

THE EFFECT OF INORGANIC ANIONS ON
THE FLOTATION OF CASSITERITE BY
SODIUM DODECYLSULFONATE

by

Christopher H. Cox

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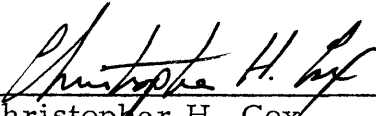
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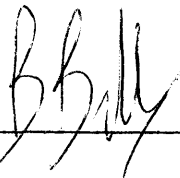
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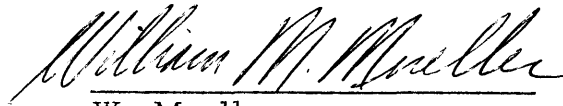
A Thesis submitted to the Faculty and the Board of Trustees
of the Colorado School of Mines in partial fulfillment of the require-
ments for the degree of Master of Science (Metallurgical Engineering).

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ABSTRACT

Micro-flotation studies were performed with cassiterite to determine its response to collection by sodium dodecylsulfonate while in the presence of various inorganic sodium salts. Electrokinetic data were developed in systems similar to those in the flotation investigations and was used in the interpretation of the recovery versus pH data.

The presence of certain inorganic sodium salts serves to shift the zero point of charge of cassiterite to lower pH values. This electrokinetic effect is reflected in the flotation behavior of cassiterite, indicating that recovery by sodium dodecylsulfonate is extremely dependent on the mineral's surface electrical characteristics.

The pK of the salt anion's conjugate acid appears to have an effect on that anion's adsorption which manifests an influence on the flotation response.

When collector dosages are of a starvation level adsorption of sulfonate appears to be governed solely by columbic attraction. Adsorption of sulfonate at higher concentration, however, seems to be a function of more than simple electrostatic forces.

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The author would like to thank Dr. Brian Ball for his guidance and counsel during the course of this investigation.

The author would also like to thank Dr. Seng Yap for the use of the electrokinetic data pertinent to this thesis.

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INTRODUCTION

The mineral cassiterite is considered to be the only important source of tin. Concentration of this mineral has been accomplished predominately through gravity operations, taking advantage of cassiterite's relatively high specific gravity and the low operating cost of processing.

However, due to the inefficiency of gravity operations in the finer size ranges, the flotation of cassiterite has received much interest. At first, flotation test work was directed toward using soaps and fatty acid as collectors with oleic acid drawing the most scrutiny (1-5). More recent studies investigated the use of alkyl-sulfonates (5, 6, 7), alkyl sulfates (5-11), long chain amines (6, 3c), sulfosuccinamate (8, 12), phosphonic acids (3, 13, 14, 15, 16, 17), mixtures of oleic acid and phosphonic acid (9), arsonic acids (5, 17, 18, 19), hydroxamic acid and hydroxamate (5, 7, 20) as collectors for cassiterite. Of the above reagents, researchers have suggested that phosphonic acid and arsonic acids are the best collectors to date with arsonic acids being the more selective of the two. These flotation studies with arsonic acid and phosphonic acid suggested that

their adsorption onto cassiterite is specific.

Yap (21) in her study of oil phase extraction of cassiterite slimes investigated the effect of the presence of different inorganic sodium salts, whose anions were similar to the polar groups of successful cassiterite collectors, on the surface electrical characteristics of cassiterite. The results of these tests showed that the presence of NaH_2PO_4 , Na_2HAsO_4 , NaHSO_3 , and Na_2SO_4 effected dramatic shifts in the zero point of charge (ZPC) of cassiterite to lower pH values.

The objective of this thesis then was to delineate the effect of the presences of these inorganic sodium salts on the flotation recovery of cassiterite using sodium dodecylsulfonate as a collector.

Tests were conducted investigating the flotation response of cassiterite as a function of pH, salt concentration and collector concentration. Electrokinetic data for the cassiterite-water-sodium salt systems and for cassiterite-water-dodecylsulfonate system developed by Yap (21) were used in the interpretation of the flotation response curves. The investigation included the use of a modified Hallimond tube so that the flotation tests could be conducted under relatively pure and controlled conditions.

