FLOTATION CHARACTERISTICS

OF

CERTAIN COPPER OXIDE MINERALS

by

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ABSTRACT

Microflotation studies with chrysocolla, malachite, and cuprite were performed to determine the response of these copper oxide minerals to flotation with potassium octyl hydroxamate and mercaptobenzothiazole as collectors. Surface charge measurements and infrared analyses were undertaken to establish the mode of collector adsorption.

The experimental results indicate that:

1) the collectors are chemisorbed onto the mineral surfaces;
2) potassium octyl hydroxamate and mercaptobenzothiazole behave in an analogous manner in the systems considered; and
3) the pH range of copper oxide mineral floatability is limited, especially in the case of chrysocolla.

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ACKNOWLEDGMENTS

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INTRODUCTION

Five general methods are available for the flotation of copper oxide minerals[1]:

1) The desired mineral is sulfidized and then floated with sulfhydryl collectors such as amyl xanthate[1] or mercaptobenzothiazole[2]. Such a process is rather delicate due to the need for proper sulfide addition and the timing of the conditioning and flotation stages. The recovery of oxides (cuprite and tenorite) exceeds that of the carbonates (malachite and azurite) while chrysocolla is not recovered.

2) Carboxylates, such as sodium oleate, are used in conjunction with gangue depressants to float the copper minerals. The problems associated with this method are not to float the desired minerals, but to prevent metal-ion

activation of the gangue minerals[3].
Rickard[4] reported good recoveries for malachite, fair recoveries with cuprite, and poor results with chrysocolla.

3) Sulfhydryl collectors, such as xanthates, are satisfactory collectors for the carbonate minerals. However, collector concentration has to be relatively large due to the microcrystalline nature of the minerals. Such a process lacks economic attractiveness and chrysocolla fails to respond to the collector action.

4) The ore is treated to precipitate copper and then flotation methods are used to produce a copper concentrate. Two processes which fall into this category are:

   (a) The leach-precipitation-flotation[5,6] process whereby the ore is leached with acid to dissolve the oxide minerals, and then reacted with iron to cement the copper. The pulp is passed through a flotation circuit to recover the copper and any sulfide minerals present. The disadvantages of such a process are

(i) acid consumption,

(ii) the cost of iron, and

(iii) the cost of the leach plant.

Franklin[7] reported that the L.P.F process capital costs are double those encountered in an equivalent conventional flotation process.

(b) In the segregation process[8], oxide-silicate ores are heated to 790 $\pm$ 30°C with sodium chloride and a reductant, such as coal. The copper minerals are converted to metallic copper, which is recovered by flotation. The objections to this process are[9]:

(i) heating the ore to 790°C is expensive;

(ii) the process is not satisfactory for all copper oxide ores; and

(iii) the segregation plant is costly.

5) Miscellaneous reagents that will chemisorb onto the oxide mineral surfaces can be used. Rickard[4] reported limited success with malachite and cuprite when using a high molecular weight

sulfonate; chrysocolla, however, showed no response. Peterson et al[10] succeeded in floating chrysocolla with potassium octyl hydroxamate and indicated that chemisorption was involved.

Oxide copper mineral deposits contain varying amounts of chrysocolla, and poor copper recoveries are generally associated with the lack of flotation response from this mineral. Of the treatment methods available, the use of collectors that chemisorb onto the mineral surfaces during flotation would, apparently, overcome most of the difficulties encountered in the preceding methods because:

1) selectivity becomes possible,
2) collector concentrations are reduced,
3) the process becomes straightforward,
4) all copper oxide minerals should respond to the treatment, and
5) the most economical methods for copper mineral concentration involve conventional flotation procedures.

The objectives of this investigation therefore became:

1) to determine the flotation characteristics of some copper oxide minerals (including chrysocolla) with potassium octyl hydroxamate and mercaptobenzothiazole as collectors; and

2) to establish the mechanism of collector adsorption on the minerals by using surface charge measurements and infrared spectrometry.

MATERIALS AND PROCEDURE

The following materials, apparatus, and procedures were used during this investigation.

Mineral Samples

The copper oxide minerals were purchased from Minerals Unlimited, Berkeley, California, and are listed below:

1) Chrysocolla ($CuSiO_3 . 2H_2O$) from New Mexico,
2) Malachite ($CuCO_3 . Cu(OH)_2$) from the Republic of Congo, and
3) Cuprite (Cu_2O) from Arizona.

Sample Preparation

Each of the above minerals was crushed in a porcelain mortar and pestle to -8 mesh and hand sorted to remove most of the obvious contaminants. The samples were then further reduced in size in the mortar. Various sizes were split from the pulverized samples and reserved for the purposes indicated in Table 1.

Table 1: Size Fractions Prepared for Various Uses.

Size Fraction	Purpose
-150 + 200 mesh	Flotation experiments.
-200	Mineral analysis.
-325	Electrophoresis and Infrared experiments.

Mineral Analyses

The analyses performed were two-fold:

1) qualitative analyses were undertaken using an emmission d-c arc technique[11] in the 2300 to 3600 angstrom region of the spectrum; and
2) quantitative chemical analyses were performed to determine the amounts of the major constituents and impurities detected during the spectrographic analyses.

The quantitative determination of the trace impurities was deemed unnecessary. The experimental techniques used during the mineral analyses are outlined in Appendix 1.

The chemical compositions of the minerals are reported in Table 2. A comparison of the theoretical and actual copper are silicon contents of the minerals appears in Table 3.

Table 2: Chemical Analyses of the Minerals used.

Element	Chrysocolla	Malachite	Cuprite
Copper	24.41	55.67	83.49
Silicon dioxide	54.78	1.34	0.72
Iron	0.14	0.14	0.12
Aluminum oxide	2.04	0.28	0.65
Calcium	0.09	Nil	Trace
Magnesium	0.04	0.03	0.01
Cobalt	Nil	0.10	Nil
Manganese	Trace	Trace	0.01
Lead	Nil	Nil	0.09
Bismuth	Nil	Nil	0.04
Beryllium	Trace	Trace	Nil
Phosphorus	Nil	Trace	Nil
Molybdenum	Trace	Nil	Trace
Silver	Nil	Nil	Trace
Zinc	Nil	Nil	Trace

Table 3: Copper and Silicon Content of the Minerals used.

Mineral	Theoretical Analysis		Actual Analysis	
	% Copper	% Silicon	% Copper	% Silicon
Chrysocolla	36.1	16.0	24.41	25.58
Malachite	57.5	--	55.67	0.63
Cuprite	88.8	--	83.49	0.34

Water

Conductivity water was used in all of the experimental work. Water, distilled from a Barnstead Still, was passed through two columns of anion-cation exchange resin (Amberlite MB-3).

Reagents

The reagents used as collectors were:

1) potassium octyl hydroxamate supplied by the Archer Daniels Midland Company; and
2) mercaptobenzothiazole (trade names: Aeropromoter 404 and Flotagen) supplied by the American Cyanamid Company.

Two frothers were used:

1) concentrated amyl alcohol in the flotation experiments conducted at elevated temperature; and

2) a 1:25 aqueous solution of Dowfroth 250 for flotation at ambient temperature.

The pH was adjusted with aqueous solutions of analytical grade hydrochloric acid and potassium hydroxide.

Commercial nitrogen gas was used to procure flotation; it was cleaned by washing it with an aqueous potassium hydroxide solution and by passing it through a column of Ascarite. This treatment removed carbon dioxide and saturated the gas with water vapor.

Microflotation Apparatus

The apparatus used in all of the flotation experiments allowed for a constant volume of purified nitrogen, under almost constant pressure, to be passed through a microflotation cell[12]. The small glass cell used in this investigation was constructed to hold 125 $\pm$ 5 ml of pulp (Figure 1).

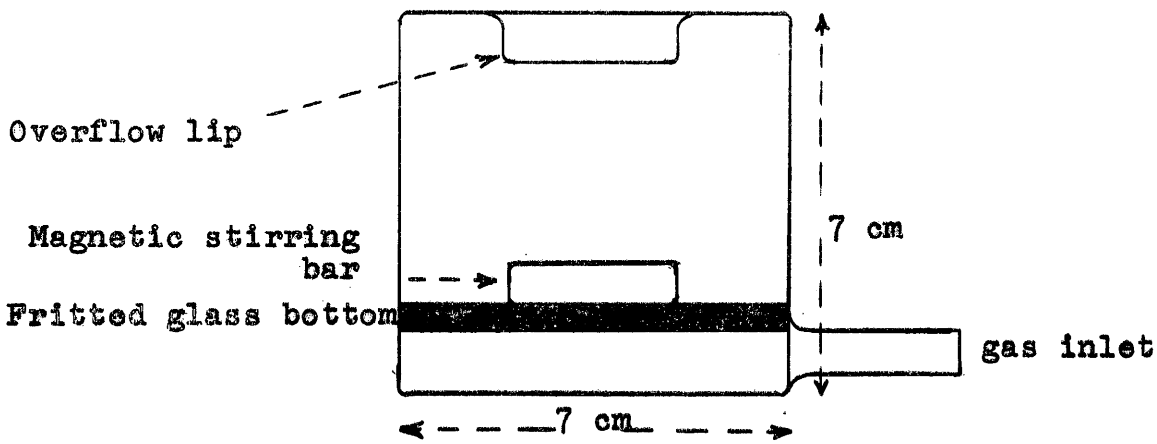


Figure 1: Schematic Diagram of Microflotation Cell.

The cell has a fritted glass bottom (with a 60-micron average pore size) for gas introduction. Controlled agitation was obtained with a variable speed magnetic stirrer and a teflon-coated stirring bar.

Nitrogen admittance to the system was controlled with a regulator valve, a water manometer, a constant head reservoir, and a gas measuring burette (by water displacement).

The usefulness of this type of apparatus lies in its ability to float small charges of pure minerals in a system free from metallic contaminants. Furthermore, operation variables such as flotation time, gas flow rate, and agitation rate, can be closely controlled. A schematic diagram of the microflotation apparatus appears in Figure 2.

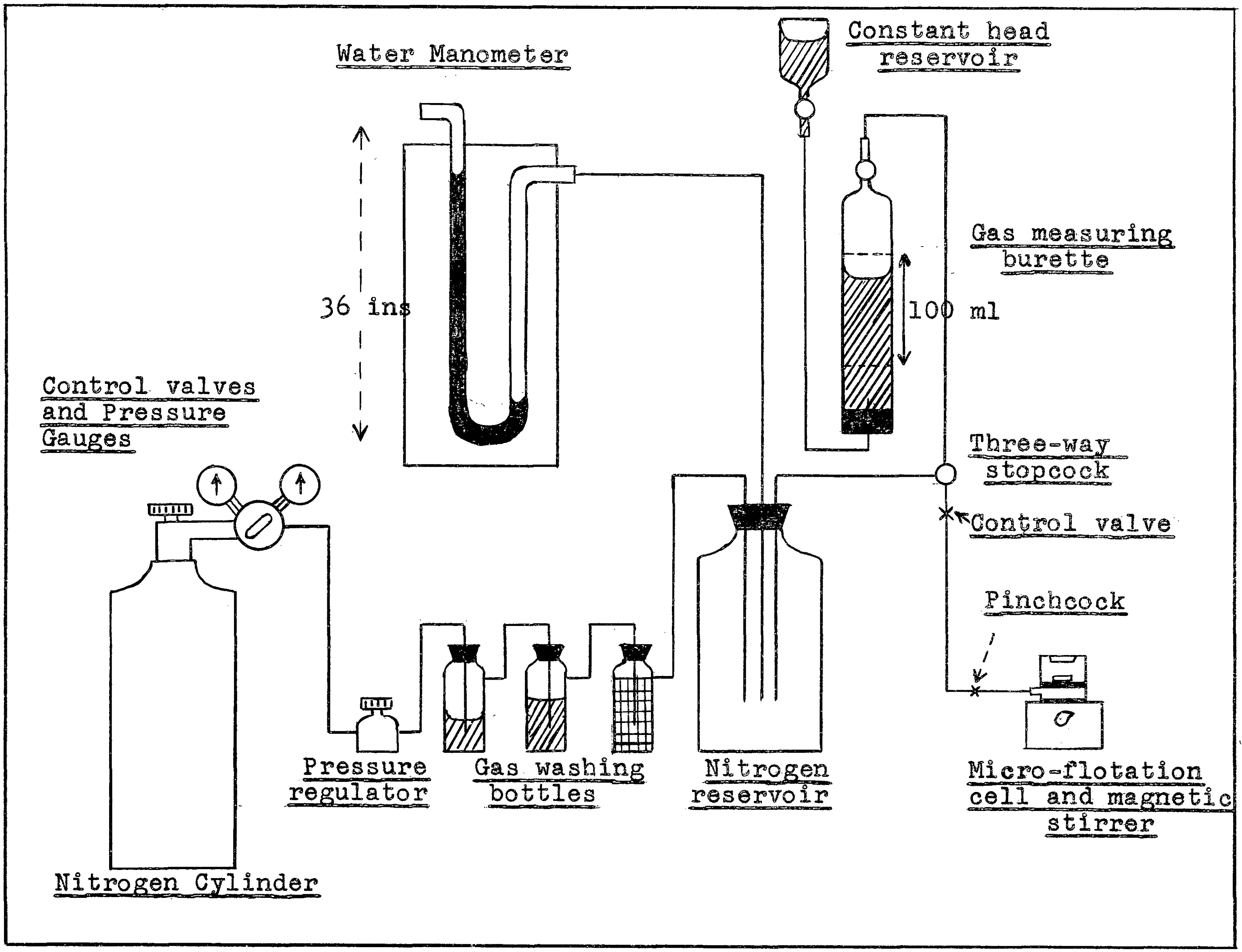


Figure 2: Schematic diagram of Micro-flotation Apparatus.

Flotation Procedure

Flotation experiments were conducted at ambient and elevated temperatures with the following procedure:

1) A predetermined volume of conductivity water (at ambient temperature or 78 $\pm$ 2°C) was combined with a measured volume of aqueous collector solution and transferred to the flotation cell.
2) The pH value of the system was adjusted to a predetermined value with hydrochloric acid or potassium hydroxide solution.
3) A 2½ gram sample of sized mineral was deslimed and transferred to the cell.
4) The agitation rate was adjusted to just prevent the settlement of particles to the cell bottom, and maintained at this setting for all the tests involving a given mineral.
5) The pulp was conditioned for 3 minutes, with regular addition of acid, or alkali, to maintain the pH near the desired value.
6) The pulp temperature was measured, termed the <u>flotation temperature</u>.
7) The pH of the pulp was measured, termed the <u>flotation pH</u>.

8) Four drops of frother were added prior to the passage of 100 ml of nitrogen through the pulp in 1 minute. The froth was collected during this period.

9) The final temperature and pH of the system were measured to check against any excessive pH or temperature changes.

10) The flotation products were transferred to 250-ml beakers and washed with hot water to remove excess reagents. The products were then dried and weighed.

11) The flotation cell frit was thoroughly cleaned with 1:1 aqueous nitric acid solution and hot water before all flotation tests.

12) Flotation recoveries were calculated from the relationship:

$$\%\ \text{recovery} = \frac{(\text{concentrate weight}) \times 100}{(\text{weight concentrate} + \text{tails})}$$

<u>The Riddick Zeta Meter</u>

The Zeta Meter[13] used in all the electrophoresis experiments permitted the determination of the electrophoretic velocity of suspended mineral particles at various pH values. The electrodes were immersed in an aqueous suspension of the mineral particles, and the velocities of discrete particles near the appropriate counting line were determined.

