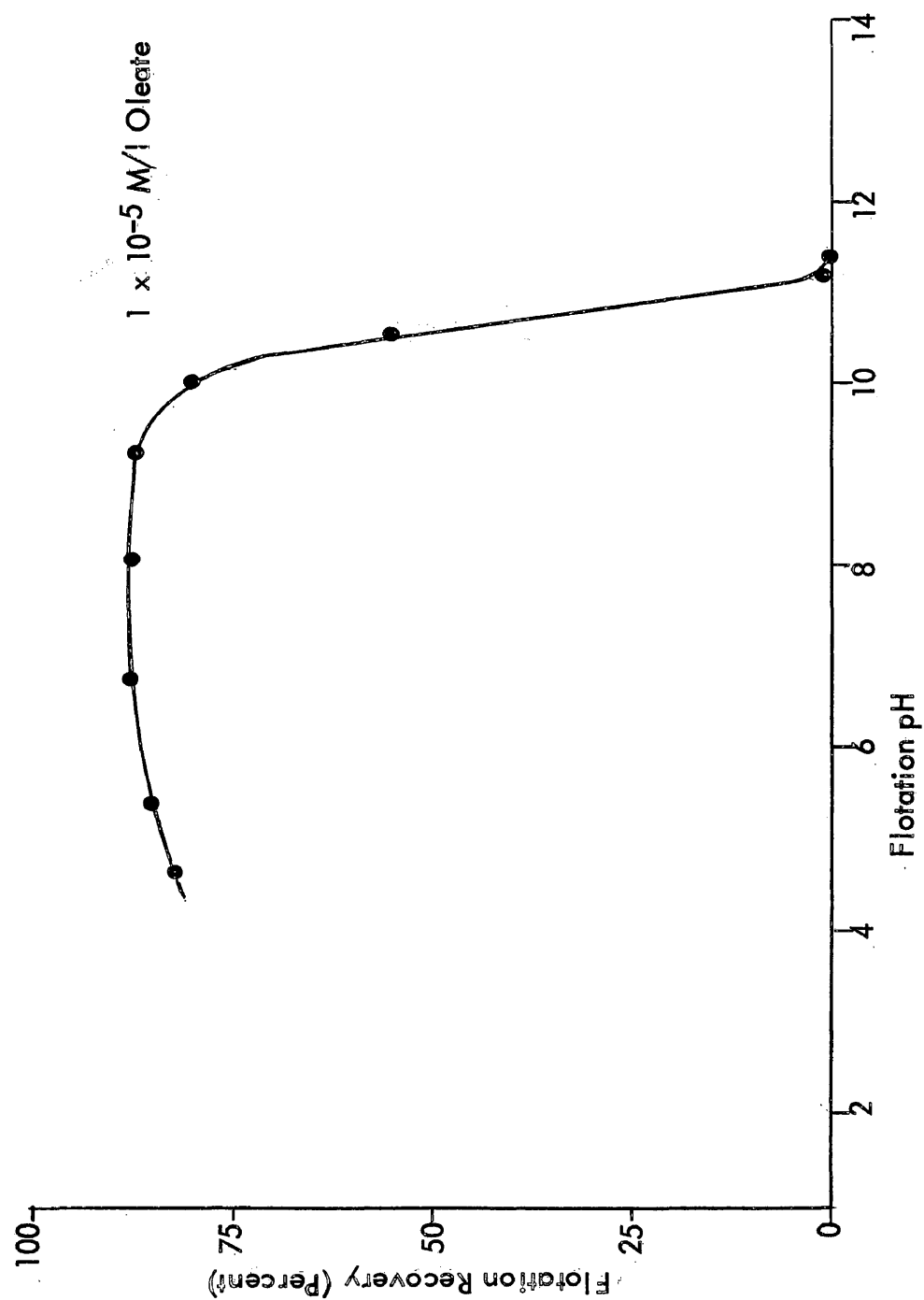


Figure 5: Cuprite Flotation Data, Recovery vs pH with Potassium Oleate as Collector

1×10^{-5} M/l Sulfonate

● No added Ca^{++}

X 1×10^{-4} M/l Ca^{++}

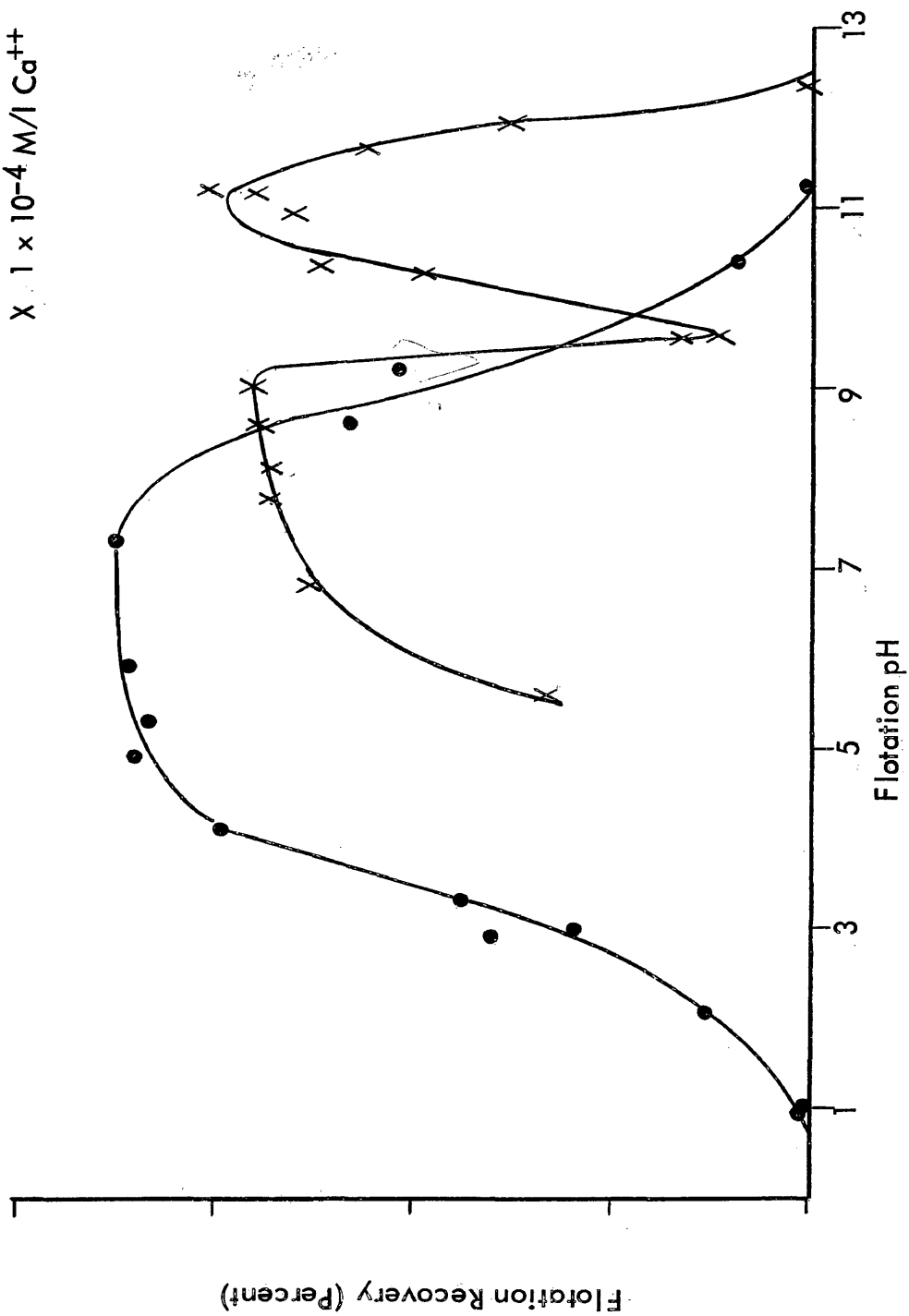


Figure 6: Cuprite Flotation Data, Recovery vs pH as a Function of Ca^{++} Addition

When oleate was used as the collector, no flotation was achieved either.

In this series of experiments, oleate concentrations of 1×10^{-5} and 1×10^{-4} M/l were used, while the pH was varied from 4 to 12.