MATERIALS AND PROCEDURES

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

Materials

Mineral Sample

The cassiterite used in this study was derived from a jig concentrate produced by Mina Polva Mines of Bolivia. The cassiterite in this sample was liberated at the 100 mesh size with pyrite and quartz being the major gangue constituents.

Water

The water used for all experimental work was triply distilled and deionized with an electrical conductivity of less than 10 μ mho.

Reagents

Reagents used in this investigation are discussed as follows:

Collector:

Sodium dodecylsulfonate: Aldrich Chemical
Company >99%

pH Control Reagents:

Perchloric acid: Baker Analytical grade

Sodium hydroxide: Baker Analytical grade

Modifiers:

Sodium perchlorate: Reagent grade

Sodium sulfate: Reagent grade

Sodium dihydrogen phosphate: Reagent grade

Sodium monohydrogen arsenate: Reagent grade

Sodium bisulfite: Reagent grade

The gas used for flotation was type T nitrogen supplied by the Linde Company. The gas was purified by passing it through a solution of potassium hydroxide, through anhydrite, and through ascorite to remove water and CO₂.

Equipment

The micro-flotation studies were conducted using a modified Hallimond tube (22, 23, 24). This apparatus allowed flotation of one gram charges of pure mineral in a system free from metallic components and frother.

The system permitted the introduction of a constant volume of purified gas at a constant pressure. Bubble dispersion was accomplished by passing purified nitrogen through a fritted disk positioned in the bottom of the tube. The disk had an average pore size of 60-microns.

A schematic of the micro-flotation equipment set up, showing the apparatus associated with the operation of the Hallimond tube is presented in Figure 1. A photograph of the equipment layout is presented in Figure 2 with a close up photograph of the Hallimond tube shown in Figure 3.

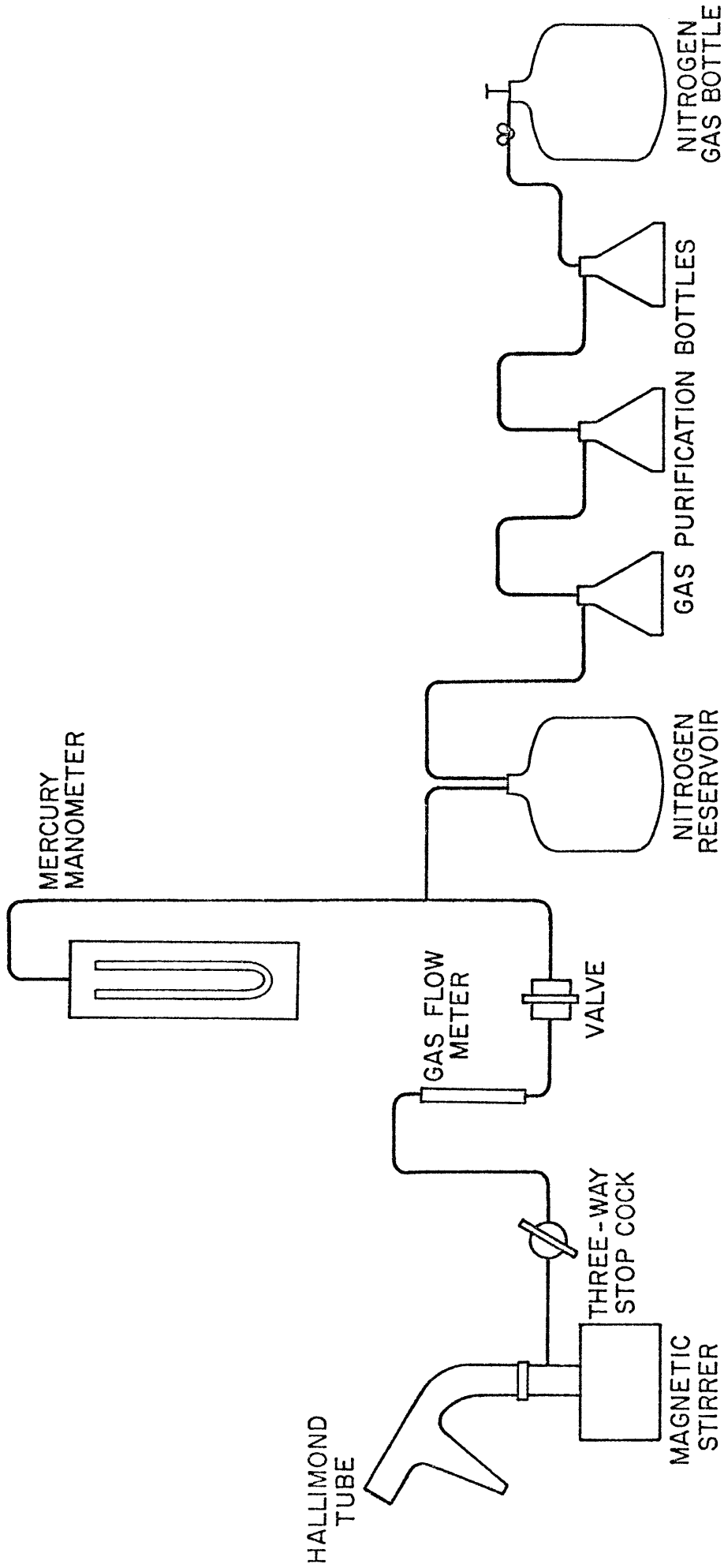
Electrokinetic measurements were conducted using a Zeta-meter supplied by the Zeta Meter Inc. of New York (29).