The Helmholtz-Smoluchowski equation used for determining the zeta potential of colloids and suspensoids is as follows:

Z.P.	=	zeta potential in esu.
	=	$\frac{(E.M.)4\pi V_t}{D_t}$, where
V_t	=	viscosity of supporting fluid in poise
D_t	=	dielectric constant of the fluid
E.M.	=	electrophoretic mobility cm/sec/esu volt
	=	$F/_H$, where
F	=	velocity of suspended particle in cm/sec
H	=	esu voltage per cm length of supporting fluid

The utility of the Zeta Meter lies in its ability to permit the determination of the zeta potential of mineral particles. The zero-points-of-charge of minerals can be determined from the pH versus zeta potential curves.

Electrophoresis Experiments

The electrophoresis experiments were conducted at ambient temperature with the following procedure:

1) A 200-mg sample of sized mineral was placed into a 250-ml beaker together with a teflon-coated stirring bar and 100 ml of water.

2) The pulp was conditioned for 5 min by controlled agitation with a variable speed magnetic stirrer. Hydrochloric acid or potassium hydroxide solution was added to maintain the pH near the desired value.

3) The stirring bar was removed, and the suspensoids were allowed to settle for the times indicated in Table 4.

Table 4: Settling Rates* and Applied EMF for Minerals used during Electrophoresis Experiments.

Mineral	Specific Gravity[14]	10 Micron Particle Settling Rate[15]	Settling Time	Applied EMF
Chrysocolla	2.41	0.41 cms/min	4 min	300 volts
Malachite	4.01	0.87	2	200
Cuprite	6.00	1.45	1	200

*The determination of settling rates is outlined in Appendix 2.

4) The temperature and pH of the suspension were measured prior to filling the electrophoresis cell with sample. Care was exercised to remove all air bubbles from

the system.

5) After the cell was placed on its holder, the 8x objective of the microscope was focused as indicated in Figure 3.

6) The alligator clips attached to the d-c output leads were connected to the cell electrodes. Ten discrete particles situated near the 8x counting line were then timed in their traverse of one ocular micrometer division (120 microns) under the influence of the applied EMF indicated in Table 4.

7) The d-c polarity switch was reversed and 10 particles were timed during movement in the opposite direction.

8) The temperature and pH value of the suspension were measured. The experimental temperature and pH were taken as the mean values of the initial and final readings.

9) Standard charts, based on the Helmholtz-Smoluchowski formula, were used to determine the electrophoretic mobilities and zeta potentials.

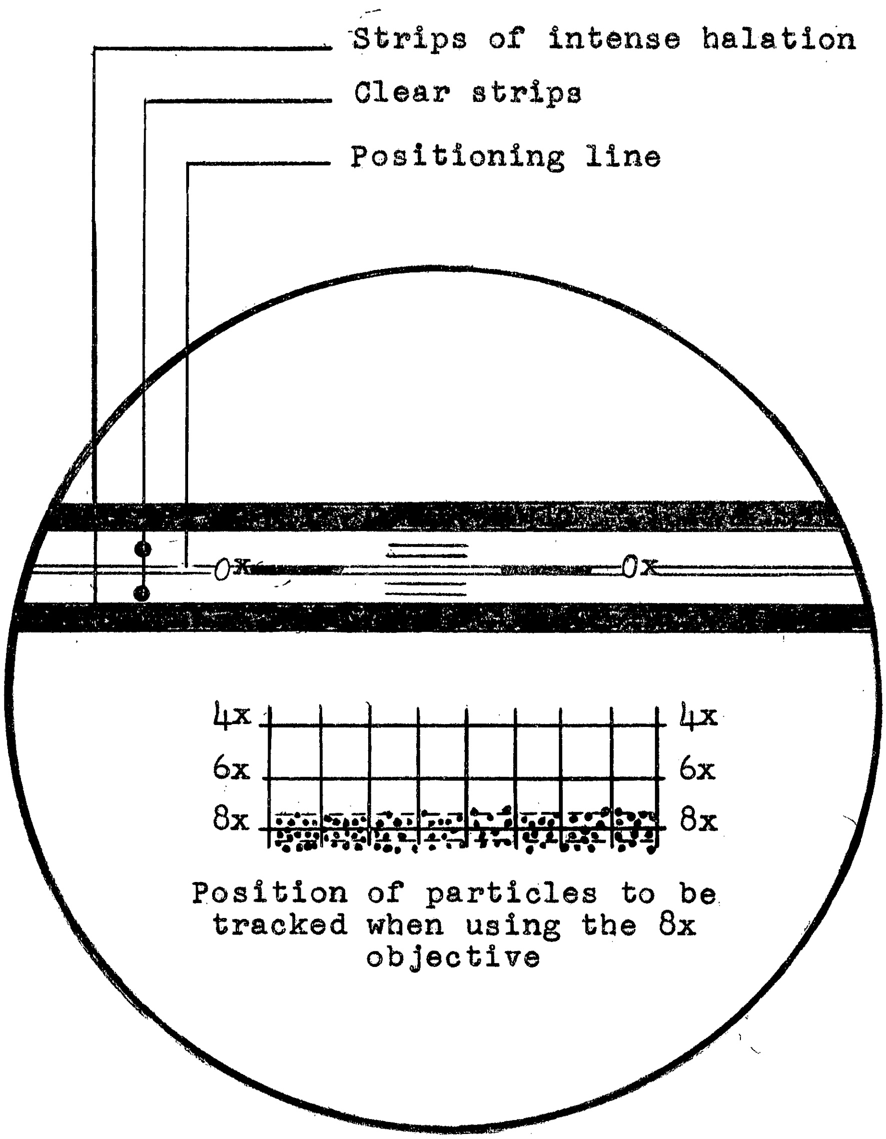


Figure 3: Schematic diagram of the focusing and positioning of the microscope and electrophoresis cell of the Zeta Meter.

The Infrared Spectrometer

Flotation reagents (collectors) are organic compounds containing various combinations of functional groups or sub-groups. Such sub-groups have characteristic absorption bands in the near infrared region of the spectrum, and their presence/absence can be determined from the nature of infrared spectra.

The Perkin-Elmer #521 Spectrometer, used in all the infrared absorption experiments, permitted the scanning of samples with successive infrared frequencies to determine the presence/absence of certain species on the mineral surfaces.

Infrared Absorption Experiments

The mineral samples and chemical compounds were prepared according to the following procedure:

1) Samples of -325 mesh minerals were ground in a mechanical mortar and pestle until 20 gm had been pulverized. The grinding rates are indicated in Table 5.

Table 5: Ceramic Mortar Charges and Grinding Rates of the Minerals used.

Mineral	Specific Gravity[14]	Ceramic Mortar Charge	Grinding Rate
Chrysocolla	2.41	3.0 gm	1.00 gm/hr
Malachite	4.01	5.0	1.66
Cuprite	6.00	7.5	2.49

2) 20-gm samples of the pulverized materials were slurried with 900 ml of water and allowed to settle for the periods indicated in Table 6.

Table 6: Settling Rates* for the Minerals used during Infrared Experiments.

Mineral	Specific Gravity[14]	5 Micron Particle Settling Rate[15]	Settling Time
Chrysocolla	2.41	0.10 cm/min	110 min
Malachite	4.01	0.22	55
Cuprite	6.00	0.36	31

*The determination of settling rates is outlined in Appendix 2.

3) The supernatent suspensions were decanted and saved for the infrared experiments. The settled materials were transferred to weighed 250-ml beakers prior to drying and weighing.
4) The slurry densities were determined by difference and are recorded in Table 7. The method of slurry density determination is outlined in Appendix 3.

Table 7: Densities of Mineral Slurries used during the Infrared Experiments.

Mineral	Slurry Density
Chrysocolla	6.1 mg/ml
Malachite	3.1
Cuprite	2.8

5) The mineral slurries were mixed thoroughly and aliquots that would yield 150 $\pm$ 10 mg solids were centrifuged. The supernatent fluid was decanted, and the remaining solids were dried in a vacuum for 24 hr.
6) 100-mg of cupric chloride dihydrate were weighed into 250-ml beakers (duplicate)

containing 10 ml of water. 40 ml of aqueous collector solution (5 mg/ml of potassium octyl hydroxamate or mercaptobenzothiazole) were added, and the mixture was agitated for 10 min. The suspension was centrifuged, the supernatent liquor decanted, and the solids dried in a vacuum for 24 hr.

7) Slurry aliquots containing 150 $\pm$ 10 mg solids were transferred to 250-ml beakers. The volumes were adjusted to 80 ml (with water), and the pH was reduced to 6.5 $\pm$ 0.5. The collector concentration was adjusted to 5×10^{-3} mole/liter, and the pulp was agitated for 10 min. The suspension was then centrifuged, the supernatent liquor was decanted, and the solids were dried in a vacuum for 24 hr.

The infrared absorption analysis procedure consisted of the following stages:

1) Portions of the dried samples, together with several drops of U.S.P Nujol, were thoroughly mixed in an agate mortar and pestle.

2) The sodium chloride windows were polished

and cleaned with rouge and ethanol. The sample slurry was spread evenly between the windows, and the windows were then clamped in the holder of the spectrophotometer.

3) The samples were scanned, and the resulting spectra were used to determine the presence or absence of certain species on the mineral surfaces.

RESULTS

The experimental work has been divided into three principal sections:

1) flotation studies involving the use of potassium octyl hydroxamate and mercaptobenzothiazole as collectors;
2) zero-point-of-charge determinations; and
3) infrared absorption studies to determine the presence of collector species on the mineral surfaces.

Flotation Experiments

Flotation experiments were conducted with each of the minerals at ambient and elevated temperatures to establish temperature effects upon flotation response. Flotation recovery was studied, both as a function of collector concentration at constant pH, and as a function of pH value at constant collector addition. Lack of sufficient amounts of samples limited the number of flotation experiments performed with malachite and cuprite.

Chrysocolla: Figure 4 depicts chrysocolla flotation recovery as a function of hydroxamate concentration at constant pH. At ambient temperature, optimum recovery was achieved with a collector concentration of $1x10^{-3}$ mole/liter. An increase in temperature to 52°C reduced the amount of collector needed for maximum recovery. At $4x10^{-4}$ mole/liter hydroxamate addition, the increase in temperature resulted in an improvement in flotation recovery.

In the next series of experiments chrysocolla flotation recovery was measured as a function of mercaptobenzothiazole concentration at constant pH (Figure 5). With the system at room temperature, complete flotation occurred at $3x10^{-3}$ mole/liter collector concentration. Elevation of the temperature to 51°C decreased the optimum collector concentration. At $7x10^{-4}$ mole/liter collector addition, the increase in temperature improved the flotation recovery appreciably.

Figure 6 shows the effect of pH upon the flotation response of chrysocolla at a constant collector addition of $3x10^{-4}$ mole/liter potassium octyl hydroxamate. Maximum

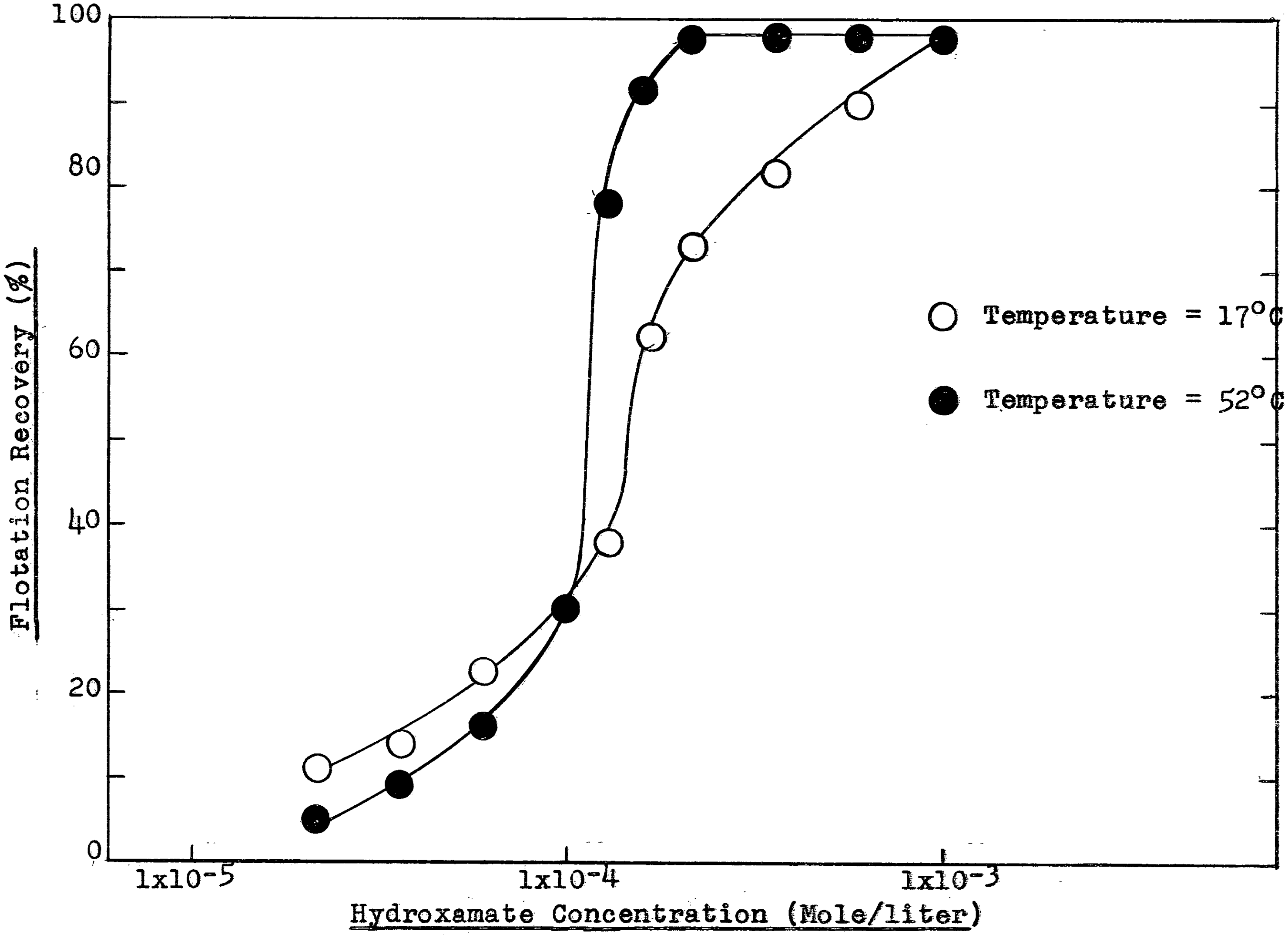


Figure 4: Chrysocolla recovery as a function of potassium octyl hydroxamate concentration (pH value = 6.2)