Experiments involving calcium ions were also performed. The sulfonate concentration was 1×10^{-5} M/l, while the calcium ion concentration was 1×10^{-4} M/l, and the pH was varied from 8 to 13. No flotation was obtained under these conditions.

All of the experiments conducted on chrysocolla with sulfonate, oleate, or calcium-sulfonate systems showed zero flotation recovery.

ADSORPTION MECHANISM EXPERIMENTS

This work was performed to determine the mechanism of adsorption of flotation collectors on the surface of these copper oxide minerals. Infrared analysis was used to determine first whether any flotation reagent was on the mineral surface and secondly how the reagent was bonded to the mineral surface^(7,8).

Materials

The minerals used in this work were the same samples used in the flotation studies. The sodium sulfonate and potassium oleate were also the same; some additional materials were used, however.

Minerals: Samples of malachite, cuprite, and chrysocolla were ground in a motor-driven mortar and pestle for two hours. These ground minerals were then slurried in two liters of conductivity water and allowed to settle for one hour. After this period of time, the mineral suspension was decanted, and the settled material discarded. The suspended mineral particles were used for the infrared studies.

Reagents: Hydrochloric acid and potassium hydroxide (reagent grade) were used for pH adjustment.

Sulfonate and oleate, in both acid and salt forms, were used as flotation reagents. The salts were those used previously. The oleic acid was chemically pure, while the sulfonic acid was prepared from sodium sulfonate. The sulfonic acid was prepared by hydrolyzing the sodium sulfonate in chloroform with hydrochloric acid at an elevated temperature⁽⁹⁾.

Copper sulfonate was prepared by precipitation with cupric nitrate from a water solution of sulfonic acid, and was subsequently dried.

The solids were suspended in U.S.P. Nujol for infrared analysis.

Procedure

Sample preparation consists of the following steps:

1. Preparing a stable suspension of the mineral containing approximately 2 gm/l solids.
2. Pipetting 20 ml of slurry into a centrifuge tube and adding the collector (1 mg collector per 10 mg solids was used in these experiments), adjusting the pH, and mixing for 3 minutes.
3. Centrifuging until all of the solids were settled and compacted.
4. Decanting the liquid and measuring the pH.

5. Placing the solids on a microscope slide and drying. The final dried sample was ready for infrared analysis.

The steps of the infrared analysis were:

1. Placing the dried sample into a small agate mortar and pestle and adding several drops of mineral oil and mixing thoroughly.
2. Placing a small amount of this mixture on a NaCl window, covering, and clamping into the sample holder.
3. Scanning the sample with an infrared spectrophotometer. The resulting spectra were used for determination of collector adsorption.

Infrared Adsorption Results

The analysis of collector-loaded minerals by infrared was accomplished by comparing the infrared spectra of pure minerals, pure collector, salts of the collector, and the loaded mineral.

Oleate Adsorption: Previous work had shown that there is a shift of an infrared adsorption peak of oleate when a salt is formed by oleic acid⁽⁷⁾. This shift can be seen in Figure 7, which shows the infrared adsorption of oleic acid and sodium oleate.

Next, a comparison was made between the pure minerals and those loaded with oleate. All three minerals were studied, and the collectors used were sodium oleate and oleic acid. The pH was set between 5.7 and 6.1. The

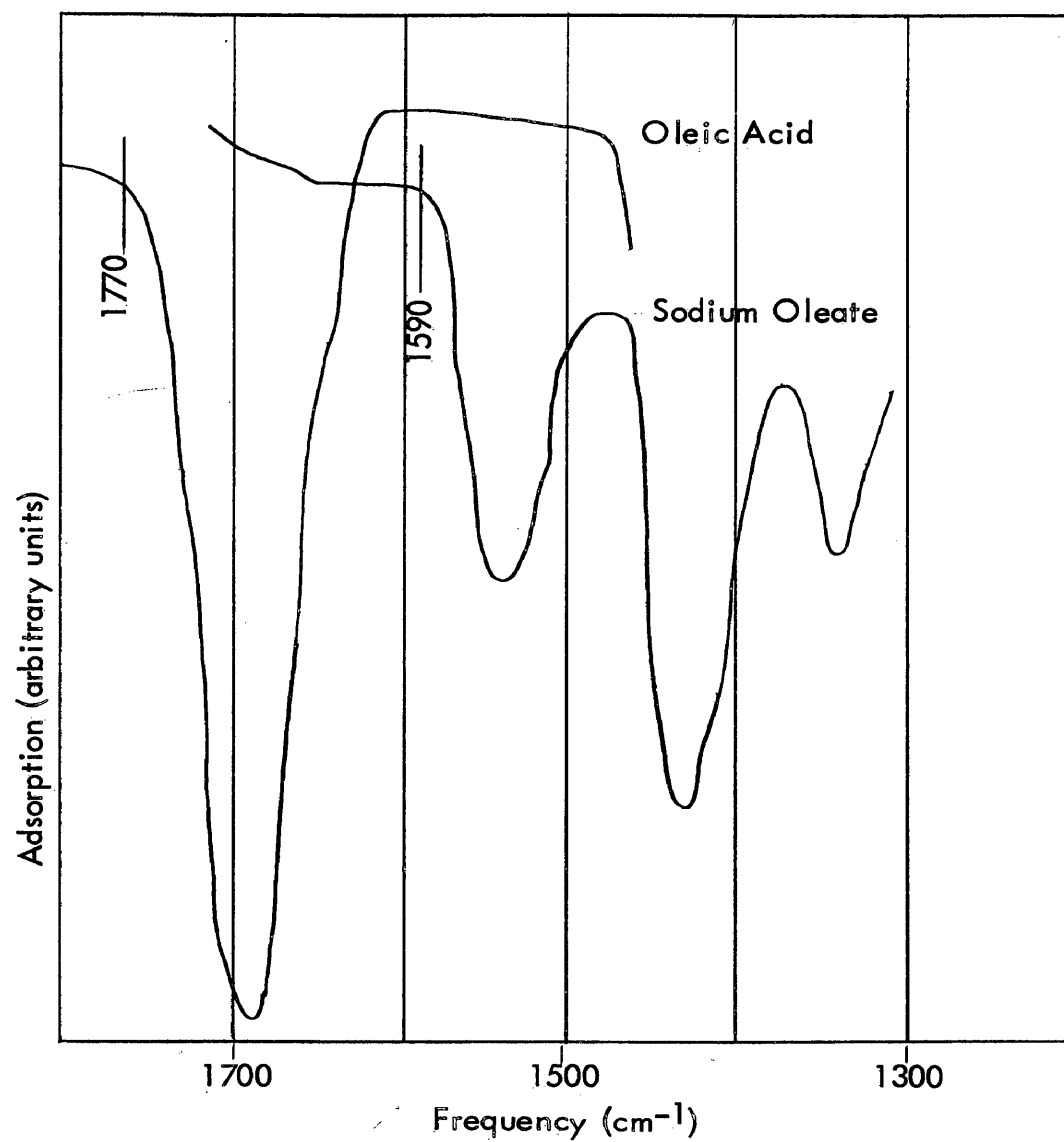


Figure 7: Infrared Adsorption vs Frequency for Oleic Acid and Sodium Oleate

spectra of the malachite-oleate system are shown in Figure 8. Note the shifts in the initial shoulders of the adsorption curves. There is a shift of the curve from 1540 cm^{-1} for the pure mineral to 1580 cm^{-1} for the loaded mineral. This shift suggests that oleate has been chemisorbed.

Figure 9 shows the infrared spectra of the cuprite-oleate system. A similar shift in the shoulder was observed for these curves which is an indication that the oleate was chemisorbed as the salt. The fact that the oleic acid was adsorbed as the salt indicates that the adsorbed salt is copper oleate. No adsorption peak was observed where oleic acid showed its characteristic peak when either cuprite or malachite were involved.

Figure 10 shows the chrysocolla-oleate system. In this figure the infrared adsorption scale has been expanded five-fold for the purpose of clarity. These curves show that neither oleic acid nor an oleate salt has been adsorbed. Further, the collector concentration used in this study was much greater than that used in flotation, but still no collector was adsorbed on the mineral surface.