Procedures

Cassiterite Sample Preparation

Microscopic examination of screen fractions produced from the jig concentrate showed 95% or greater liberation of the cassiterite occurring at the 100-Tyler mesh size. This determination led to the selection of the -100 + 150 mesh size fraction of the jig concentrate for micro-flotation studies. This size fraction was removed from the bulk sample and subjected to a flotation operation to remove any sulfides present. This procedure was conducted using sodium ethyl xanthate as collector while calcium hydroxide was used to maintain the pulp at a pH of 9.0.

After flotation the cassiterite product was washed in acetone, dried, and subjected to a heavy liquid separation, using 'Clerici' solution at a specific gravity of 4.2, to remove any quartz or cassiterite-gangue middlings. The sink product from the heavy



SCHEMATIC OF MICRO FLOTATION APPARATUS

FIGURE 1

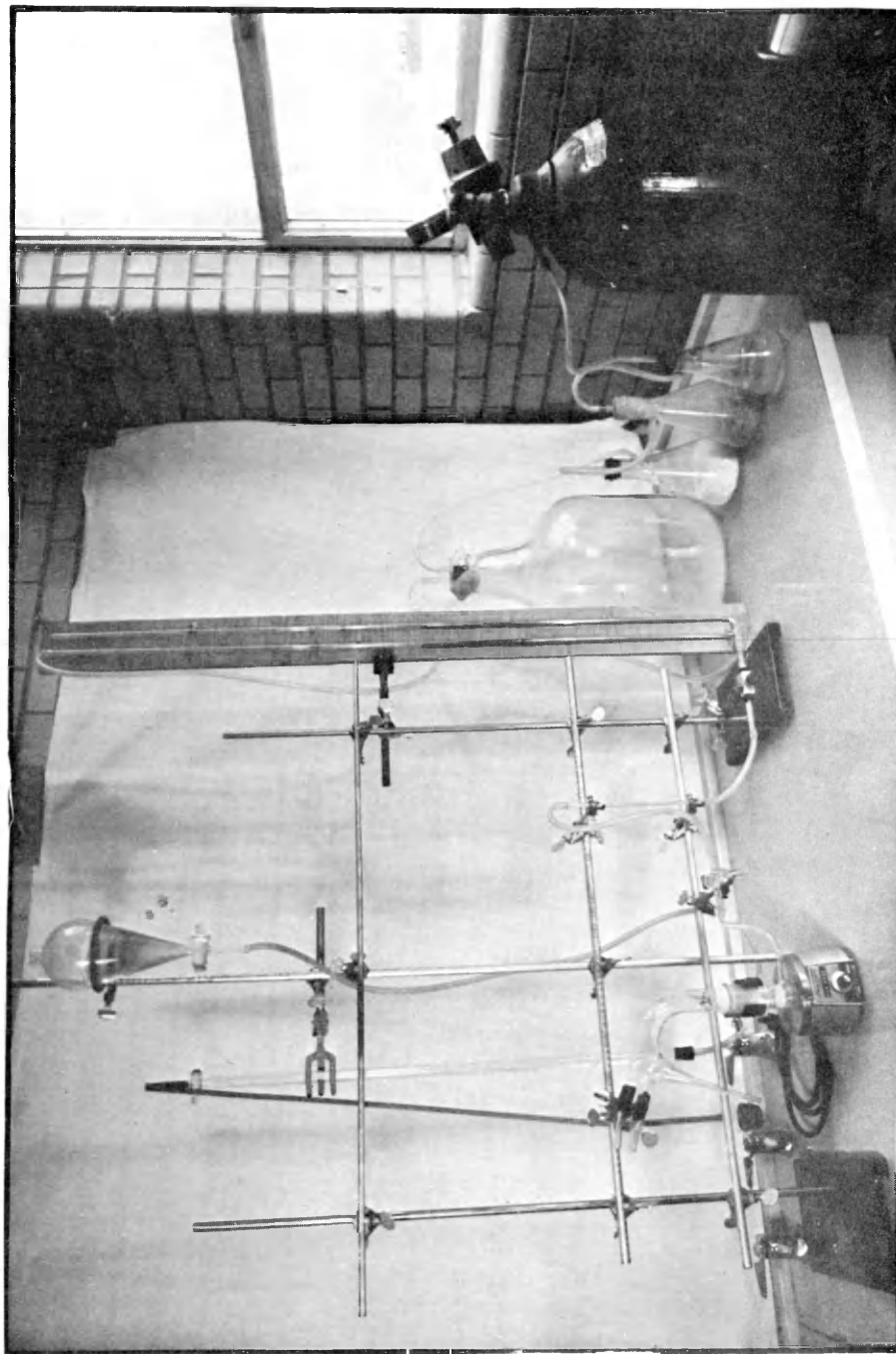


FIGURE 2

Photograph of Micro-Flotation Apparatus

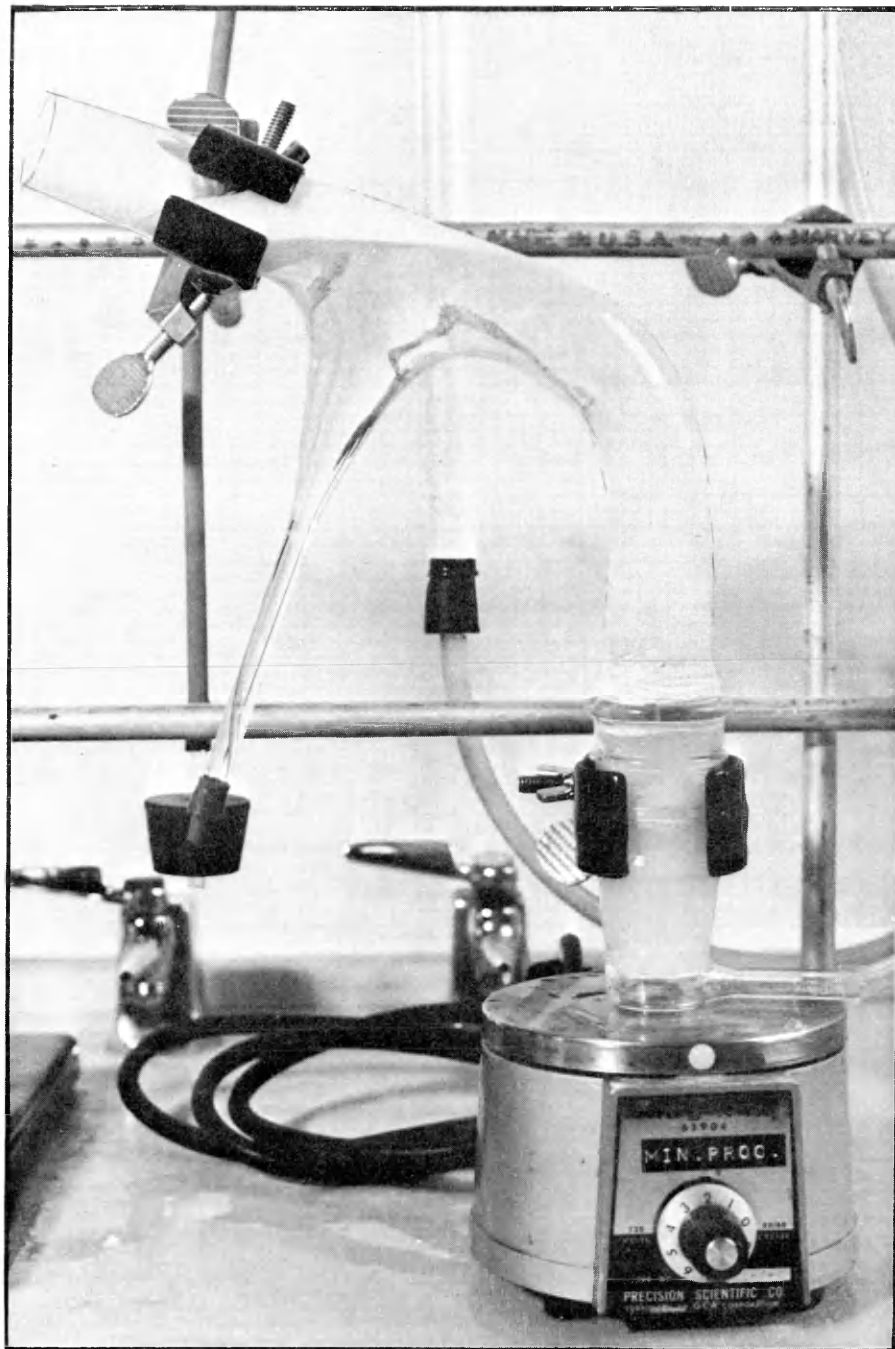


FIGURE 3

Photograph of Modified Halimond Tube

liquid operation was washed with acetone, dried and cleaned magnetically using a Reading laboratory magnetic separator.

The nonmagnetic fraction was leached with analytical grade concentrated hydrochloric acid for ten hours, under reflux, to remove any residual sulfide mineralization and residual particulate iron. The leached cassiterite was washed with conductivity water until the wash solution and filtrate had equal electrical conductivities. After washing the material was dried and stored in sealed plastic vials for flotation test work.

Mineral Analysis

A sample of the purified -100 + 150 mesh screen fraction was subjected to x-ray diffraction analysis to confirm mineral structure. The diffraction pattern produced from sweeping between 2θ angles of 10° and 100° matched the pattern discussed in the ASTM card file for cassiterite.

Mineral purity was determined by a semiquantitative emission spectrographic scan of a sample of the purified screen fraction. Results of this analysis are shown in Table 1.

Table 1. Spectrographic Analysis of -100+150 M Purified Cassiterite Screen Fraction

<u>Element</u>	<u>Amount, %</u>
Al	0.2
B	0.5
Co	<0.001
Cu	0.01
Fe	2.0
Mn	<0.001
Si	0.1
Ti	<1.0
Sn	>70.0
W	0.2
V	0.01
Zr	0.01
Ca	0.01
Mg	0.5

Flotation Experiments

The flotation experiments were conducted in the following manner:

1. 300 ml of conductivity water containing the designated sodium salt of desired concentration was prepared and adjusted to a specific pH using perchloric acid or sodium hydroxide.
2. 50 ml of solution, described in step 1, was removed and placed along with 1 gram of prepared cassiterite sample in an 80 ml beaker. The cassiterite and solution were agitated by means of a magnetic stirrer bar for 5 minutes.
3. After 5 minutes, a specific amount of sodium dodecyl-sulfonate, in solution with the same concentration of sodium salt as the solution discussed in 1, was introduced into the 800 ml beaker. The cassiterite sample was allowed to condition with the collector for 10 minutes. The pH of the system was measured after conditioning; the value obtained was considered flotation pH.
4. The remaining 250 ml of this solution discussed in step 1 was brought up to desired sulfonate strength.
5. After conditioning, the cassiterite sample and flotation solution were transferred to the modified Hallimond

tube and 35 ml of purified nitrogen were passed through the pulp in 60 seconds. During this time the pulp was stirred magnetically and the floated material collected in the upper chamber.

6. The final pH was recorded to check for any excessive change.
7. The flotation products were dried and weighed, and the recoveries were calculated.

Electrokinetic Measurements

The mobility of cassiterite at various pH values in the presence of NaH_2PO_4 and of Na_2HAsO_4 at fixed concentrations was determined by means of the zeta-meter at 25°C . The suspensions for the mobility measurements were prepared as follows:

1. A weighed amount of cassiterite was introduced into a 50-ml Erlenmeyer flask and 1.0 ml of water was added. The suspension was dispersed for 1 minute in an ultrasonic bath.
2. 39 ml of known concentration of the sodium salt was added and the pH adjusted by addition of HClO_4 or NaOH .
3. The flask was stoppered, immersed in a water bath of $25^\circ \pm 1^\circ\text{C}$ and agitated by means of a magnetic stirrer bar for 15 min.

4. After 15 min. a 5 to 10 ml aliquot of the suspension was taken for pH determination.
5. The mobility was determined after 20 min of agitation.
6. The zeta-potential was then determined from the mobility by means of the Helmholtz-Smoluchowski equation (29). Under the conditions employed the equation reduced to:

$$\text{Zeta-potential} = 12.8 \times \text{mobility (m volt)}$$

EXPERIMENTAL RESULTS

Presented in this section are the results of flotation investigations studying the effects of selected inorganic electrolytes on the response of the cassiterite-sodium dodecylsulfonate system. These tests were directed toward delineating the recovery of cassiterite as a function of the following parameters:

1. pH
2. Inorganic electrolyte type
 - A. NaClO_4
 - B. NaH_2PO_4
 - C. Na_2HAsO_4
 - D. NaHSO_3
 - E. Na_2SO_4
3. Inorganic electrolyte concentration
4. Sodium dodecylsulfonate concentration

Also presented are some electrokinetic data for the NaH_2PO_4 and Na_2HAsO_4 systems. An explanation of the results follows.

NaClO₄ System

The flotation recovery of cassiterite as a function of pH for collector concentrations of 10^{-4} M and 10^{-5} M sulfonate in the presence of a fixed NaClO₄ molarity of 10^{-3} is depicted in Figure 4.

For a collector concentration of 10^{-4} M complete flotation is observed in the acid range up to a pH value of 5.5. As the pH is increased above this value flotation recovery drops rapidly and goes to 0% at a pH of 11.

With a concentration of 10^{-5} M sulfonate in this system the flotation recovery is decreased over the whole pH range. At a pH of 1.0 cassiterite recovery is only 82%, dropping almost linearly to zero at a pH value of approximately 9.0.

NaH₂PO₄ System

A) Flotation Results

The flotation response of cassiterite, as a function of pH, for 10^{-4} M sulfonate in the presence of 10^{-3} M, 10^{-4} M and 10^{-5} M NaH₂PO₄ is expressed graphically in Figure 5. Also shown in this figure is the recovery curve for 10^{-5} M sulfonate when in solution with 10^{-3} M NaH₂PO₄.

For a sulfonate concentration of 10^{-4} M in conjunction with NaH₂PO₄ at a 10^{-3} M level complete flotation is only encountered below pH 1.8. The recovery curve drops rapidly as pH is

Figure 4. Recovery of cassiterite vs pH for various concentrations of sodium dodecylsulfonate in the presence of 10^{-3}M NaClO_4 .