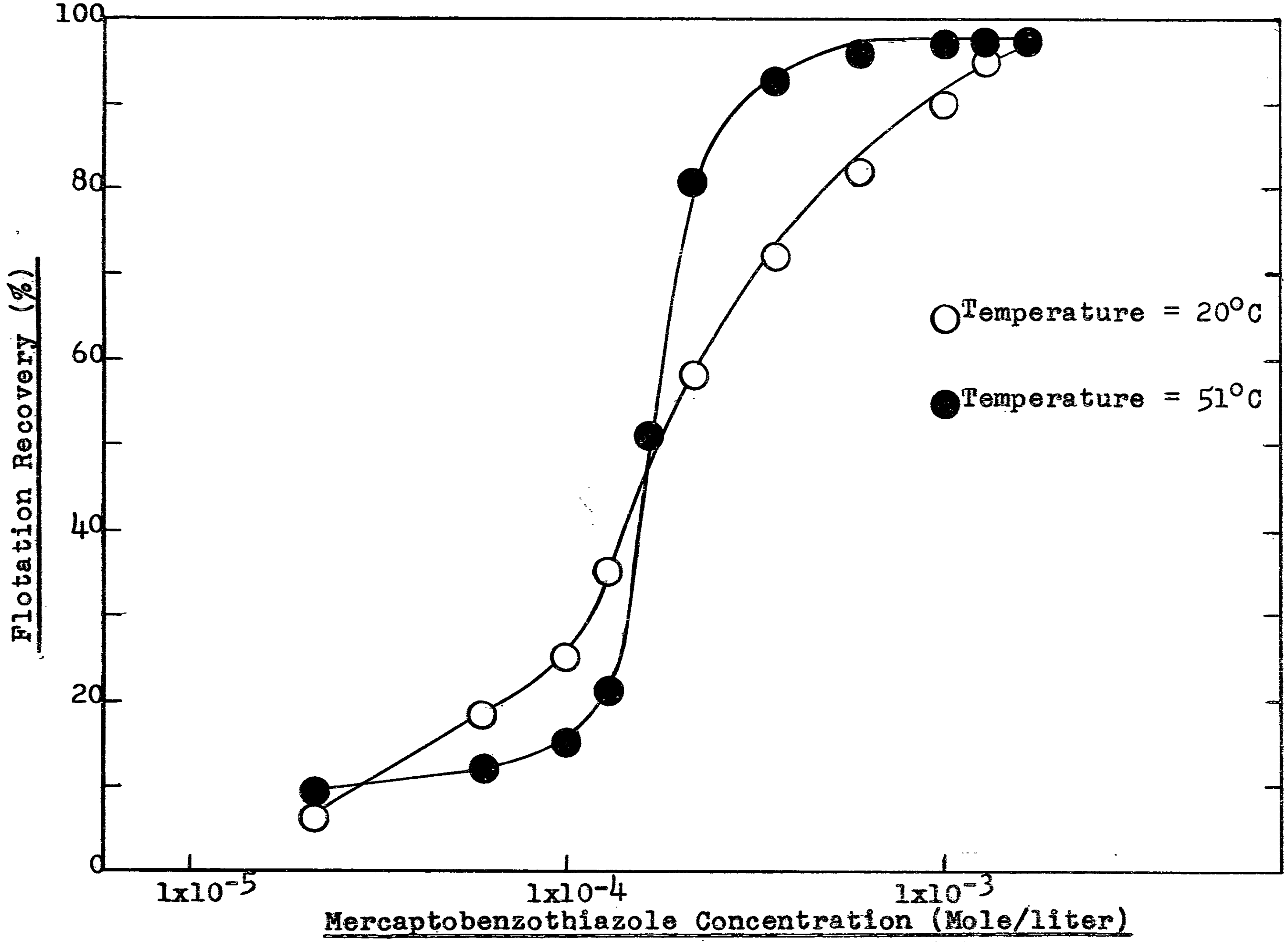


Figure 5: Chrysocolla recovery as a function of mercaptobenzothiazole concentration (pH value = 6.2)

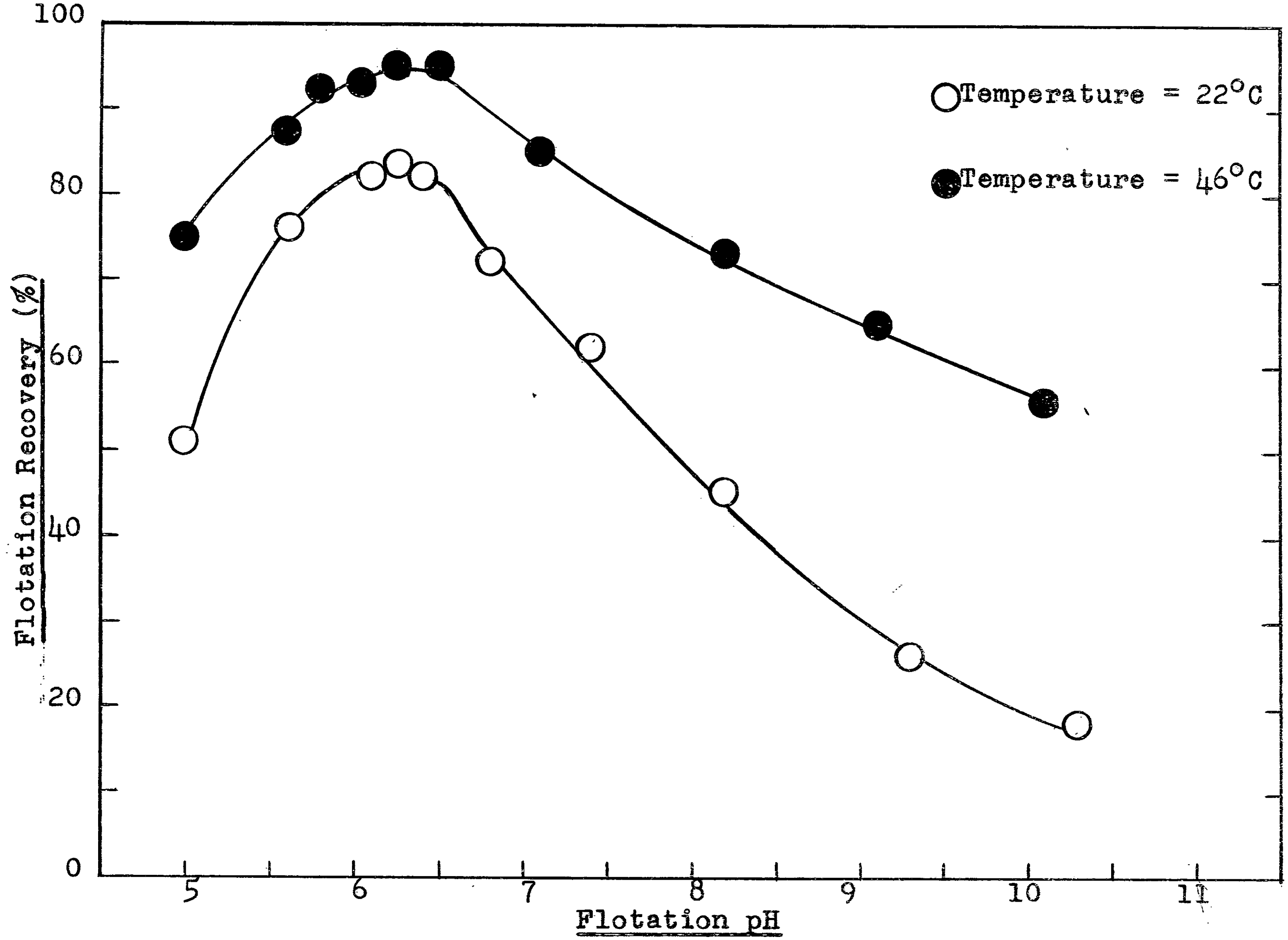


Figure 6: Chrysocolla recovery as a function of pH with potassium octyl hydroxamate addition of $3x10^{-4}$ mole/liter.

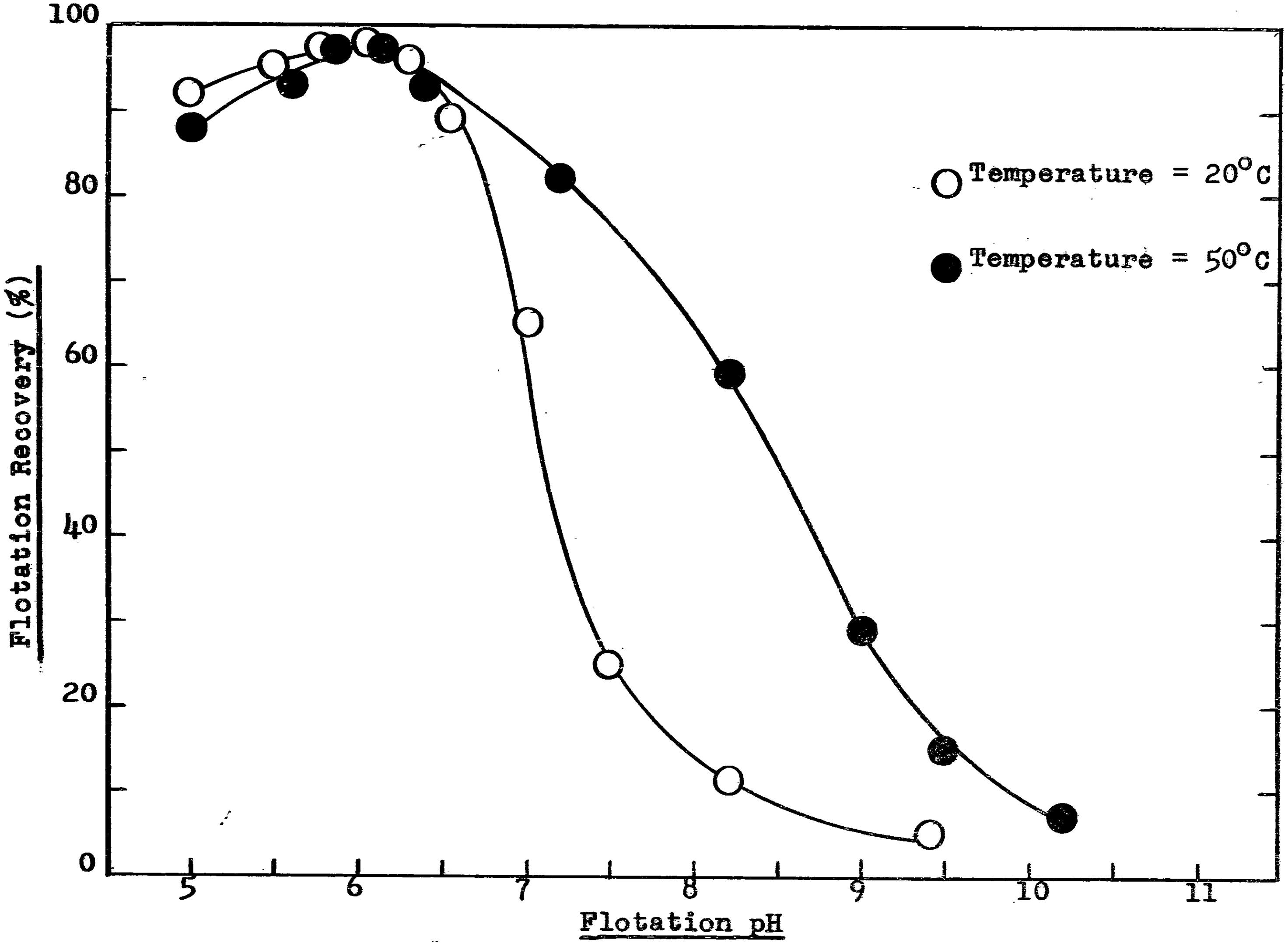


Figure 7: Chrysocolla recovery as a function of pH with mercaptobenzothiazole addition of 9×10^{-4} mole/liter.

flotation response occurred between pH 5 and pH 7, and an increase in temperature improved the recovery. System depression occurred at pH values below 5 and above 8.

Chrysocolla flotation recovery as a function of pH with a mercaptobenzothiazole addition of 9×10^{-4} mole/liter appears in Figure 7. Maximum flotation recovery was achieved between pH 5 and pH 7. Elevation of the temperature improved the flotation response. The system was depressed above pH 8.5.

Malachite: Figure 8 represents malachite flotation recovery as a function of hydroxamate concentration at constant pH. The improvements effected by an increase in the system temperature are noteworthy. Optimum flotation response at $52^\circ C$ occurred at 2×10^{-4} mole/liter collector concentration.

Malachite recovery as a function of mercaptobenzothiazole concentration was also considered (Figure 9). The improvements obtained in flotation response due to a temperature increase were again evident, and optimum recovery was obtained with 3×10^{-4} mole/liter collector addition at $52^\circ C$.

In the next series of experiments malachite recovery was determined as a function of pH with a potassium hydroxamate addition of 1×10^{-4} mole/liter. Maximum flotation response occurred between pH 6 and pH 10.5 with the system temperature at 52°C (Figure 10). The system was depressed outside of this pH range.

Figure 11 portrays malachite flotation recovery as a function of pH with a mercaptobenzothiazole concentration of $3x10^{-4}$ mole/liter. Flotation recovery was at a maximum in the pH 6 to pH 9.5 range at a temperature of 50°C. Depression occurred below pH 5 and above pH 9.5. Malachite flotation experiments were terminated at this stage due to exhaustion of the sample supply.

<u>Cuprite</u>: Figure 12 shows cuprite flotation recovery as a function of pH with a potassium octyl hydroxamate addition of $1x10^{-4}$ mole/liter. A temperature increase improved the flotation response, and maximum recovery occurred in the range of pH 6 to pH 10. Depression occurred below pH 6 and above pH 10.

Cuprite flotation with mercaptobenzothiazole as a function of pH is shown in Figure 13. Flotation was obtained over the pH 5 to pH 12 range. Elevation of the temperature improved the flotation response to a limited extent. No further experiments were performed due to exhaustion of sample supply.

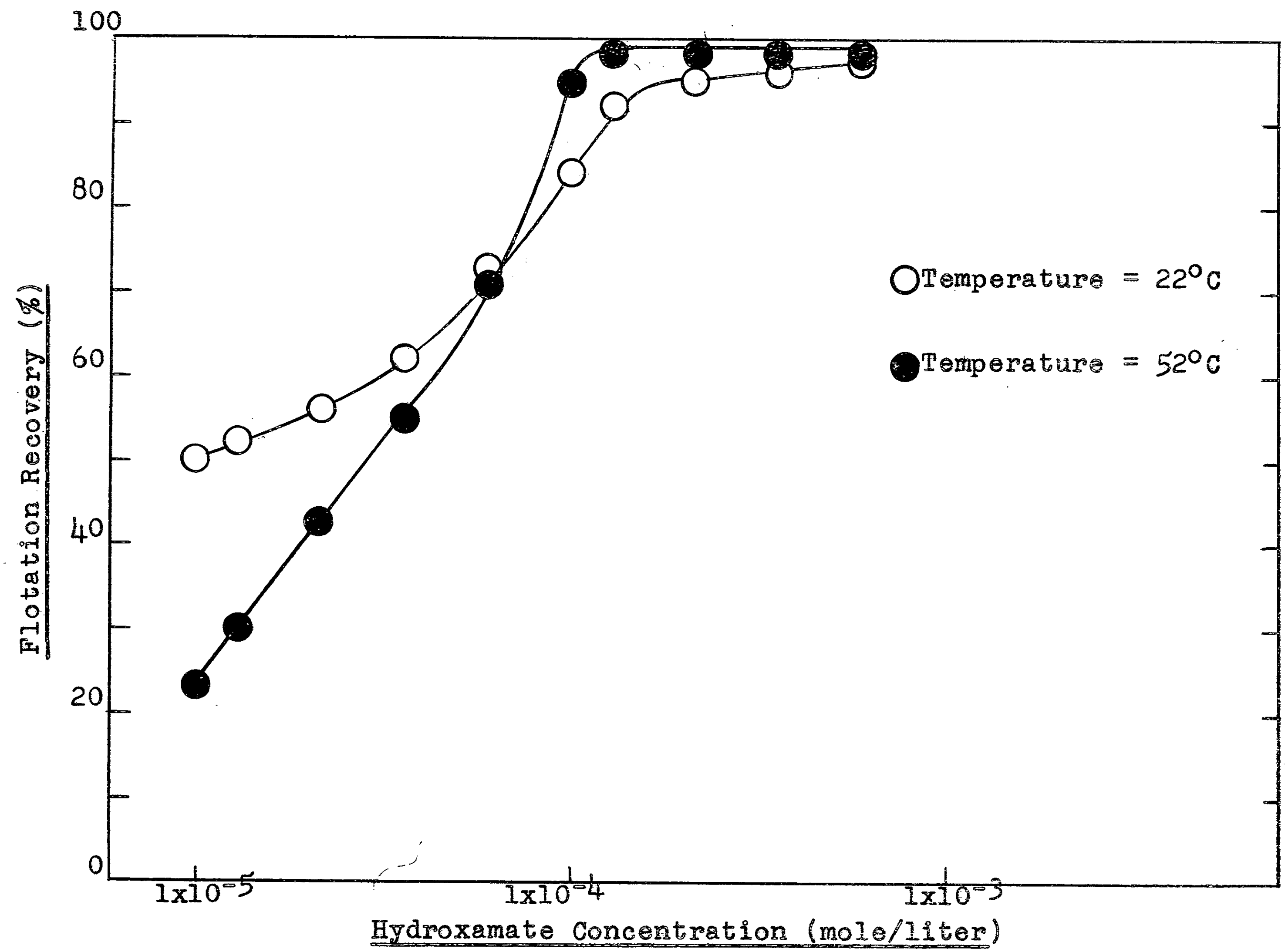


Figure 8: Malachite recovery as a function of potassium octyl hydroxamate concentration (pH value = 6.5)