Sulfonate Adsorption: Infrared analysis of adsorbed sulfonate has not been reported previously on any flotation system, which increases the difficulty of interpretation, since no frequency assignments have been made or shifts of frequency observed.

The infrared adsorption spectra of sulfonic acid, sodium sulfonate, and cupric sulfonate were obtained by means of the same procedure as that used in the oleate

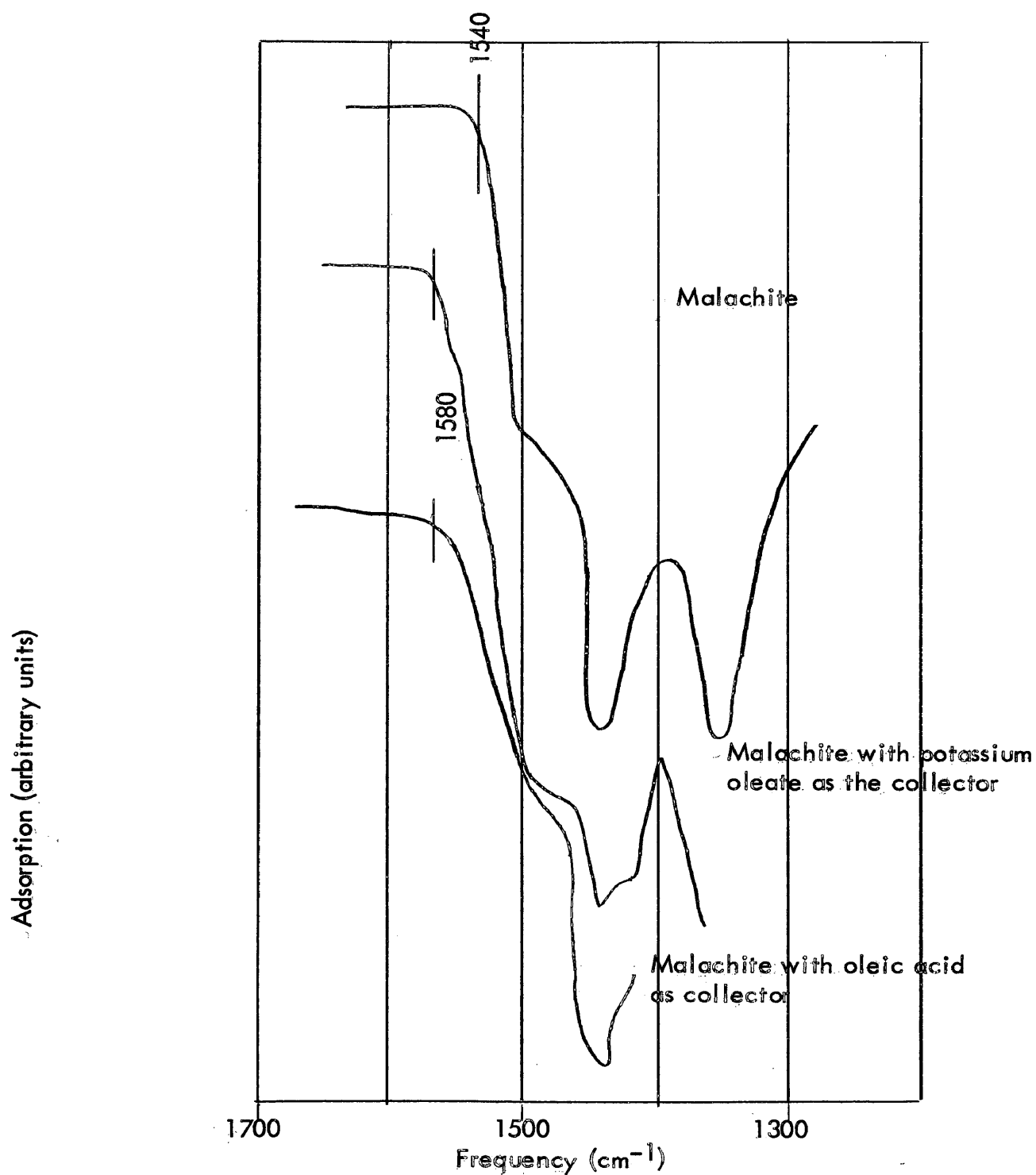


Figure 8: Infrared Adsorption vs Frequency for Malachite-Oleate System

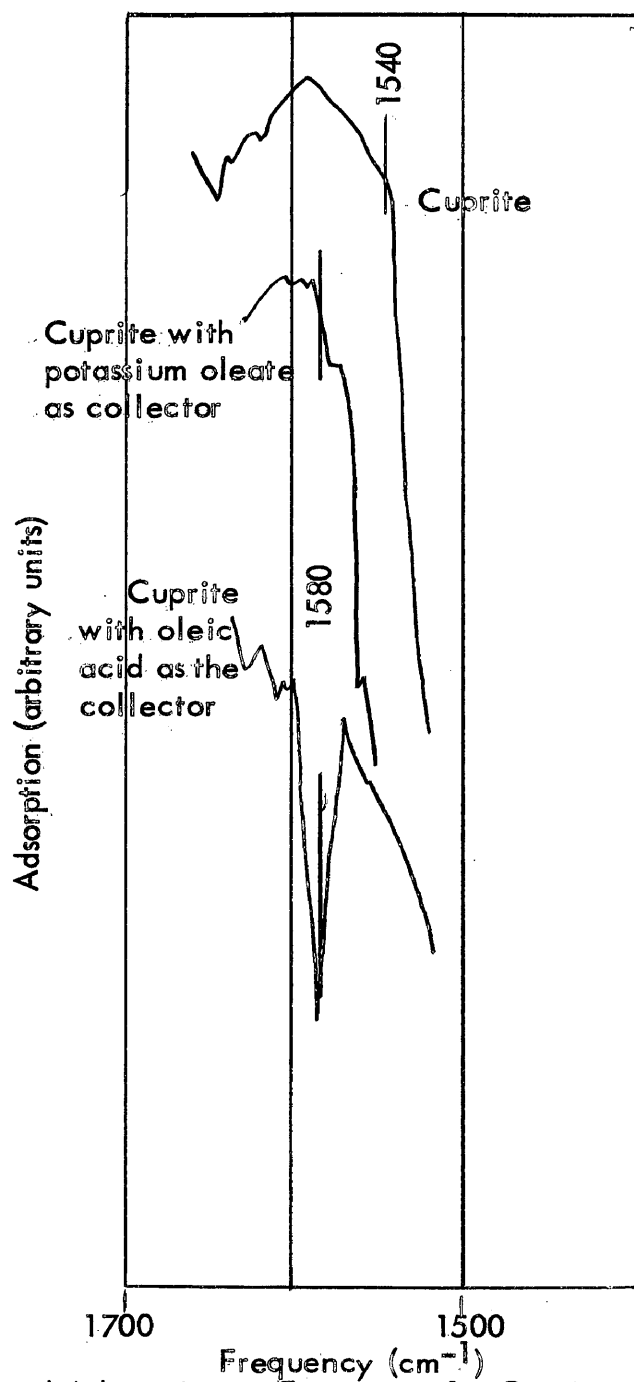


Figure 9: Infrared Adsorption vs Frequency for Cuprite-Oleate System

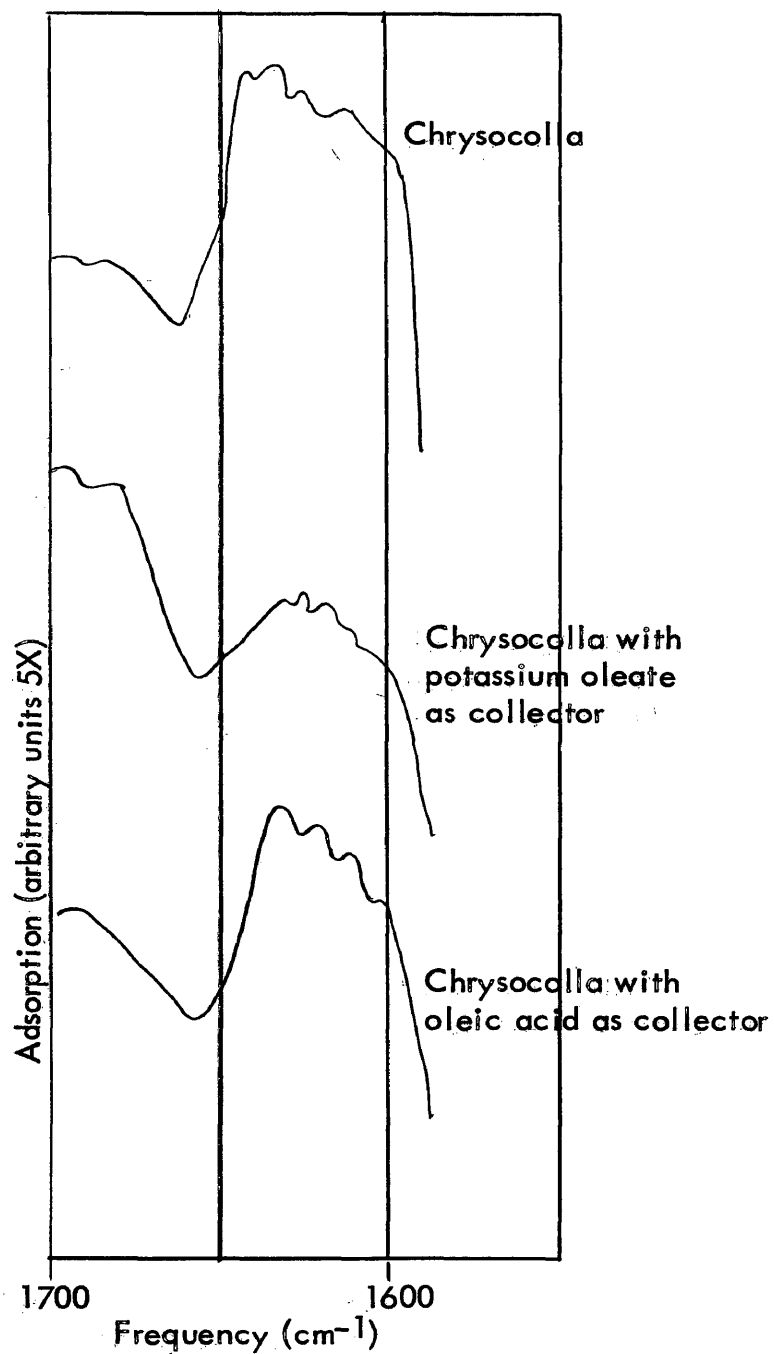


Figure 10: Infrared Adsorption vs Frequency for Chrysocolla-Oleate System

system. These data are shown in Figure 11. Note the weak double peak for sulfonic acid (1180 cm^{-1}), the absence of a double peak and frequency shift for sodium sulfonate, and the strong double peak and shift to lower frequencies (1140 cm^{-1}) for cupric sulfonate. The strong doublet and frequency shift were used to identify copper sulfonate on the mineral surfaces.

Malachite-sulfonate and cuprite-sulfonate infrared spectra are shown in Figures 12 and 13, respectively. In both cases a five-fold expansion of infrared adsorption scale was used. The doublet appeared in both cases at the expected frequency of 1140 cm^{-1} , which indicates the formation of copper sulfonate on the mineral surface.

The chrysocolla-sulfonate system shows no indication of any adsorption on the mineral surface (see Figure 14).

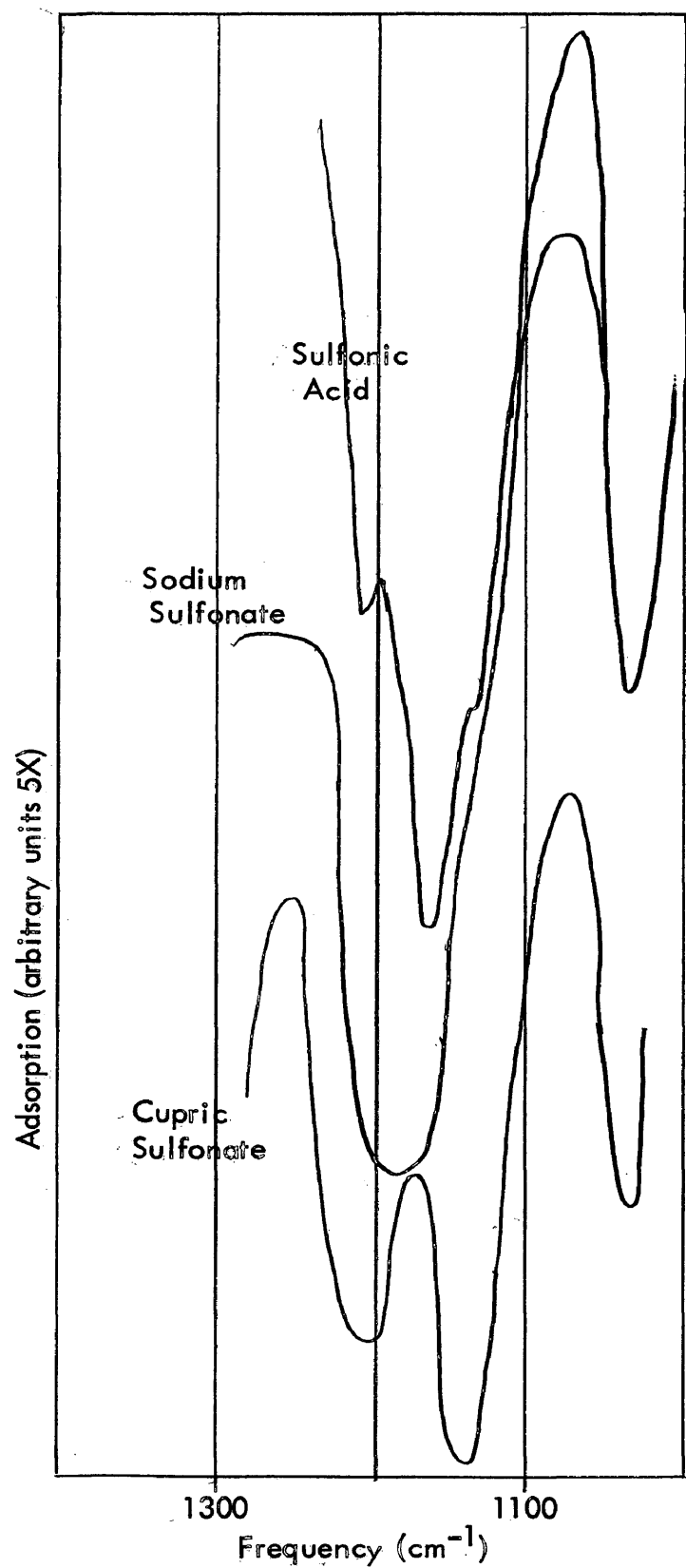


Figure 11: Infrared Adsorption vs Frequency for Sulfonic Acid, Sodium Sulfonate, and Cupric Sulfonate