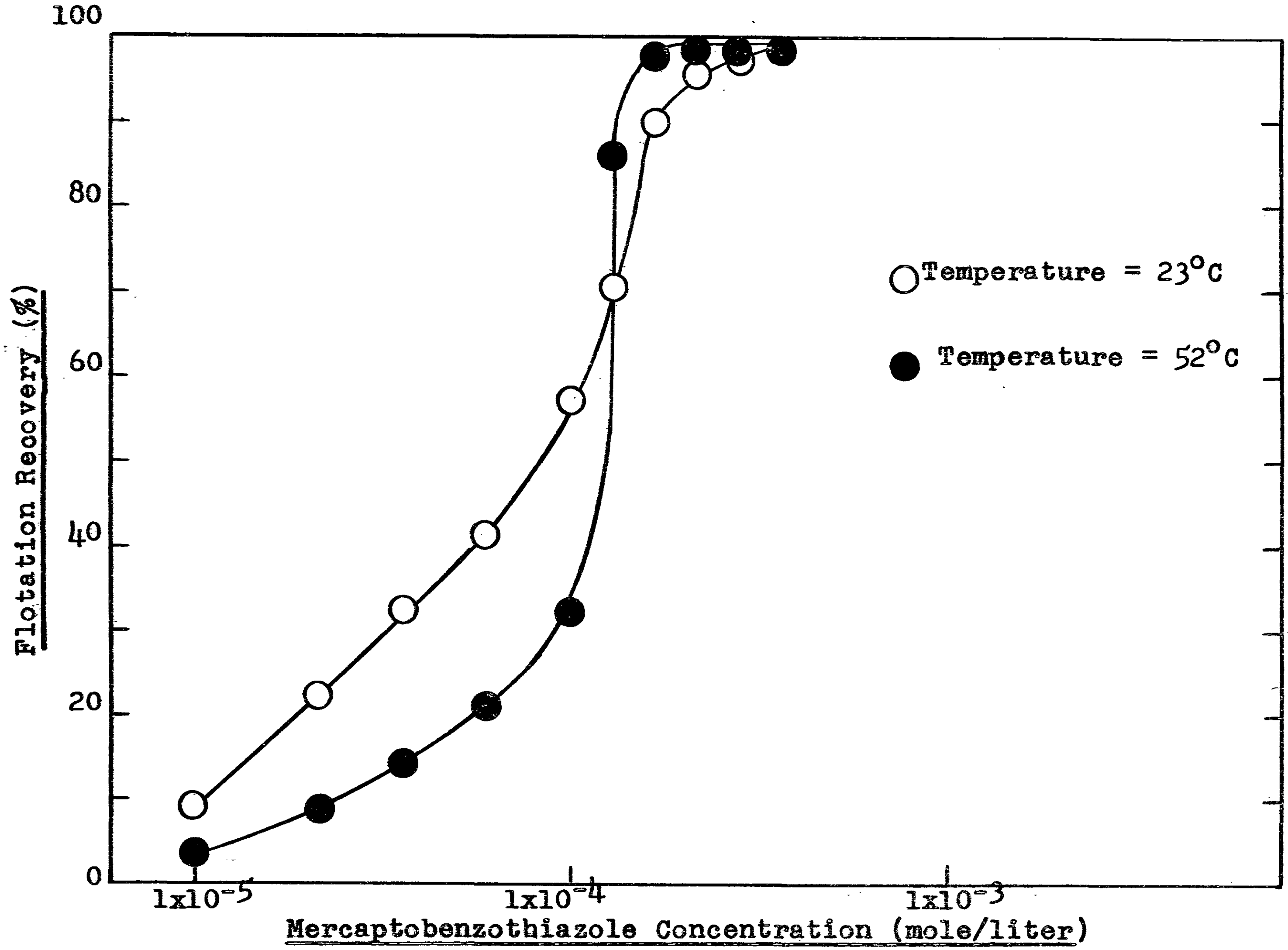


Figure 9: Malachite recovery as a function of mercaptobenzothiazole concentration (pH value = 6.5)

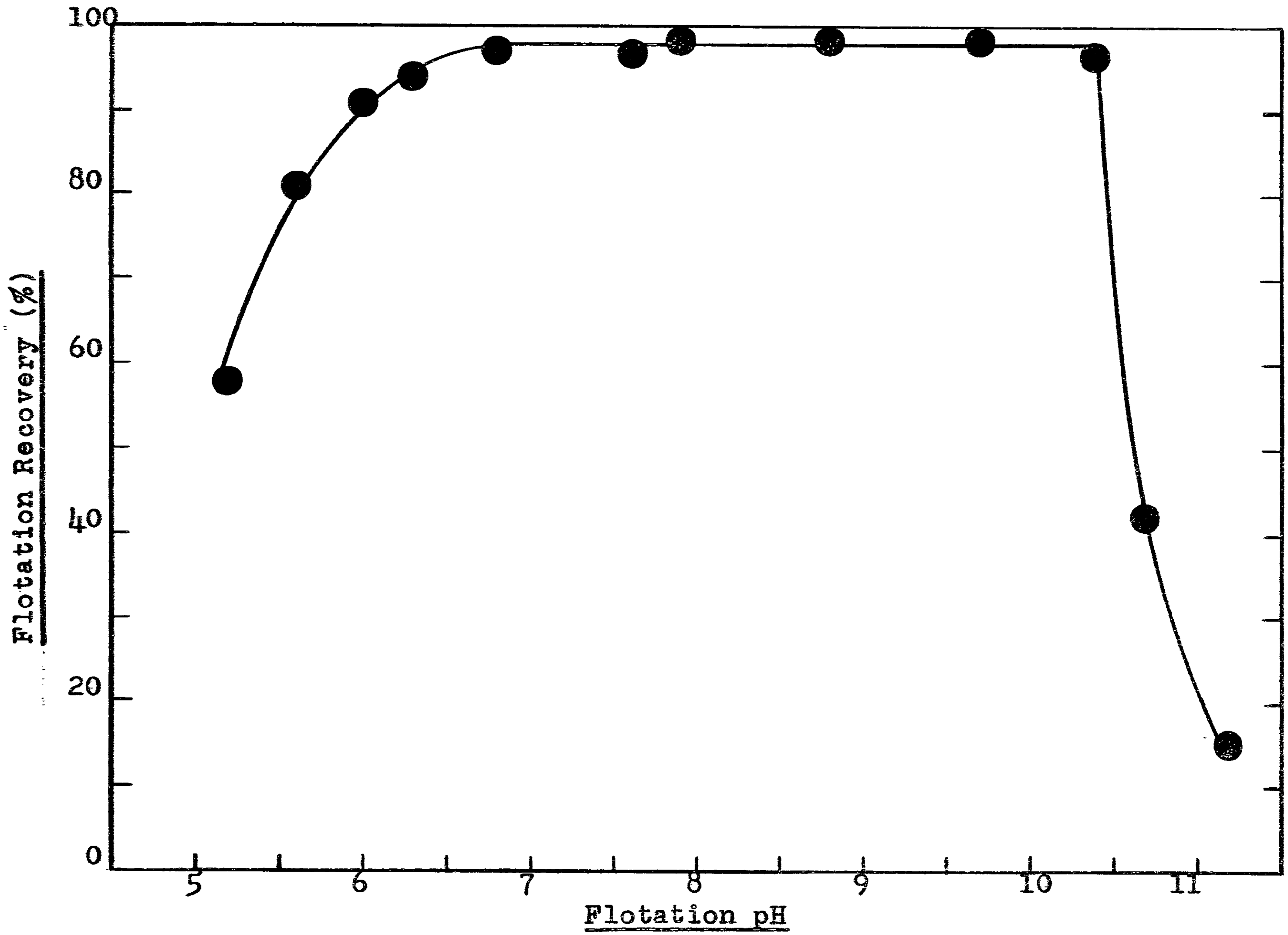


Figure 10: **Malachite recovery as a function of pH with potassium octyl hydroxamate addition of $1x10^{-4}$ mole/liter (Temperature = $52^{o}C$)**

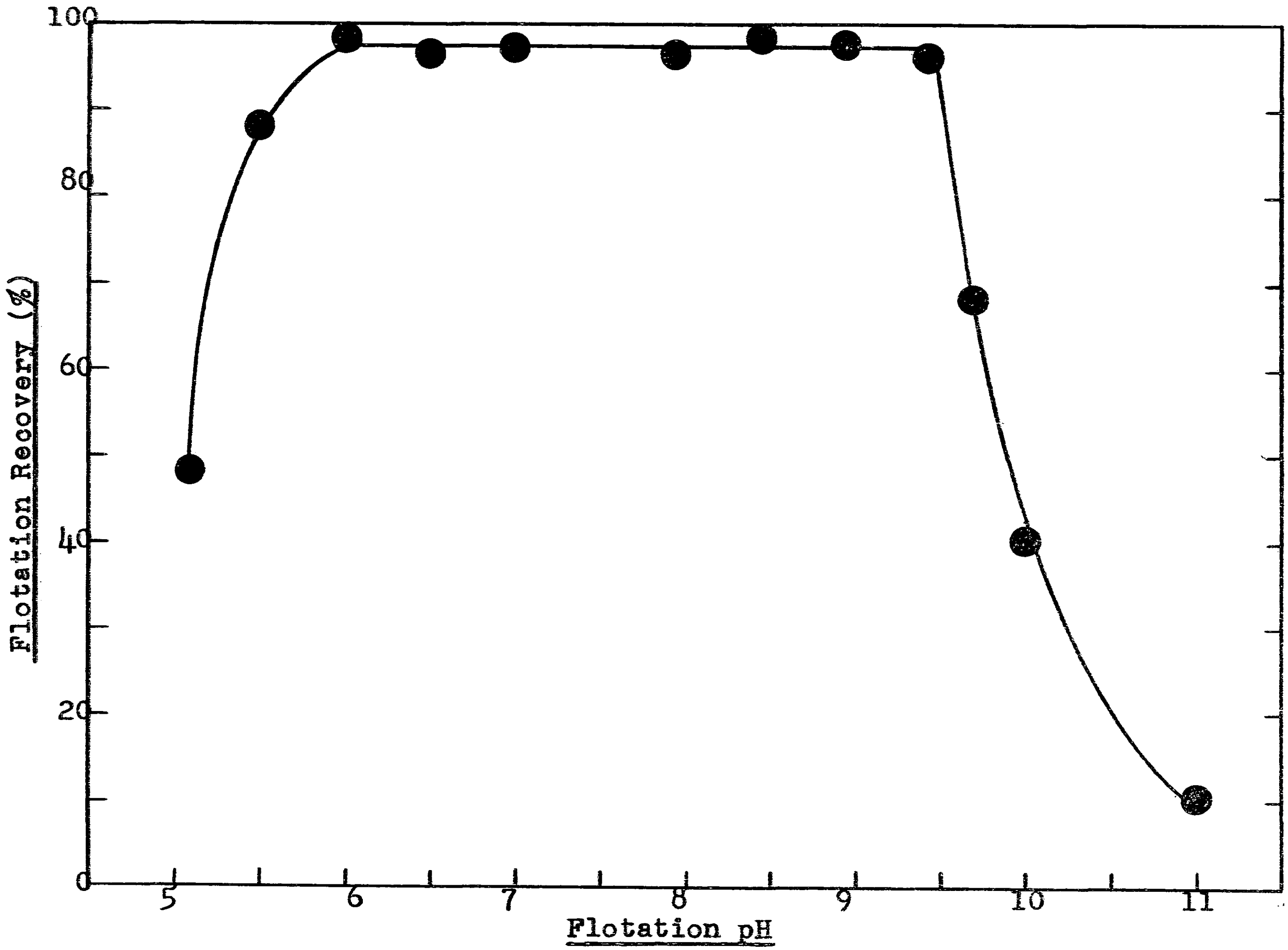


Figure 11: Malachite recovery as a function of pH with mercaptobenzothiazole addition of $3x10^{-4}$ mole/liter (Temperature = 50^oC)

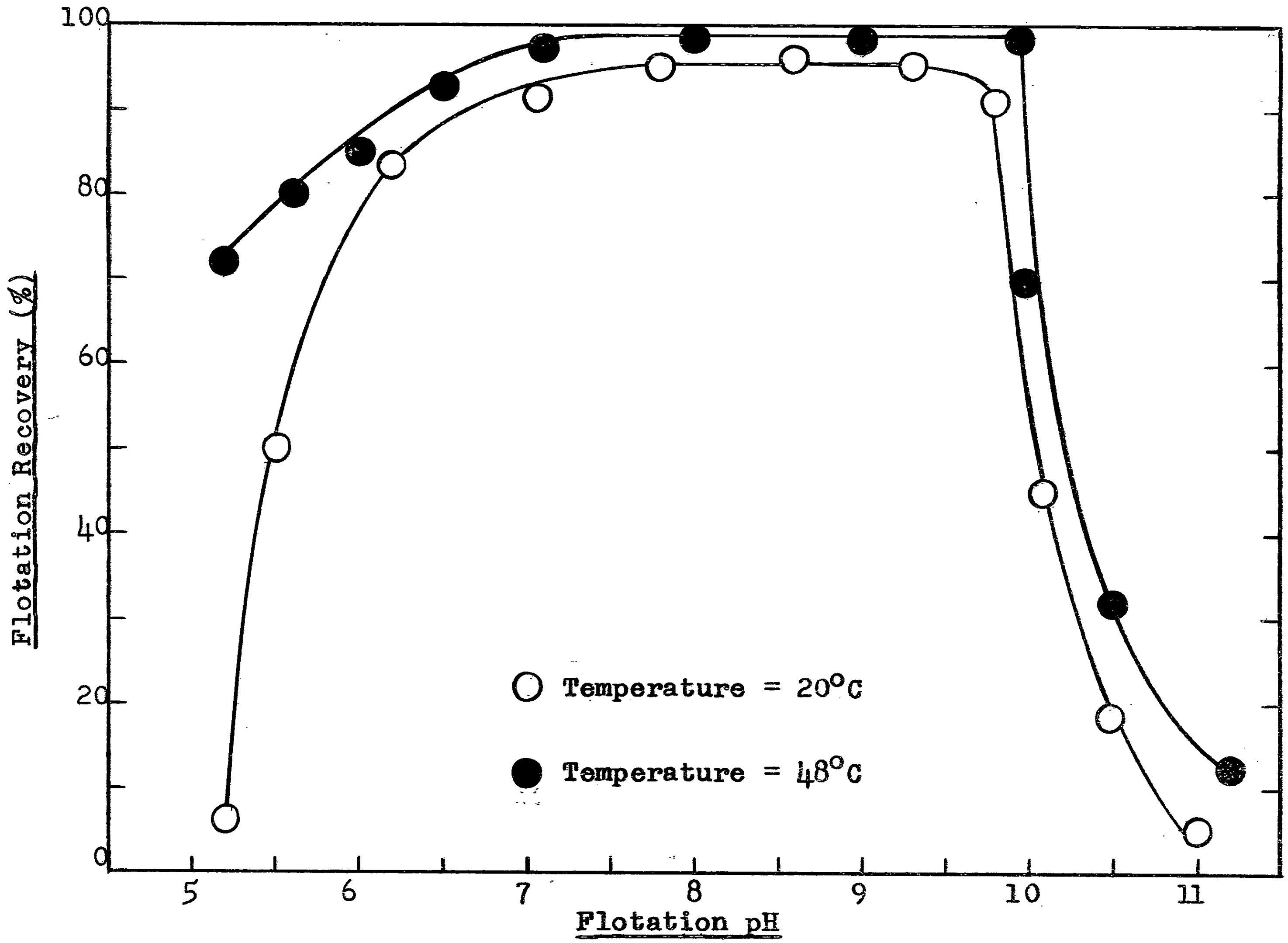


Figure 12: Cuprite recovery as a function of pH with potassium octyl hydroxamate addition of 1×10^{-4} mole/liter.