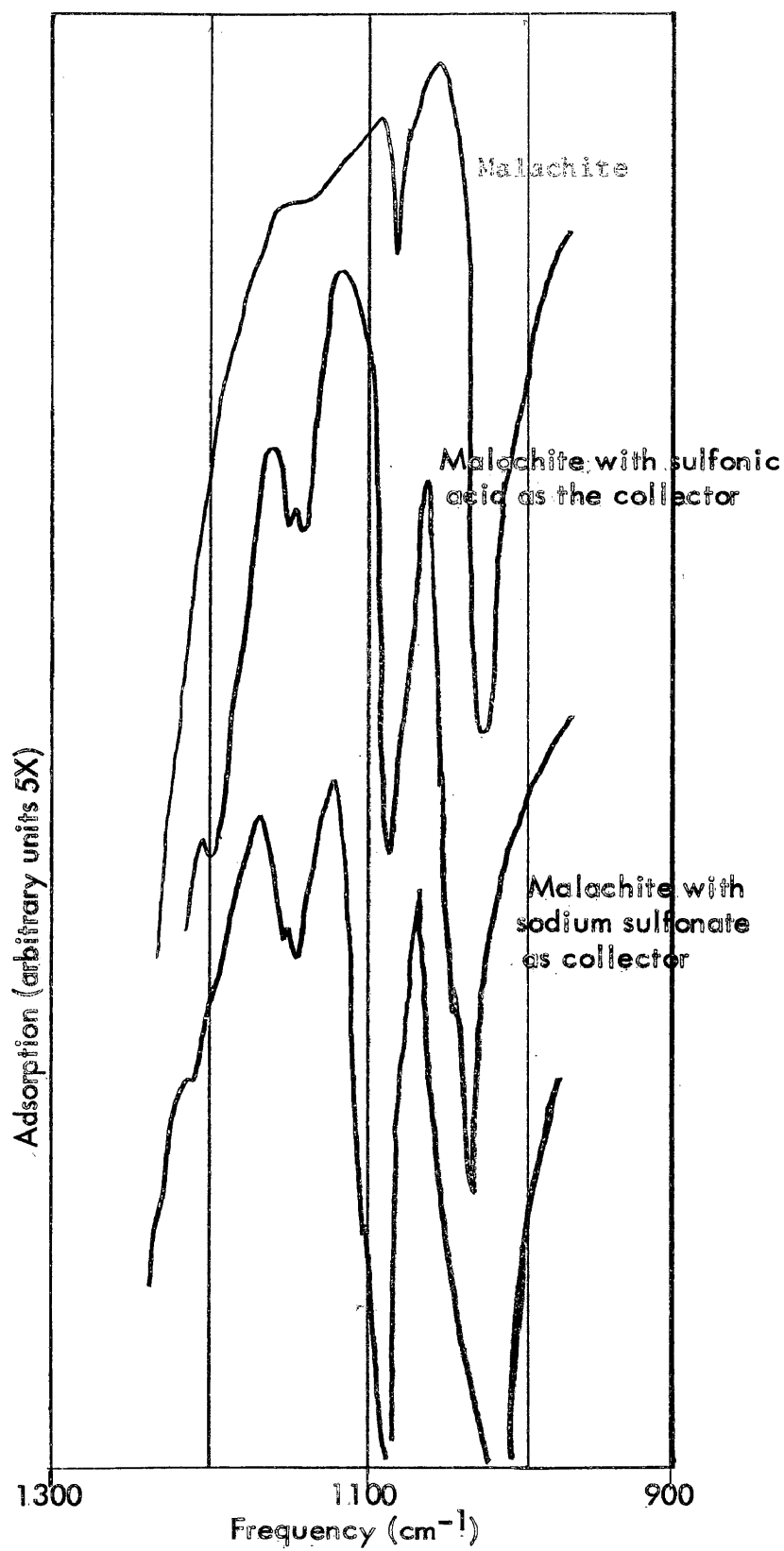


Figure 12: Infrared Adsorption vs Frequency for the Malachite-Sulfonate System

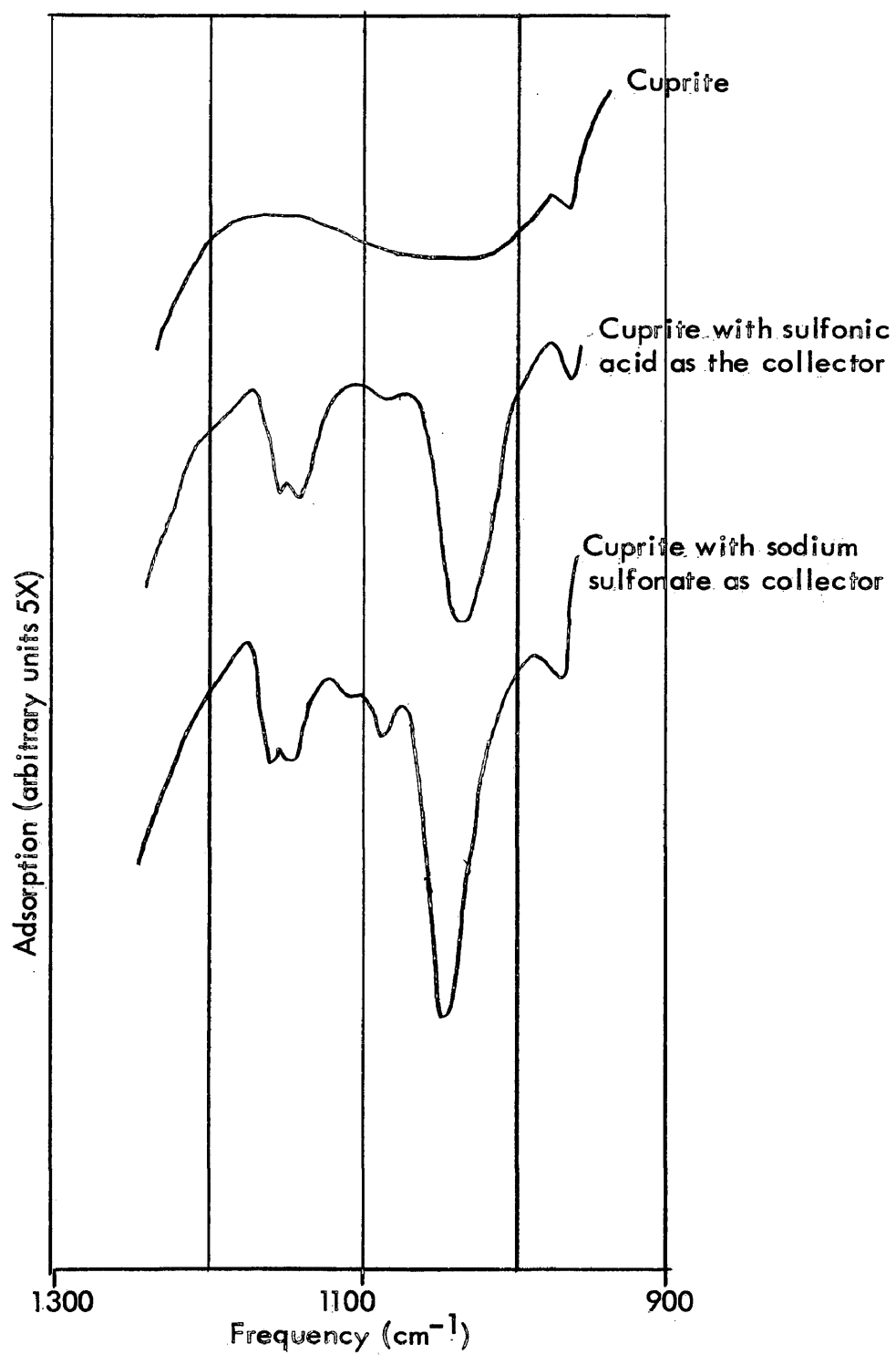


Figure 13: Infrared Adsorption vs Frequency for the Cuprite-Sulfonate System

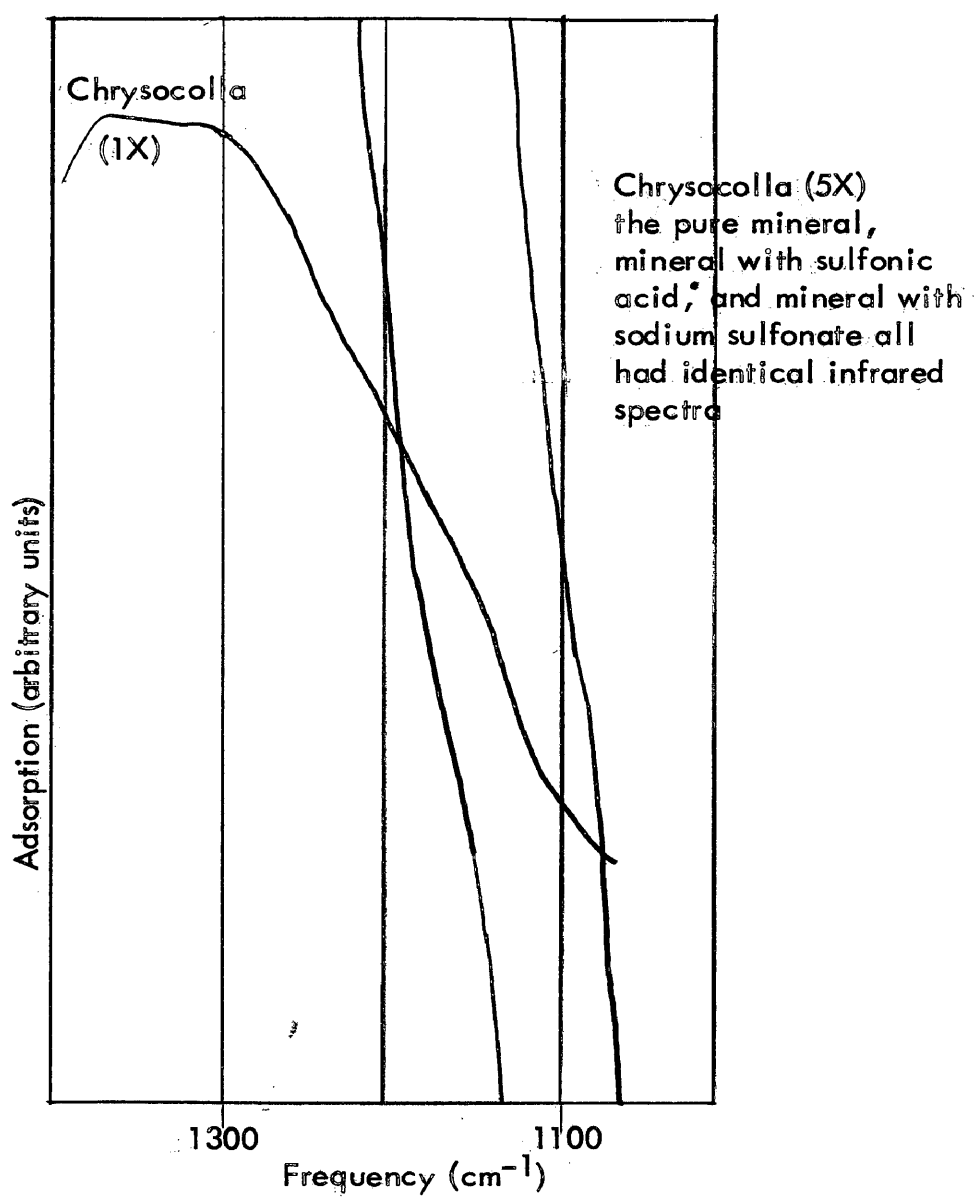


Figure 14: Infrared Adsorption vs Frequency for Chrysocolla-Sulfonate System

QUANTITATIVE COLLECTOR ADSORPTION EXPERIMENTS

Ultra-violet studies were used to obtain a quantitative measure of the amount of sulfonate adsorbed on each of the mineral surfaces.

Materials

The same reagents and minerals, used for the flotation experiments, were used in these studies.

Minerals: Samples of the same mineral were used in this study. They were, however, hand-ground with a porcelain mortar and pestle to -100+120 mesh size and then wet screened and deslimed with conductivity water.

Apparatus

A Beckman DK Spectrophotometer with hydrogen lamp was used to measure the ultra-violet absorption in the range of 260 to 220 mμ.

Procedure

The procedure employed can be divided into two parts. The first of these involves obtaining a standard curve. The second involves measuring the amount of flotation reagent adsorbed on the mineral surfaces.

In order to produce the standard curve of percent absorption as a function of concentration of sulfonate in solution, several different concentrations of sulfonate were prepared. The absorption of each of these solutions was measured from the spectra, some of which are shown in Figure 15. From these data, the standard curve shown in Figure 16 was produced.

Next, the adsorption of the collector on the various minerals was determined in the following manner:

1. A given volume of 1×10^{-5} M/l sulfonate was measured (in these cases, 100 ml).
2. The pH was adjusted to the value where maximum adsorption occurred, as determined from flotation data.
3. Two and one-half grams of mineral (-100+200 mesh) was added to the solution and agitated for 5 minutes.
4. The mineral was allowed to settle, and liquid samples were carefully collected by decanting.
5. The ultra-violet absorption of these samples was measured at 236 mμ.

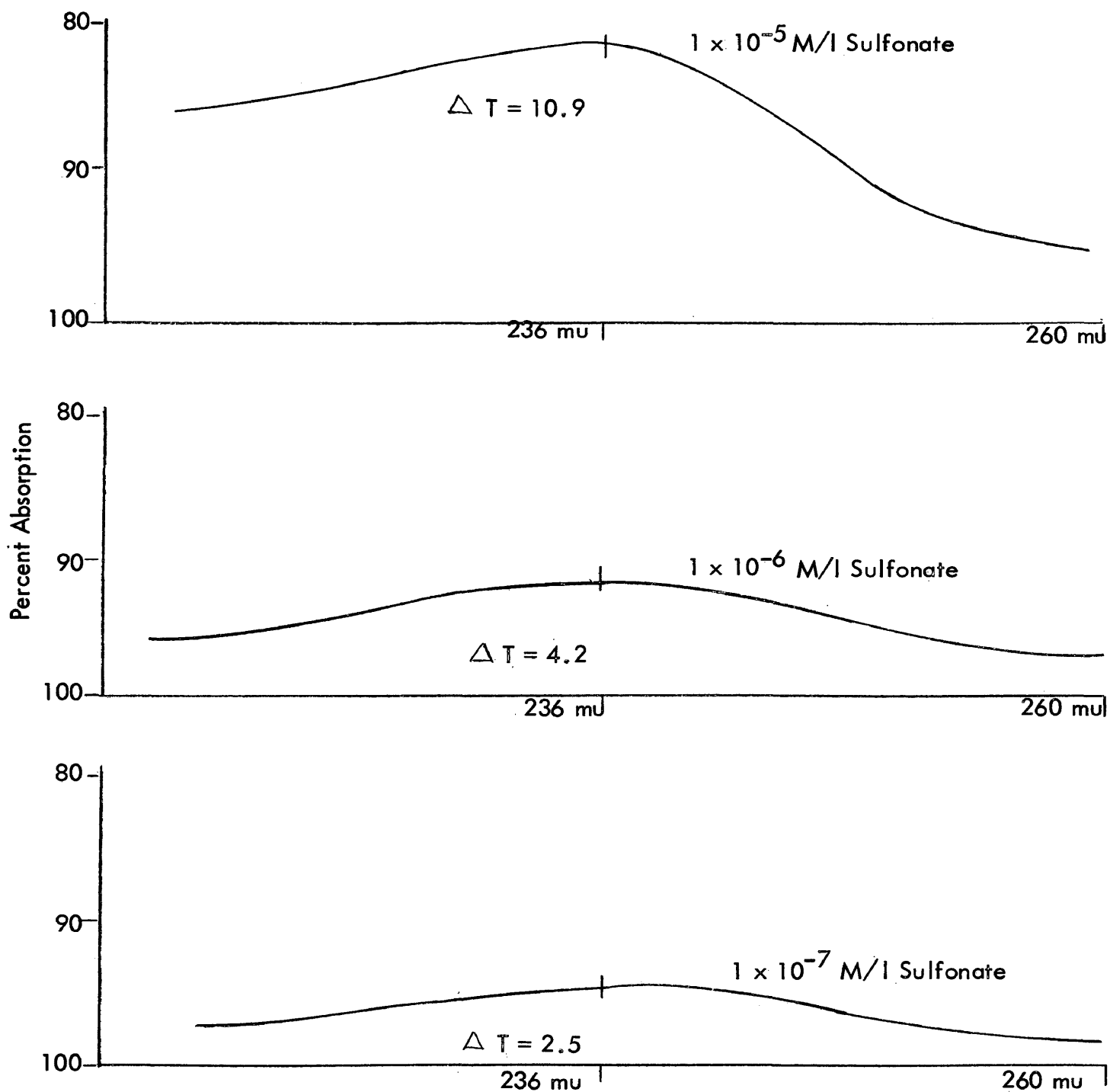


Figure 15: Percent Transmission vs Wavelength. Ultra-violet Spectra of Standard Sulfonate Solutions