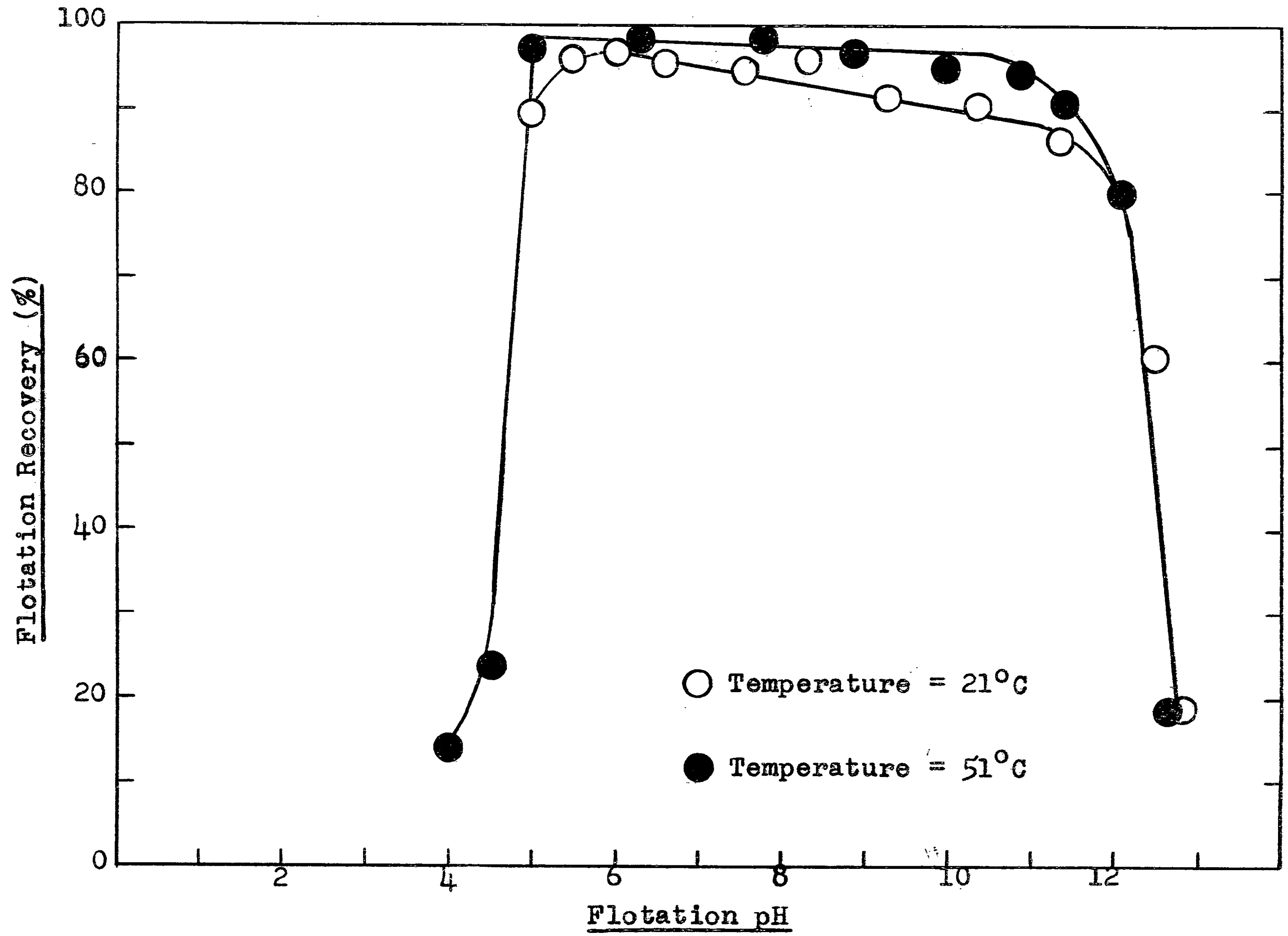


Figure 13: Cuprite recovery as a function of pH with mercaptobenzothiazole addition of $3x10^{-4}$ mole/liter.

Electrophoresis Experiments

Zero-points-of-charge were determined for each of the minerals used in the investigation. The surface charges on the samples in conductivity water were measured with a Zeta Meter.

Chrysocolla: The zeta potential of chrysocolla is depicted as a function of pH in Figure 14. The zero-point-of charge of chrysocolla is pH 3.0.

Malachite: In the next series of electrophoresis experiments, the zero-point-of-charge for malachite was determined to be pH 9.7 (Figure 15).

Cuprite: The electrophoresis data for cuprite are recorded in Figure 16. The zero-point-of-charge of cuprite is pH 9.4.

Infrared Absorption Experiments

The analysis of the collector-loaded minerals with infrared spectrometry was accomplished by comparing the infrared spectra of the pure minerals, the copper salts of the collectors, and the loaded minerals. The initial scans at 1x scale expansion indicated that the characteristic

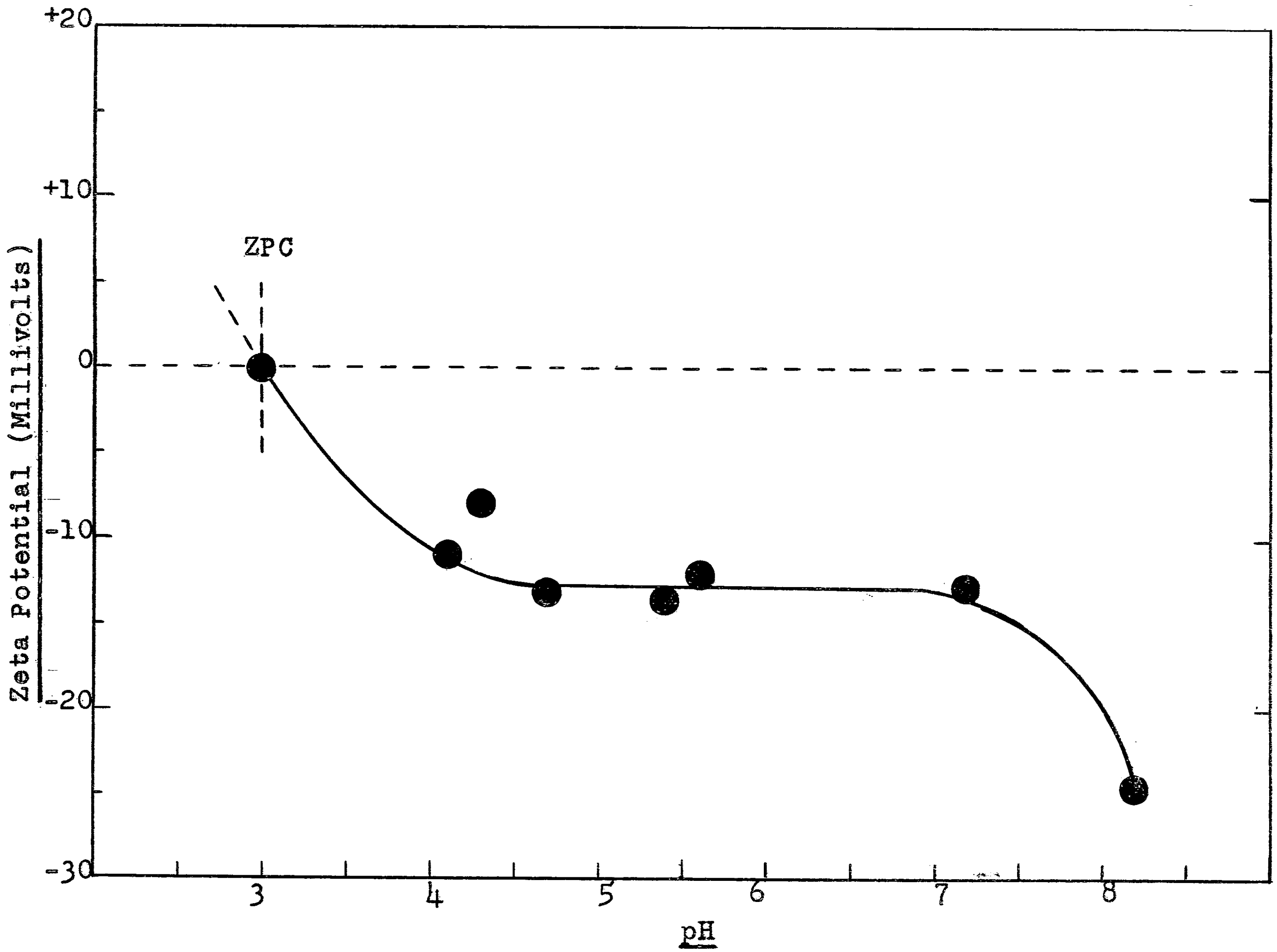


Figure 14: The zeta potential of chrysocolla as a function of pH.

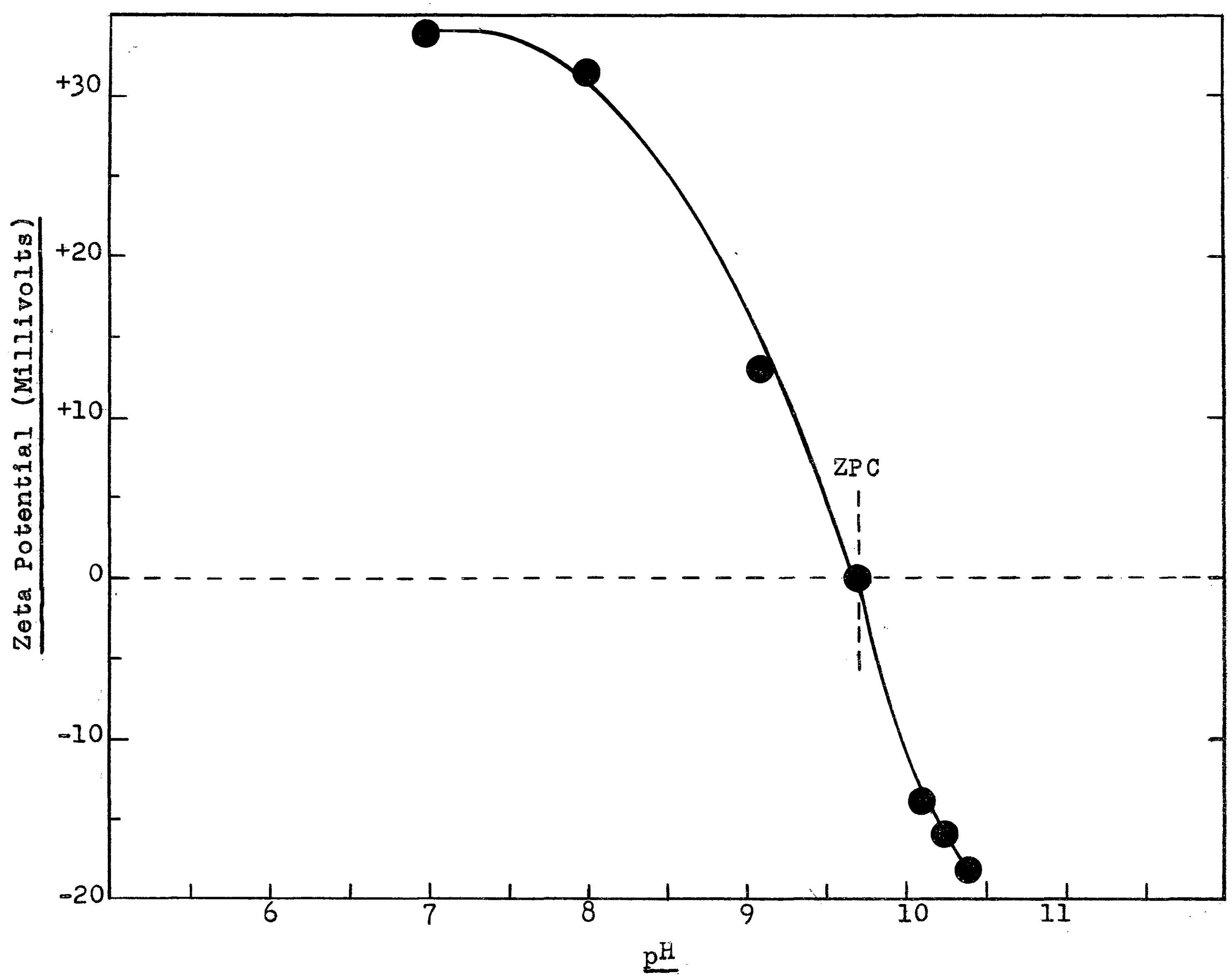


Figure 15: The zeta potential of malachite as a function of pH.