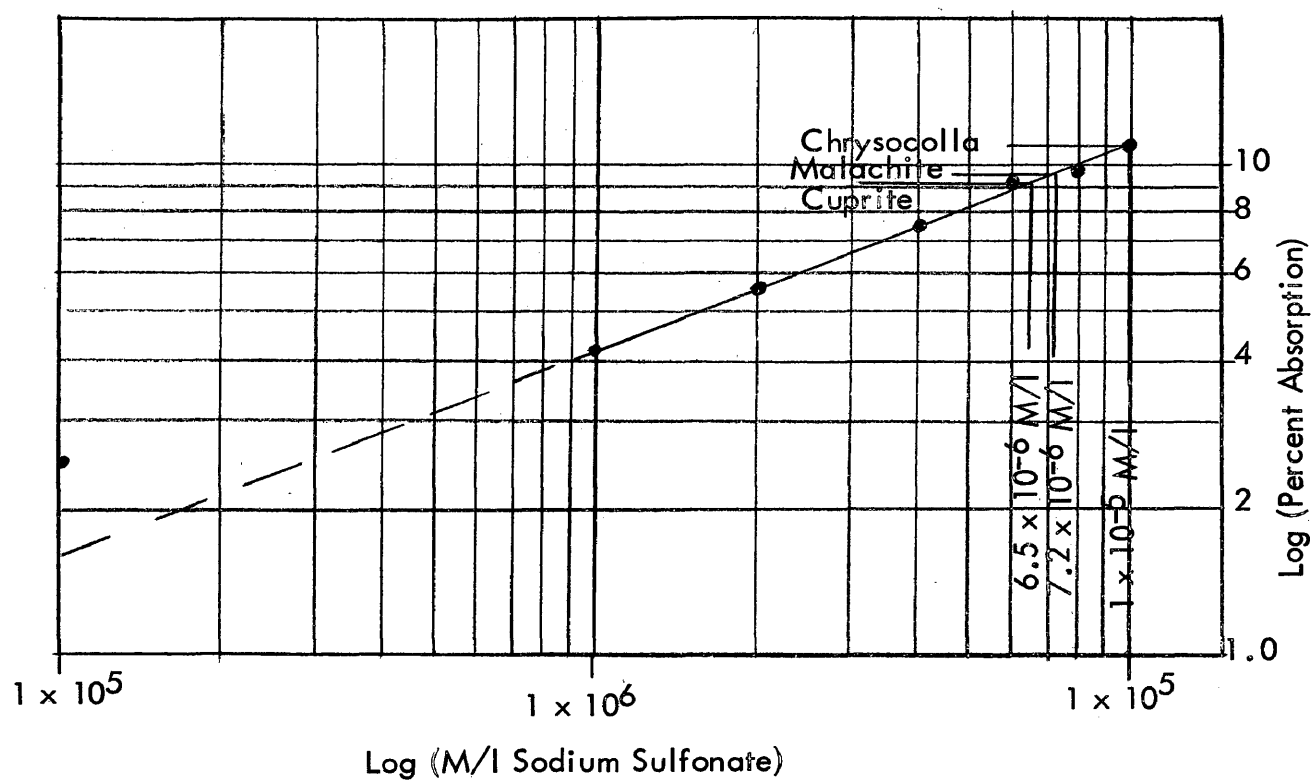


Figure 16: Log (Percent Ultra-violet Absorption at 236 mμ) vs
Log (M/I Sodium Sulfonate)

6. The measured ultra-violet absorption was then compared with the standard curve, and the sulfonate concentration in solution after contact with the mineral was determined.
7. The adsorption on the mineral surface was calculated from this ultra-violet absorption measurement and an estimate of the surface area of the mineral particles.

Results of Adsorption Studies

The adsorption spectra of the standard solutions are shown in Figure 15; the standard curve (Figure 16) was produced from these measurements.

The residual solutions were analyzed for sulfonate by ultra-violet techniques (absorption spectra are presented in Figure 17) and by the use of the standard curve. The absorption values of the residual solutions, which are plotted on the standard curve Figure 16, yield the final concentration of sulfonate in the residual solution. Then, by difference, the amount of sulfonate adsorbed on two and one-half grams of mineral can be calculated. These adsorption data are tabulated in Table 2.

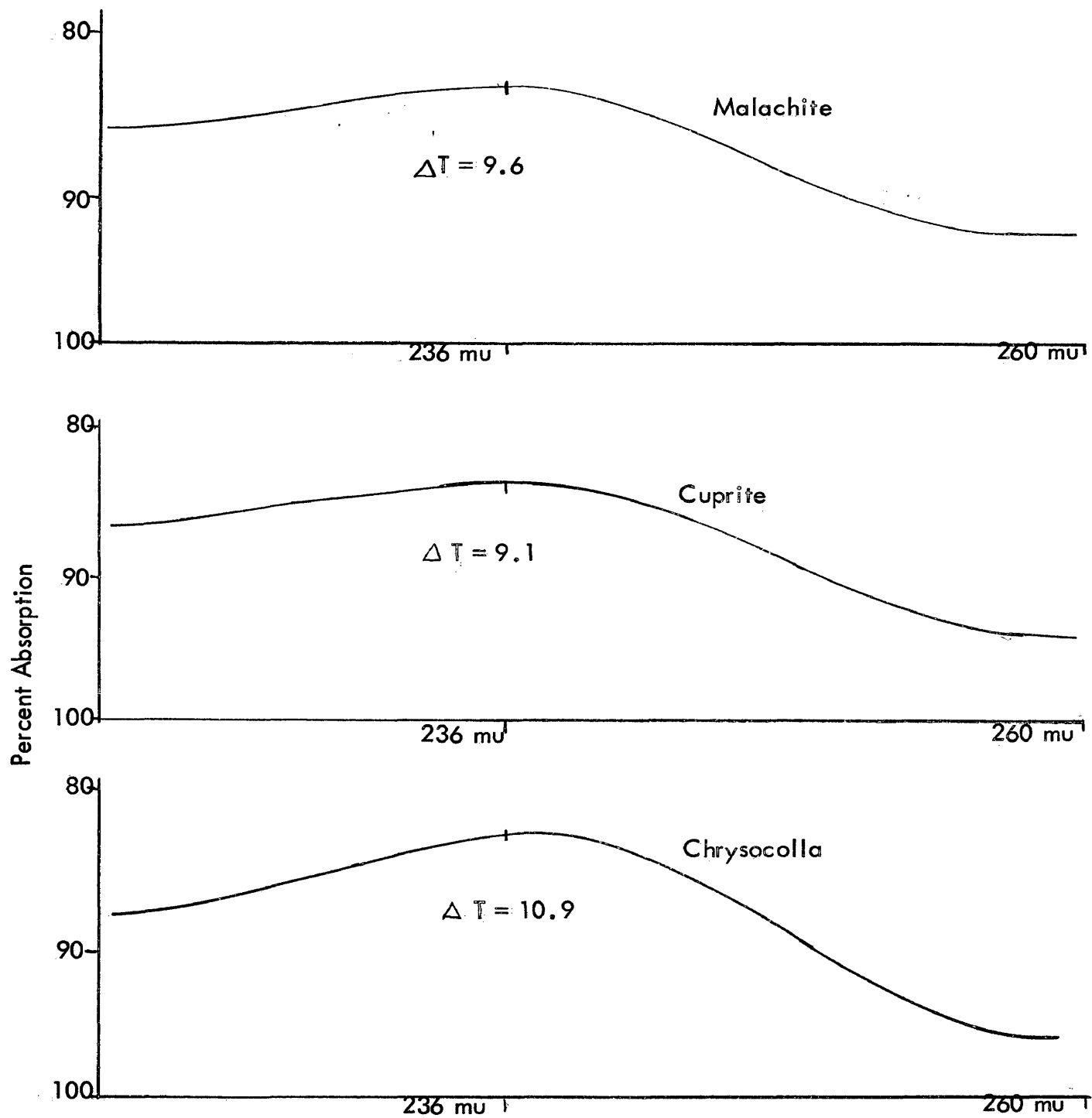


Figure 17: Percent Transmission vs Wavelength. Ultra-violet Spectra of Residual Solution from Mineral Contact

Table 2 – Mole of Sulfonate Adsorbed from 100 ml of
a 1×10^{-5} M/l Solution on 2.5 gm of Mineral

<u>Mineral</u>	<u>Mole Sulfonate Adsorbed</u>
Malachite	2.8×10^{-7}
Cuprite	3.5×10^{-7}
Chrysocolla	none

DISCUSSION OF RESULTS

In this section the observed results will be discussed and their significance pointed out.