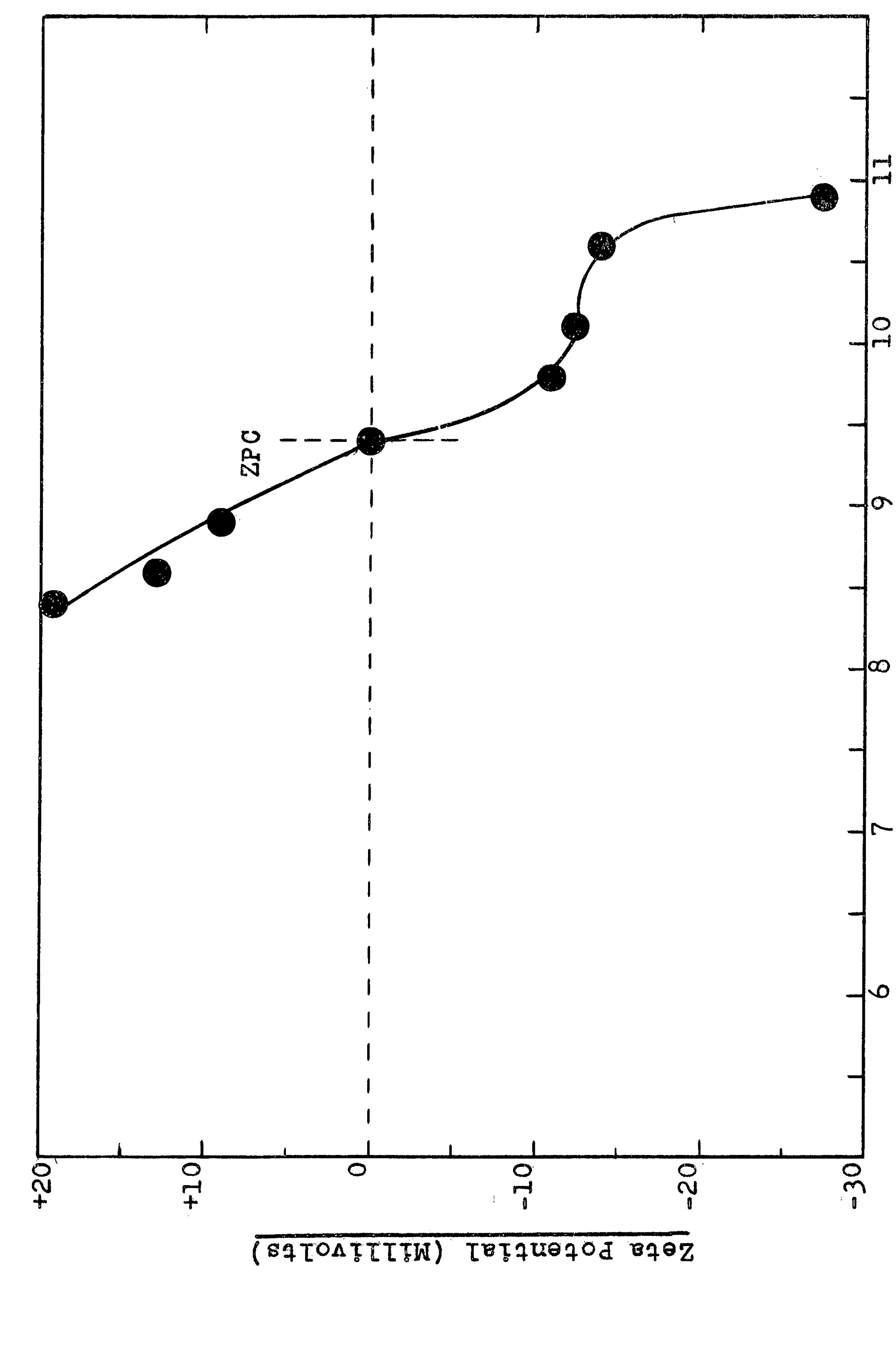


Figure 16: The zeta potential of cuprite as a function of pH.

absorption frequencies of octyl hydroxamate were situated in the 1500 to 1700 cm^{-1} region, while those for mercaptobenzothiazole occurred in the 900 to 1100 cm^{-1} region. Infrared spectra were then traced across these regions with 5x scale expansion.

Chrysocolla: The characteristic absorption frequencies for the chrysocolla-hydroxamate systems are shown in Figure 17. By examining the spectra of copper hydroxamate and chrysocolla loaded with hydroxamate, it can be seen that the characteristic bands are distorted and/or displaced upon the adsorption of the collector onto the mineral surface.

Figure 18 depicts infrared absorption frequencies for the chrysocolla-mercaptobenzothiazole system. The characteristic bands have been distorted and displaced when the collector adsorbs onto the mineral.

Malachite: In Figure 19 it can be seen that the unique absorption frequencies for copper hydroxamate are distorted and shifted when the collector species reacts with the mineral surface.

Figure 20 shows a similar displacement for the characteristic frequencies of the malachite-mercaptobenzothiazole system.

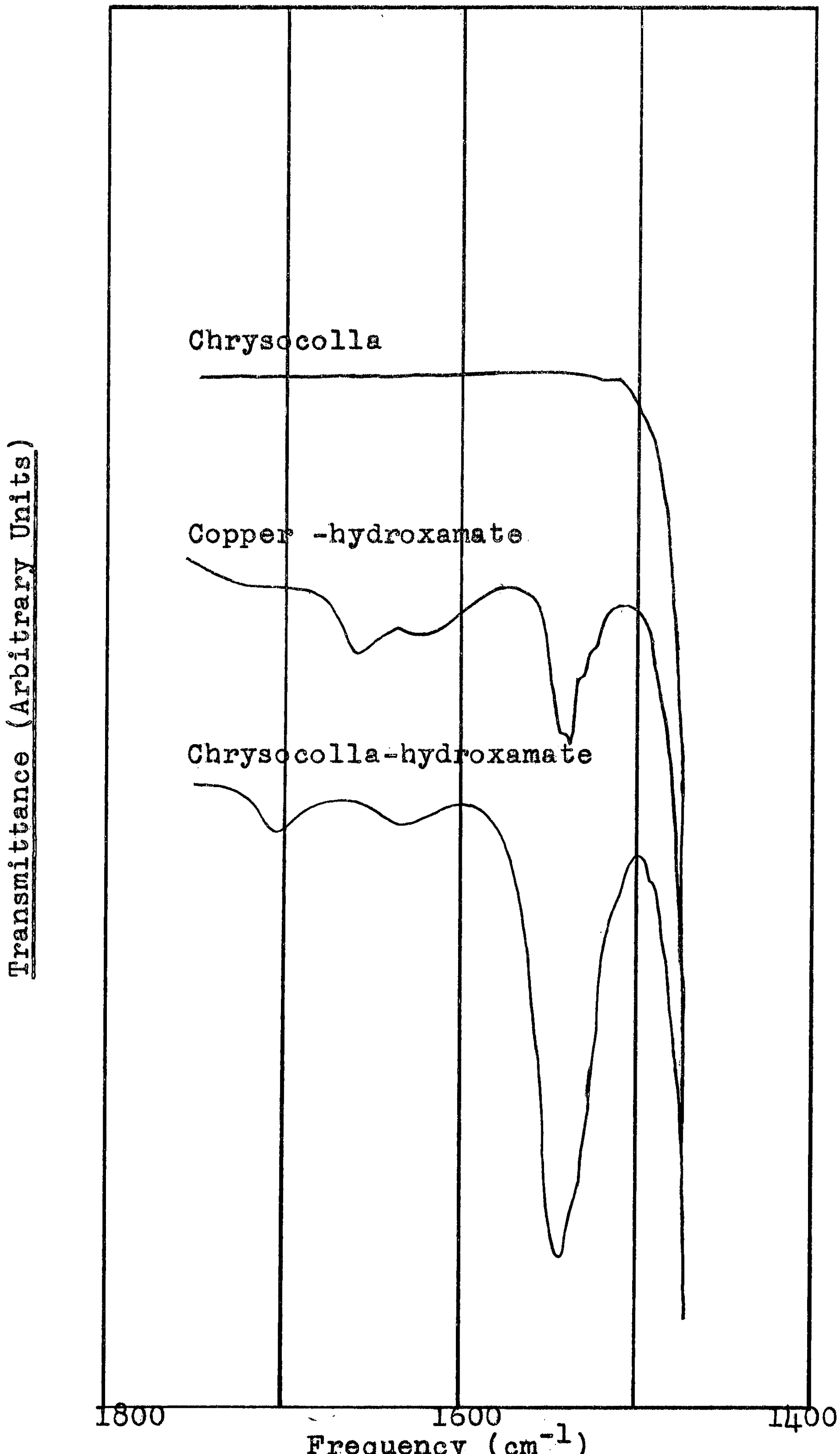


Figure 17: Infrared absorption versus frequency for the chrysocolla-hydroxamate system.

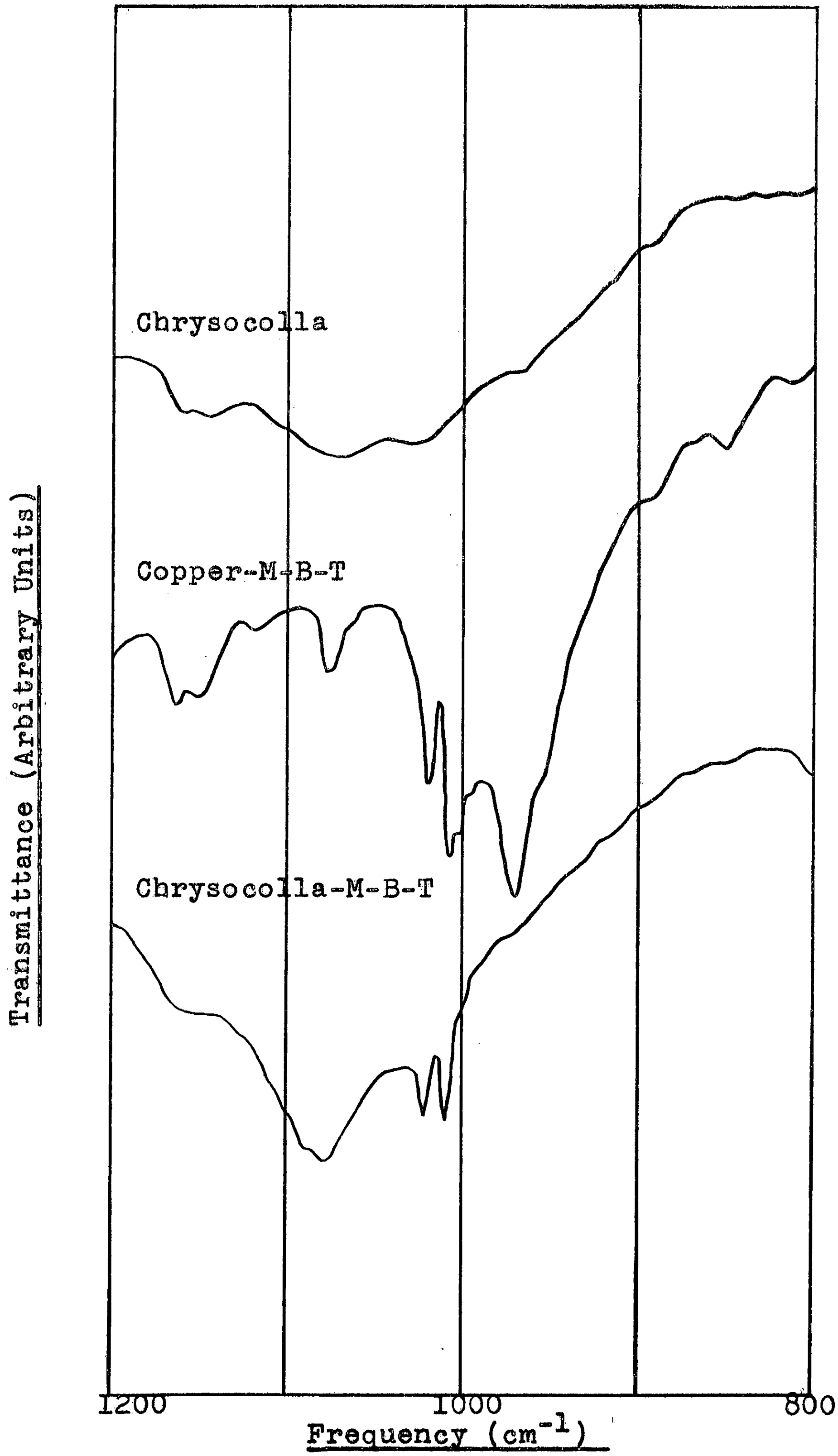


Figure 18: Infrared absorption versus frequency for the chrysocolla-mercaptobenzothiazole system.

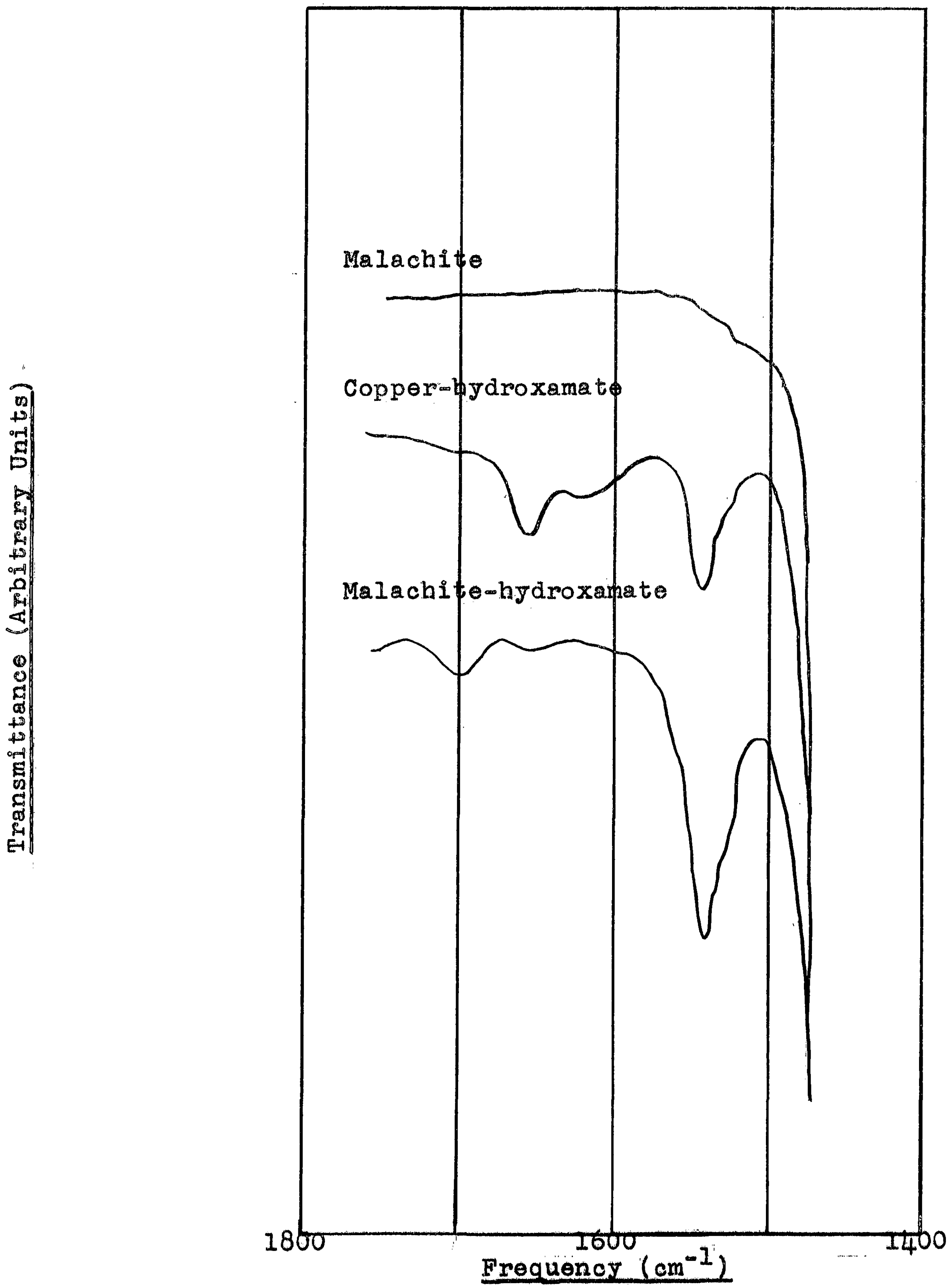


Figure 19: Infrared absorption versus frequency for the malachite-hydroxamate system.

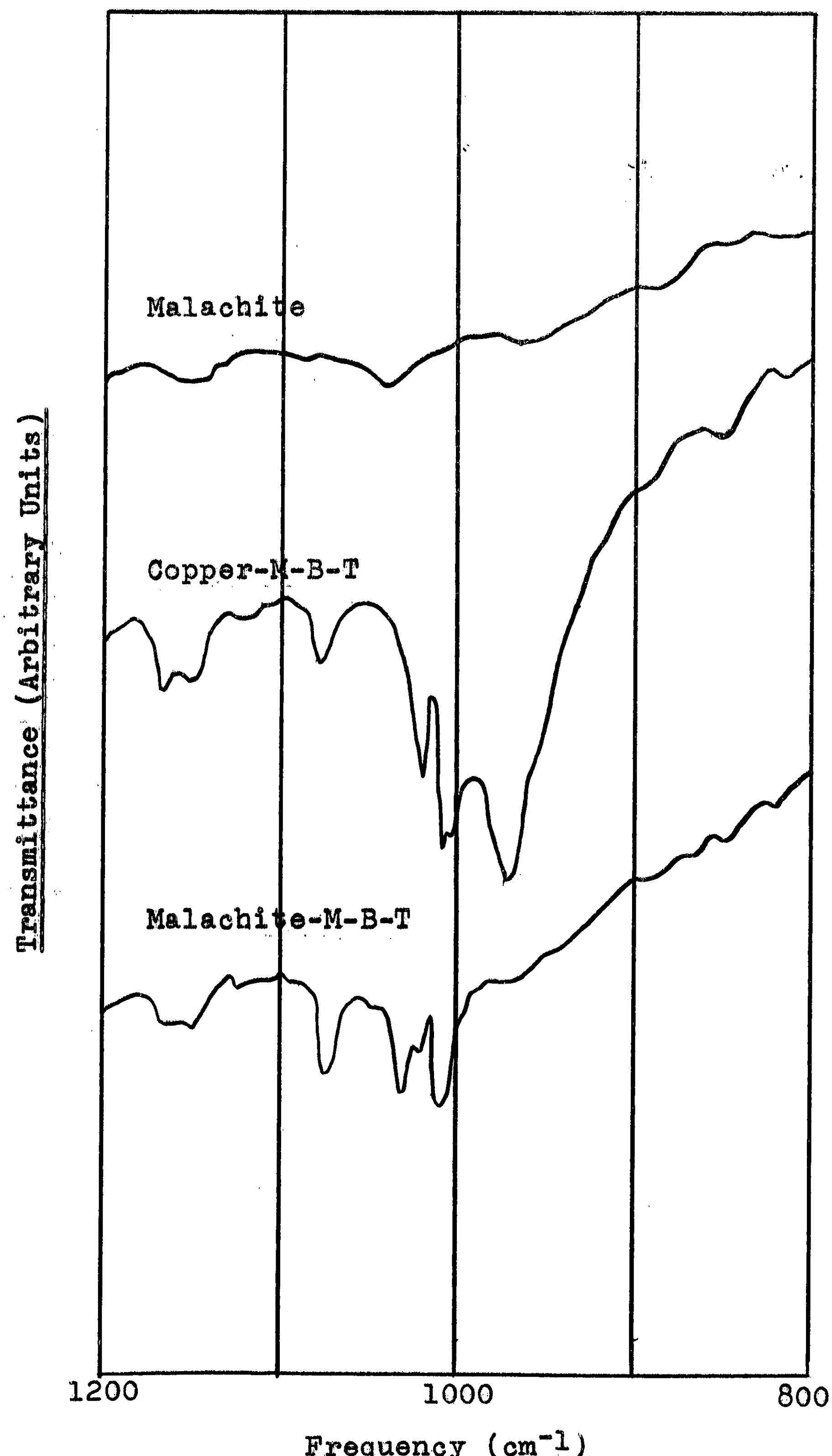


Figure 20: Infrared absorption versus frequency for the malachite-mercaptobenzothiazole system.

<u>Cuprite:</u> The characteristic absorption frequencies for the cuprite and copper-collector species have been drawn in Figures 21 and 22. In both cases the characteristic absorption bands have been displaced and distorted when the collectors adsorbed onto the mineral surfaces.

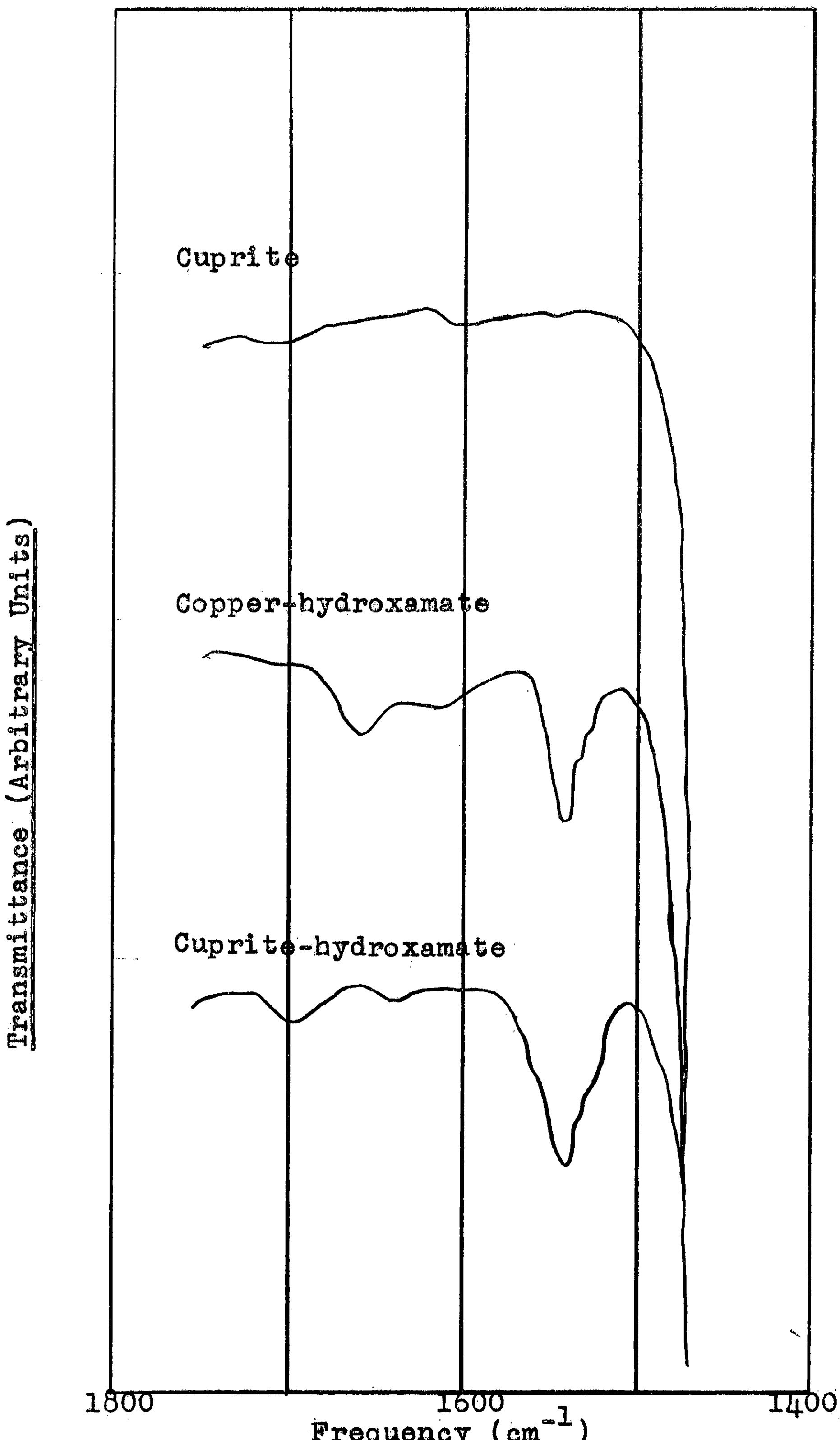


Figure 21: Infrared absorption versus frequency for the cuprite-hydroxamate system.

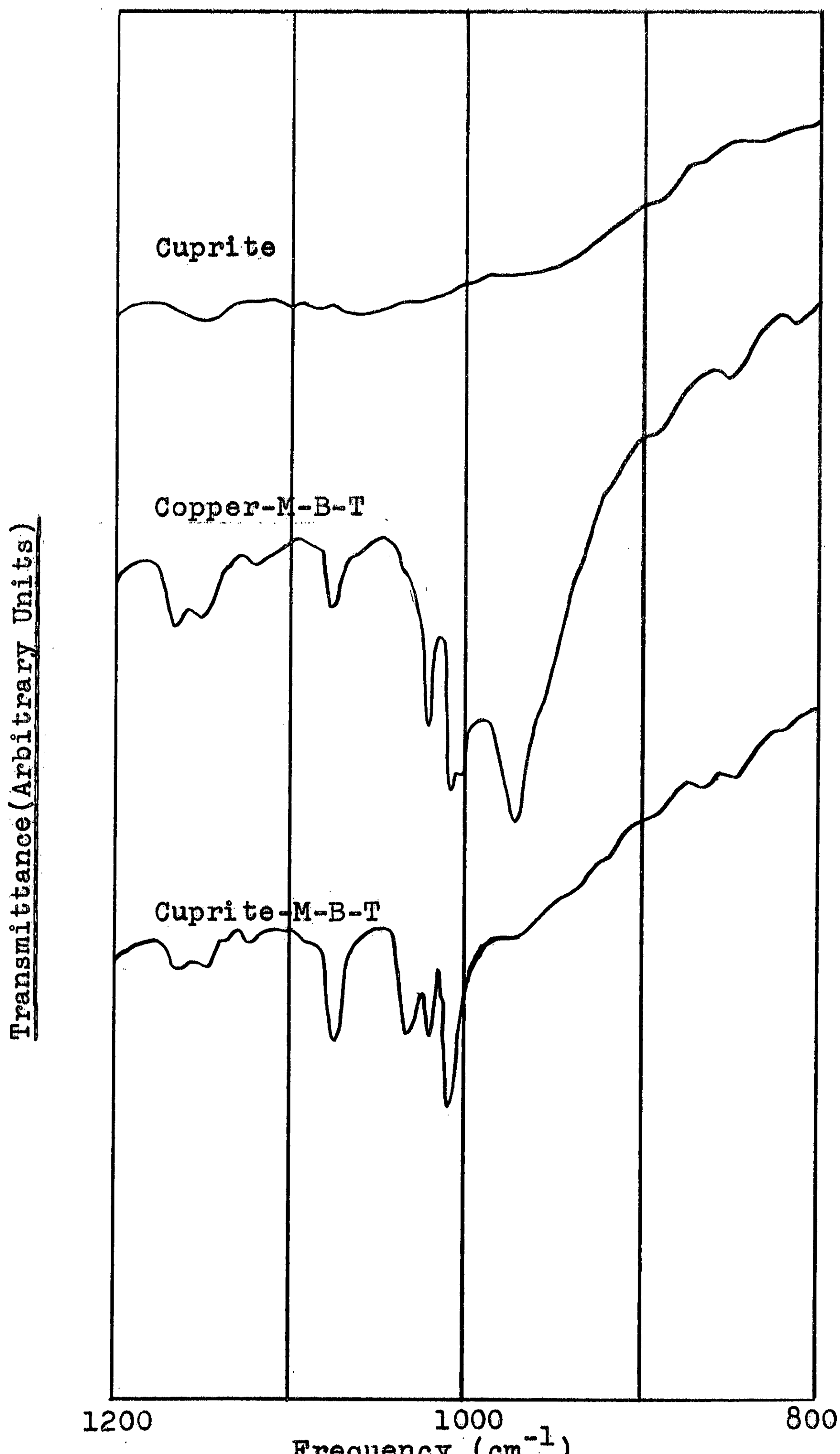


Figure 22: Infrared absorption versus frequency for the cuprite-mercaptobenzothiazole system.

DISCUSSION OF RESULTS

The experimental results obtained with the oxide copper minerals chosen for this investigation suggest that collector action is due to the formation of chemical bonds between surface copper ions and the anionic collector molecules. The observed results will be discussed and their significance pointed-out in the following sections.

Flotation

The flotation experiments showed several features that warrant consideration; these features can be listed as:

1) the effects of increased temperature upon flotation response as a function of collector concentration at constant pH;

2) the effects of increased temperature on flotation recovery as a function of pH at

constant collector addition;

3) the decrease in flotation response when the pH value falls below 5;

4) the depression of the system at high pH; and

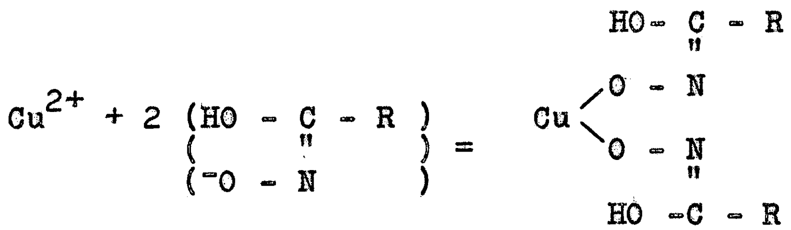
5) the relatively narrow region in which chrysocolla responds to the collectors.

In all flotation systems, flotation response is affected by ions in solution; consequently an endeavour will be made to explain the above phenomena according to the principles of solution chemistry.

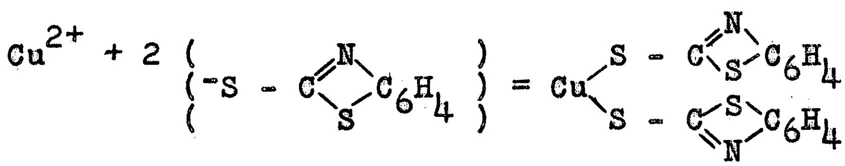
Consideration of the data pertaining to the flotation recoveries of chrysocolla and malachite as functions of collector concentrations (Figures 4, 5, 8, and 9) reveals that analogous effects were obtained from an elevation in temperature:

1) At low collector concentrations, the recoveries at room temperature exceed those recorded at elevated temperatures. These effects are probably due to the enhanced mineral solubilities at the higher temperatures and the consequent increase of cupric ion in solution. The collector ion concentrations are

then lowered according to the reactions:



(precipitate)



(precipitate)

2) At higher collector concentrations, the increase in temperature improved the flotation recoveries considerably and resulted in an appreciable reduction in the optimum collector concentration. These temperature effects appear to substantiate the premise that chemical reactions on the mineral surfaces are responsible for collector action, because chemical reactions tend to be enhanced by an increase in temperature (16).

Unfortunately, the lack of sufficient sample prevented the performance of similar flotation tests with cuprite.

The effect of a temperature increase upon the flotation response of chrysocolla and cuprite as functions of pH at constant collector additions (Figures 6, 7, 12, and 13) was to improve the flotation recoveries. The effects for cuprite are not pronounced, probably because of the fact that the collector concentrations used were in excess of the optimum values for the respective reagents. This reasoning is supported by the fact that the low and high temperature curves tend to approach each other as the reagent concentrations exceed the optimum values in Figures 4, 5, 8, and 9. Once again the lack of sufficient sample prevented the performance of similar flotation experiments with malachite.

A comparison of the mineral flotation responses as a function of pH value at constant collector addition (Figures 6, 7, 10, 11, 12, and 13) indicates that flotation recoveries fall-off at pH less than 5.

There are several possible explanations for this behavior:

1) The supply of collector ions is being depleted, either by hydrolysis[10], or by the decomposition of the collector ions

$$\begin{matrix} R - C - OH \\ \| \\ N - O^- \end{matrix} + H_2O = \begin{matrix} R - C - OH \\ \| \\ N - OH \end{matrix} + OH^-$$

2) The minerals are soluble in acid media, and the resulting cupric ions tie-up collector ions as an insoluble precipitate. This concept is substantiated by the formation of a film on the surface of the flotation pulp during the flotation experiments performed under these conditions.

3) Both of the above phenomena probably contribute towards the observed depression, but evidence has been advanced[10] which indicates that the lack of flotation response is due to the absence of chemisorbed hydroxyl ions on the surface (especially on chrysocolla).