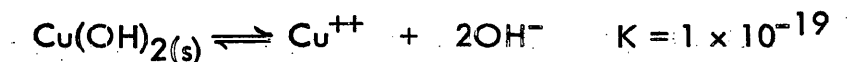
Flotation

The flotation work showed several features which warrant explanation; these are:

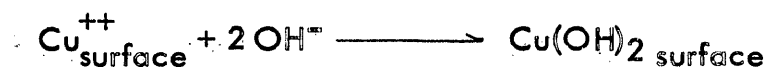
1. the depression of flotation at high values of pH,
2. the optimum value of pH for flotation observed with malachite,
3. the lack of flotation at low values of pH,
4. the lack of flotation of chrysocolla at any pH.

Flotation is directly affected by pH and ions in solution; this effect has been established in previous work^(4,6,10). To explain these flotation phenomena, principles of solution chemistry are used to suggest possible mechanisms responsible for flotation.

The depression of the copper oxide minerals at high values of pH is probably related to hydrolysis of cupric ion. This relationship can be seen from the equilibrium between $\text{Cu}(\text{OH})_2(\text{s})$, Cu^{++} and hydroxyl ions, which is as follows⁽¹¹⁾:



At high values of pH, it is obvious that for a nominal addition of Cu^{++} (1×10^{-4} M/l) to water, most of the copper ions will be precipitated as copper hydroxide. It can be expected that a similar reaction would take place at an ionized surface copper atom:



This would prevent the formation of a copper-collector compound at the surface; this compound is necessary for flotation.

At the surface, when a collecting agent is present in solution, there will be competition between:



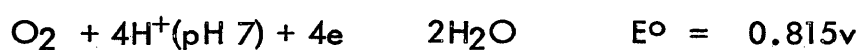
It is now just a matter of which of the two solid compounds are more stable under the conditions employed. The equilibrium constant for the hydroxide formation shows that it is very insoluble (stable) in the range above pH 9. The depression of copper oxide flotation in the high pH range is probably due to this hydroxide formation on the mineral surface.

The lack of flotation in the acidic region is probably due to different mechanisms for malachite and cuprite. The flotation response of malachite was poor in this region simply because it was dissolving. This rapid dissolution would prevent a stable surface for the formation of a collector layer, so flotation was depressed.

The observed optimum for malachite flotation shown in Figure 1 can be explained by considering the two causes of flotation depression just discussed. The peak is simply the point where mineral dissolution and the collector-hydroxide equilibrium effects are the most favorable for collection.

With cuprite the lack of flotation in the acidic region is quite different from the reason for malachite depression since cuprite is not readily soluble in weak (pH 2-4) hydrochloric acid.

Flotation is dependent upon the formation of an insoluble metal collector at the surface of the mineral. It was found to be impossible, with reasonable concentrations in aqueous media, to form an insoluble cuprous sulfonate. Flotation would then seem to be improbable for this mineral unless oxidation of surface copper ions occurs. Air introduced into the system during conditioning is the probable oxidant. The existence of the cupric surface ion can be inferred by the similar results obtained at high values of pH with malachite and cuprite. The following equations show the applicable oxidation-reduction equations⁽¹¹⁾:



Therefore, cuprite flotation probably occurs by: 1) the oxidation of the surface cuprous ion to cupric ion and 2) the formation of a metal collector salt at the mineral surface.

Non-flotation of chrysocolla is explained by the lack of collector adsorption on the mineral surface. This was indicated by I.R. examination of the surface of treated chrysocolla and by analysis of solution after equilibration. The actual reason for this inability of the collectors to attach to the surface is not known at the present time. It may be due to the lack of ionizable surface copper atoms, in other words, the insoluble nature of the mineral.

One other point brought out in the flotation work is that the floatable copper minerals can be activated by a suitable metal ion in solution in a pH region where the mineral is normally depressed and the ion is undergoing hydrolysis. This extended pH range of floatability is due to the partially hydrolyzed metal ion combining with a collector ion to produce an insoluble metal-hydroxy-sulfonate. It is postulated that this complex molecule is adsorbed on the mineral by hydrogen bonding through the hydroxyl ligand^(4,6).

The inability of this mechanism to float chrysocolla is rather outstanding. Many chemically inert minerals can be floated in this manner, so it is very surprising that it fails on chrysocolla^(5,6,12). This failure could be due to the amorphous character of the mineral preventing adsorption. Surface characteristics, in general, are believed to be responsible for this behavior. The reasons

for this inability to float chrysocolla by activation with metal ions cannot be explained at present.

Adsorption Mechanism

In the flotation work it was stated that copper sulfonate or copper oleate was formed on the mineral surface. This infrared analysis was performed to determine the actual mechanism of adsorption and the species adsorbed.

The method used to obtain the infrared spectra was a solid-oil mull technique. This technique introduced some adsorption peaks that covered the peaks that were to be observed. However, the initial shoulder where the curve broke was characteristic and could be used for analysis. This interference was true in general for the oleate systems. However, the sulfonate characteristic peaks were on a broad slope of the mineral-oil spectra and could be distinguished.

The two cases where adsorption of oleate was observed showed a shoulder at 1580 cm^{-1} . This frequency is much too low to be oleic acid, and is also shifted to a lower value than sodium oleate, indicating that this adsorbed oleate is a salt of copper^(7,8). One other feature which would indicate that the collector is adsorbed as a salt of copper is that with both the acid and sodium salt form of the collector, the spectra produced was the same and different than that of either the oleic acid or sodium oleate. These characteristics of the curves and the frequency shifts show that the mechanism of adsorption is probably the

formation of the copper oleate salt or the mineral surface, or in other words, chemisorption.

In the sulfonate system, the characteristics of the infrared spectra of the various forms of sulfonate are diagnostic. The sulfonic acid shows a weak doublet with the major peak at 1160 cm^{-1} . The spectra of sodium sulfonate shows no doublet, and has a major peak at 1180 cm^{-1} . The copper salt has a strong doublet, and it has a major peak at 1140 cm^{-1} . It is these peak doublets and peak frequencies that were used to analyze the spectra and show the presence of copper sulfonate. The doublet is probably due to a dimer, a hydrogen-bonded dimer in the case of the acid and a double sulfonate dimer in the case of the copper salt.

Where flotation occurred (malachite and cuprite), the characteristic doublet was present, and the major peak frequency was 1140 cm^{-1} . These data indicate that the mechanism is chemisorption and that copper sulfonate is formed at the mineral surface.

Chrysocolla showed no adsorption, physical or chemical, of any of the sulfonate species.

One other fact is that the form (acid or salt) of the collector, prior to flotation, does not change the adsorbed species or adsorption mechanism. It would have been possible for the acid form to be hydrogen bonded to the surface

of the mineral. This hydrogen bonding was definitely not observed in the case of oleic acid or sulfonic acid.

Quantitative Collector Adsorption

The flotation work showed that a collector was adsorbed on the mineral. Ultra-violet analysis was used to estimate the extent of adsorption of the collector. To make this measurement two factors had to be determined: a) the amount of collector removed from solution and b) the surface area of the particular solid. Ultra-violet was used to determine the quantity of sulfonate adsorbed. The area could not be measured, so it was calculated from the assumed average particle size, mineral specific gravity, and weight of the sample, and an assumed shape factor of 1.43 was used. The area determination has a probable error; therefore, the adsorption value calculated has the range of values given in Table 4.

Table 4 - Adsorption Density of Sulfonate on Various Copper Oxide Minerals

<u>Mineral</u>	<u>Mole Sulfonate per Square Centimeter</u>
Malachite	$4.3 \times 10^{-10} \pm 0.2 \times 10^{-10}$
Cuprite	$7.4 \times 10^{-10} \pm 0.2 \times 10^{-10}$
Chrysocolla	none

SUMMARY AND CONCLUSIONS

In the preceding work, several facts about the chemistry of copper oxide flotation become apparent. These are summarized in the following conclusions:

1. Malachite and cuprite float by chemisorbing the collector on the surface. Chemisorption is accomplished by the formation of an insoluble copper-collector compound on the mineral surface.
2. The mechanism of metal-ion activation is applicable to malachite and cuprite flotation.
3. Complete hydrolysis of the mineral surface cation sites prevents flotation.
4. The concentration of chemically adsorbed sulfonate is between 10^{-9} and 10^{-10} mole per square centimeter.

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