The depression of copper oxide minerals at high pH is probably related to the hydrolysis of cupric ion on the mineral surface. Consideration of the equilibrium relationship[17]

$$Cu(OH)_2(s) = Cu^{2+} + 2\ OH^- : K = 1.6 \times 10^{-19}$$

indicates that for a nominal addition of cupric ion (1×10^{-3} mole/liter) to water, the majority of the copper ions will be precipitated as cupric hydroxide at a pH value in excess of 9. It can be expected that a similar reaction will take place at an ionized surface copper atom at high pH, and we therefore have two possible reactions in the flotation system:

$$Cu^{2+} \text{ (surface)} + 2OH^- = Cu(OH)_2 \text{ (surface)}$$

$$Cu^{2+} \text{ (surface)} + 2HA^- = Cu(HA)_2 \text{ (surface)}$$

Flotation response now becomes a function of which these two surface compounds is the most stable under the conditions employed. The lack of flotation at high pH values (Figures 6, 7, 10, 11, 12, and 13) is probably due to the fact that the mineral surfaces will not react with collector ions at the expense of hydroxyl ions. In the case of cuprite with mercaptobenzothiazole (Figure 13), it was noted that the system was depressed at pH greater than 12. This effect was probably due to the fact that the collector concentration was in excess of the optimum value and caused an extension of the flotation range.

The reason for the relatively narrow pH range for chrysocolla flotation response can be seen by considering the data recorded in Table 8.[10]

Table 8: Concentrations of various cupric ion species as a function of pH for an addition of 1×10^{-3} mole/liter of cupric chloride to water.

pH Value	Cu^{2+}	$Cu(OH)^+$	$Cu(OH)_2(s)$
5.0	1.0×10^{-3}	1.0×10^{-6}	--
5.6	1.0×10^{-3}	4.0×10^{-6}	--
5.8	1.0×10^{-3}	6.3×10^{-6}	--
6.0	9.9×10^{-4}	9.9×10^{-6}	--
6.2	6.4×10^{-4}	1.0×10^{-5}	3.5×10^{-4}
6.4	2.5×10^{-4}	6.4×10^{-6}	7.4×10^{-4}
7.0	1.6×10^{-5}	1.6×10^{-6}	9.8×10^{-4}

The maximum concentration of the initial hydroxy complex of copper in the solution occurs in pH range of 5.8 to 6.4, and the hydrolysis of the cupric ions is virtually complete at pH 7. Similar reactions are capable of occurring on the chrysocolla surface, and the chemisorption of the collector onto the mineral can follow the reactions indicated below:

$$Cu^{2+}\ (\text{surface}) + H_2O \ = \ Cu(OH)^+\ (\text{surface}) + H^+$$

$$Cu(OH)^+(\text{surface}) + \begin{array}{c} HO - \underset{\|}{C} - R \\ {}^-O - N \end{array} = \begin{array}{c} Cu\begin{array}{l} \diagup O - \underset{\|}{C} - R \\ \diagdown O - N \end{array} \\ (\text{surface}) \end{array} + H_2O$$

A comparison of the optimum collector concentrations (Figures 4, 5, 8, and 9) indicates that, for chrysocolla and malachite, the optimum mercaptobenzothiazole addition is approximately double that for octyl hydroxamate under similar conditions. This behavior is probably associated with the greater solubility of copper-mercaptobenzothiazole compared to copper-hydroxamate. The collector action of mercaptobenzothiazole can probably be improved by rendering the collector less soluble through the synthesis of a short hydrocarbon chain (2-carbon or 3-carbon) onto the benzene structure. Further research work in this field is advocated.

Finally, complete flotation of the minerals was never attained due to the fact that they contained impurities (See Tables 2 and 3, pages 8 and 9).

Electrophoresis Studies and Zeta Potential

Zeta potential is of importance with respect to the behavior of solids dispersed in liquids, especially in flotation pulps. In general, the mineral particles are charged under flotation plant conditions, and the sign and magnitude of the zeta potential influences the adsorption characteristics of collectors. A schematic diagram of the zeta potential concept is shown in Figure 23[13].

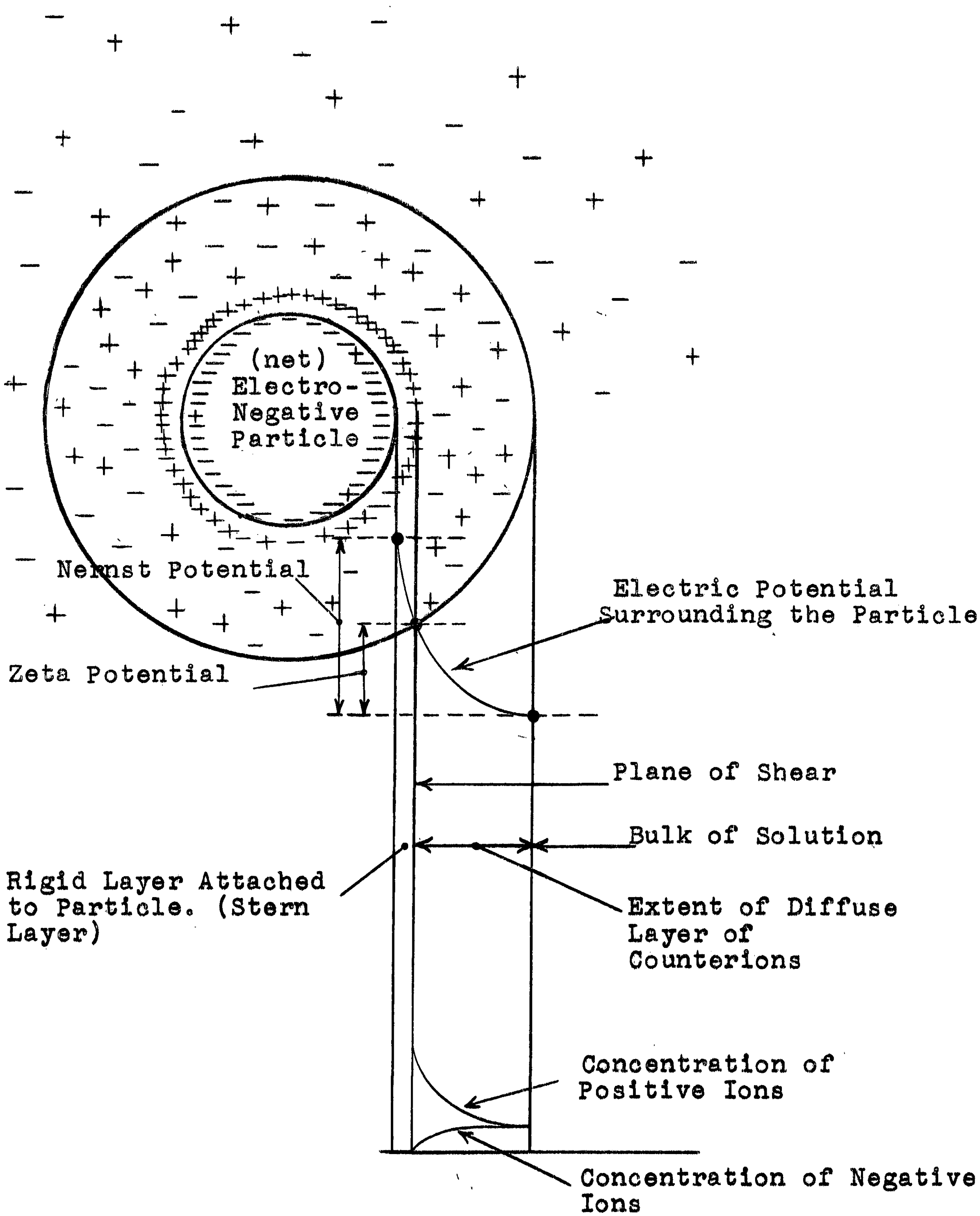


Figure 23: Concept of the Zeta Potential and the Double Layer.

The diagram depicts an electronegative particle surrounded by negative and positive ions. It can be seen that the zeta potential represents the difference in electrical potential between the rigid layer of ions attached to the mineral particle and the bulk of solution. The zeta potential is developed from the tendency of ions in the particle surface and ions within the diffuse layer to establish equilibrium. Three different situations are possible:

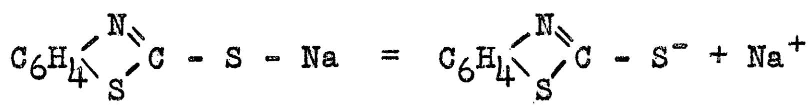
1) a negative zeta potential indicates that the mineral surface is negative, and adsorption of cations takes place;
2) a positive zeta potential shows that the mineral surface is positive, and adsorption of anions results; and
3) at the zero-point-of-charge the surface will be equally influenced by cations and anions.

The two collectors used for this investigation can be classified as anionic reagents because the ions carrying the hydrocarbon groups are anions.

1) Potassium octyl hydroxamate.

$$\begin{array}{lll} H - O - \underset{\|}{C}\ (CH_2)_6\text{-}CH_3 & = H - O - \underset{\|}{C} - (CH_2)_6\text{-}CH_3 & \\ K - O - N & \quad {}^{-}O - N & + K^{+} \end{array}$$

2) Mercaptobenzothiazole.



The collector ions are negatively charged and will be electrically repulsed by a negative mineral surface (i.e. in a flotation pulp where the pH value exceeds the ZPC). Such a system will not respond to flotation unless a chemical reaction occurs (on the mineral surface) whereby this force of repulsion can be overcome by the decrease in free energy resulting from the reaction. Such a reaction between the collector ions and the mineral is called chemisorption because the adsorbate is bound to the mineral surface by chemical forces.

The pH ranges yielding maximum flotation response in the mineral systems studied, and the zero-points-of-charge for the respective minerals have been recorded in Table 9.

Table 9: The optimum flotation pH ranges and the ZPC's of the minerals used.

Mineral	Collector	pH Range	ZPC
Chrysocolla	Hydroxamate	5 - 7	3.0
	M.B.T.	5 - 7	
Malachite	Hydroxamate	6 - 10.5	9.7
	M.B.T.	6 - 10	
Cuprite	Hydroxamate	6 - 10	9.4
	M.B.T.	5 - 12	

It can be seen that both the collector responses were independent of the surface charges on the minerals. This evidence indicates that the collectors are chemisorbed onto the mineral surfaces.

Adsorption Mechanism

The temperature effects upon flotation response and the zeta potential studies both indicate that the collector ions were probably chemisorbed onto the minerals during flotation. Furthermore, such chemisorption reactions probably involve the formation of copper hydroxamate and copper mercaptobenzothiazole on the mineral surfaces. The infrared absorption experiments were therefore performed to establish the presence of these copper compounds on the mineral surfaces.

The recorded data (Figures 17, 19, and 21) indicate that the adsorption of hydroxamate onto chrysocolla, malachite, or cuprite involves the same mechanism because:

1) the copper hydroxamate curve showed a shoulder at 1570 cm^{-1} that was displaced to 1600 cm^{-1} upon reaction with the minerals; and
2) the copper hydroxamate absorption bands at 1620 cm^{-1} and 1660 cm^{-1} were shifted to 1650 cm^{-1} and 1700 cm^{-1}, respectively, when adsorption onto the minerals took place.

The remaining data (Figures 18, 20, and 22) show that mercaptobenzothiazole adsorption onto the minerals possesses similar frequency displacements in the 970 to 1020 cm^{-1} region.

The characteristics of all the infrared curves, and the frequency shifts produced during adsorption of collectors onto the minerals, substantiated the postulates that copper hydroxamate and copper mercaptobenzothiazole are formed on the mineral surfaces. Consequently, chemisorption reactions must be involved in the three mineral systems considered in this investigation.

CONCLUSIONS

Several conclusions regarding the flotation characteristics of chrysocolla, malachite, and cuprite developed from this investigation, viz.,

1) The flotation response of the copper oxide minerals is due to the formation of an insoluble copper-collector compound on the mineral surfaces (i.e. a chemical reaction is involved).
2) The system temperature plays an important part in improving the flotation recoveries.
3) The flotation pH has to be controlled in the 6.5 ± 0.5 region for optimum response, especially for chrysocolla.
4) Conventional flotation of copper oxide minerals (including chrysocolla) with economical reagent additions is possible.

APPENDIX 1

The Experimental Techniques used for Mineral Analyses

Qualitative Emission Spectrographic Analysis (11)

1) Excitation Parameters

d-c arc power	6
capacitance	0.0025 uF
inductance	300 uH
analytical gap	4 mm
slit width	25 u
spectral range	2300 - 3600 A
plate type	Kodak S.A #3 x 2 ins
electrode types	AGKSP # L 4006, and AGKSP # L 3951.

2) Exposure Parameters

Rack Position	Samples	Exposure
600	malachite	5 sec preburn
520	cuprite	30 sec exposure
440	chrysocolla	
560	iron rod	5 sec preburn
480	iron rod	3 sec exposure d-c power = 3.

3) Plate Development

D.19 developer .... 4 min at 20°C

short stop .... 30 sec

fixer .... 5 min

water rinse .... 30 min.

Quantitative Analyses

Mineral samples were forwarded to the Messina (Transvaal) Development Company Laboratories in Messina, South Africa, for the determination of the major constituents and impurities.

APPENDIX 2

The Determination of Mineral Settling Rates from Stoke's Law

Stoke's Law gives the rate of fall of a small sphere in a viscous fluid[15]

V = free-falling velocity of a particle in cm/sec

$$= \frac{d^2 . g . (D_p - D_f)}{18\ n} \text{ cm/sec where....}$$

d = Stoke's diameter of the particle in cm

g = Gravitational acceleration in c.g.s. units

= 981 cm/sec^2

D_p = density of the particle in gm/ml

D_f = density of the fluid in gm/ml

n = absolute viscosity of the fluid in dyne sec/cms^2 (poise).

For 10 Micron Particles

$$V = \frac{(10 \times 10^{-4})^2 \ 981\ (D_p - 1.00)}{18 \times 0.0113} \text{ cm/sec}$$

$$= (4.82 \times 10^{-3})(D_p - 1.00) \text{ cm/sec}$$

$$= 17.4\ (D_p - 1.00) \text{ cm/hr.}$$

Mineral	Specific Gravity	10 Micron Particle Settling Rate
Chrysocolla	2.41	24.5 cm/hr
Malachite	4.01	52.4
Cuprite	6.00	87.0

For 5 Micron Particles

$$V = \frac{(5 \times 10^{-4})^2 \, 981 \, (D_p - 1.00)}{18 \times 0.0113} \text{ cm/sec}$$

$$= (1.21 \times 10^{-3})(D_p - 1.00) \text{ cm/sec}$$

$$= 4.32 \, (D_p - 1.00) \text{ cm/hr.}$$

Mineral	Specific Gravity	5 Micron Particle Settling Rate
Chrysocolla	2.41	6.1 cm/hr
Malachite	4.01	13.1
Cuprite	6.00	21.8

APPENDIX 3

The Determination of Mineral Slurry Densities for Infrared Absorption Work

Mineral	Amounts of Settled Solids	Amounts of Suspended Solids/850 ml	Slurry Density
Chrysocolla	14.83 gm	5.17 gm	6.1 mg/ml
Malachite	17.34	2.66	3.1
Cuprite	17.64	2.36	2.8

Sample calculation

Amount of suspended solids/850 ml slurry

= original weight - amount of settled solids

= 20.00 - 14.83

= 5.17 gm

Slurry density = amount of solids/unit volume

$$= \frac{5.17 \times 1000}{850} \text{ mg/ml}$$

= 6.1 mg/ml

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