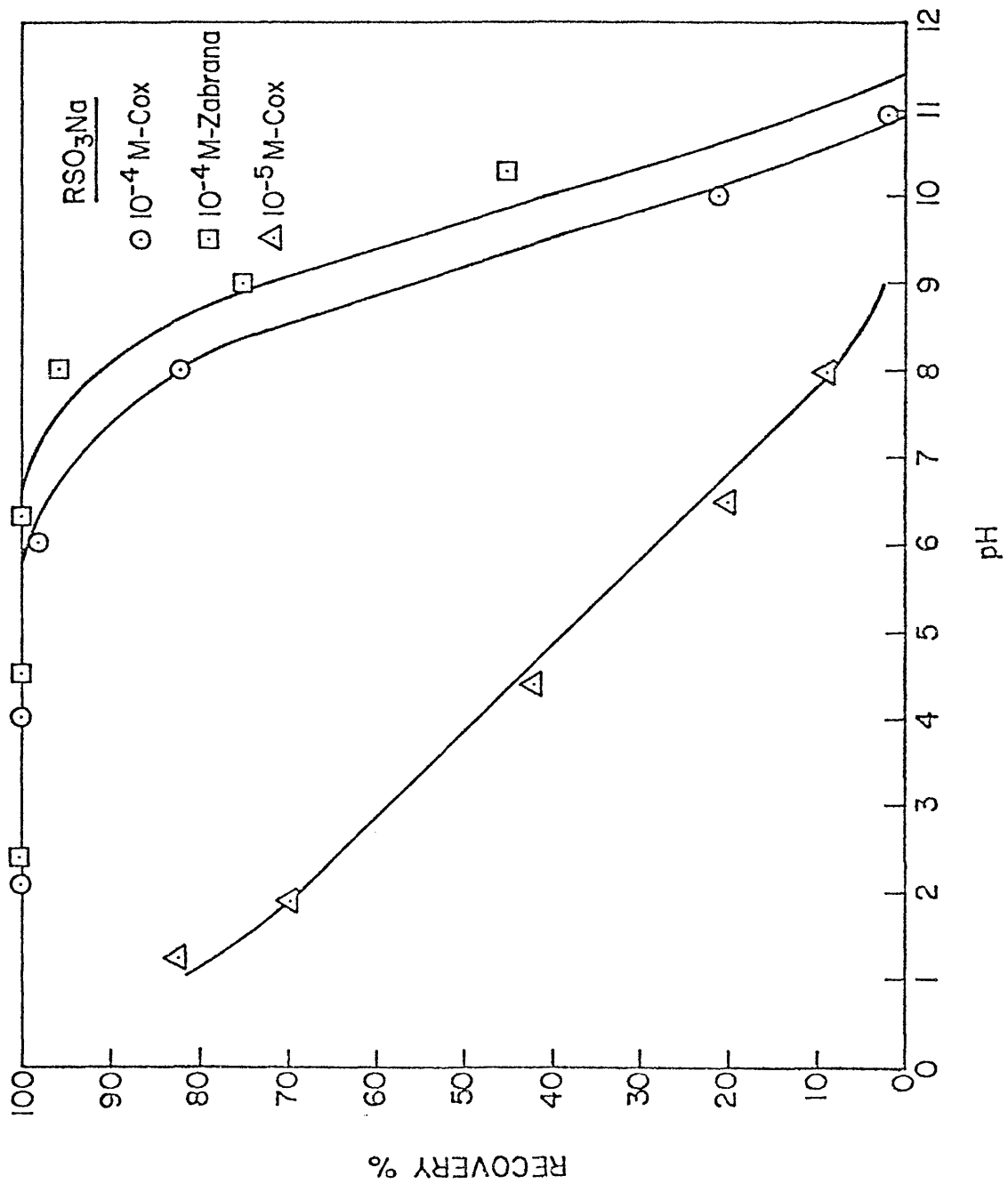
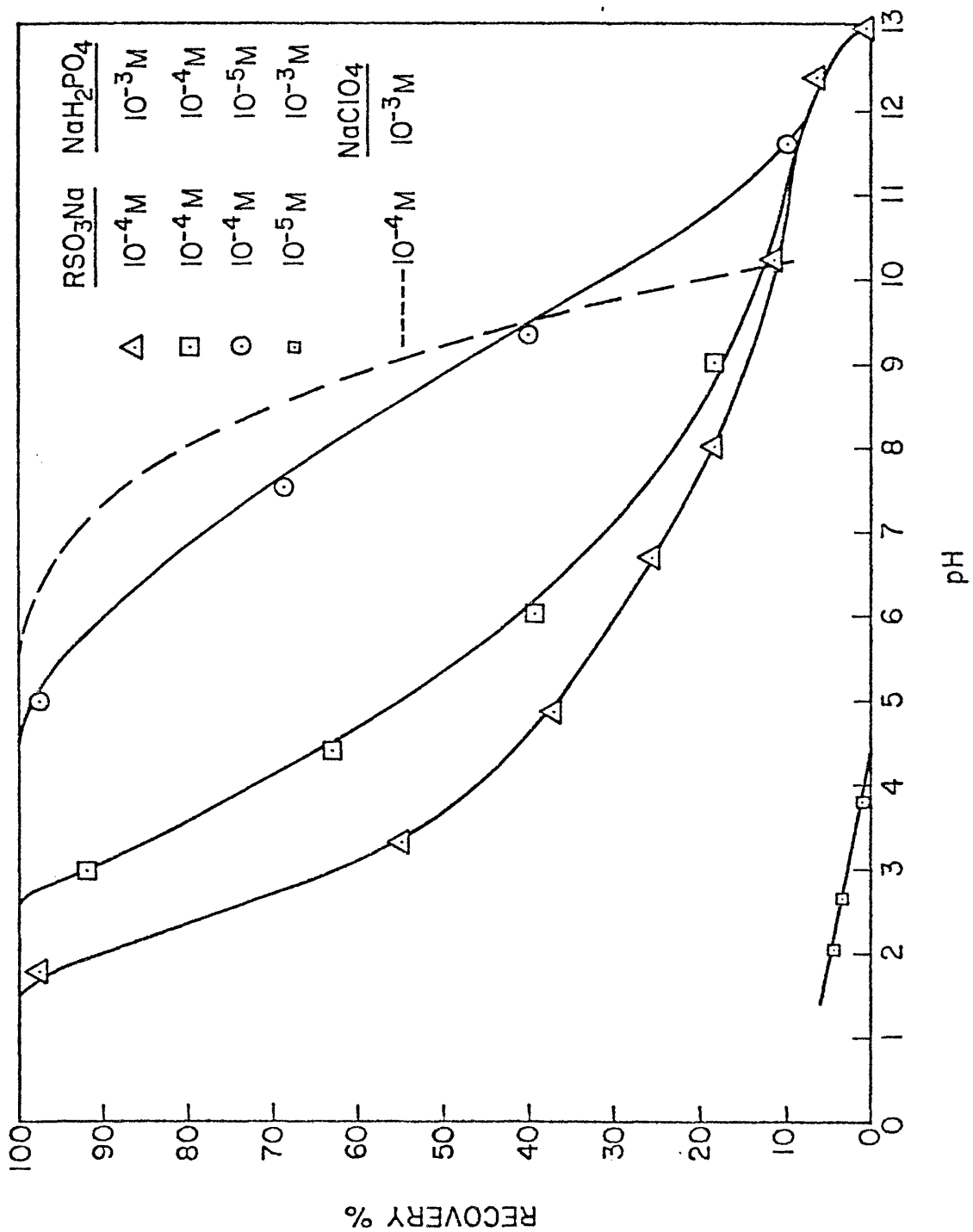


Figure 5. Recovery of cassiterite vs pH for 10^{-4} M and 10^{-5} M sodium dodecylsulfonate in the presence of various concentrations of NaH_2PO_4 .



increased but began to flatten in slope when passing through neutral pH. The curve continues to level until reaching a basic pH of approximately 12.5, where the flotation trend changes and falls to 0% at pH 13.

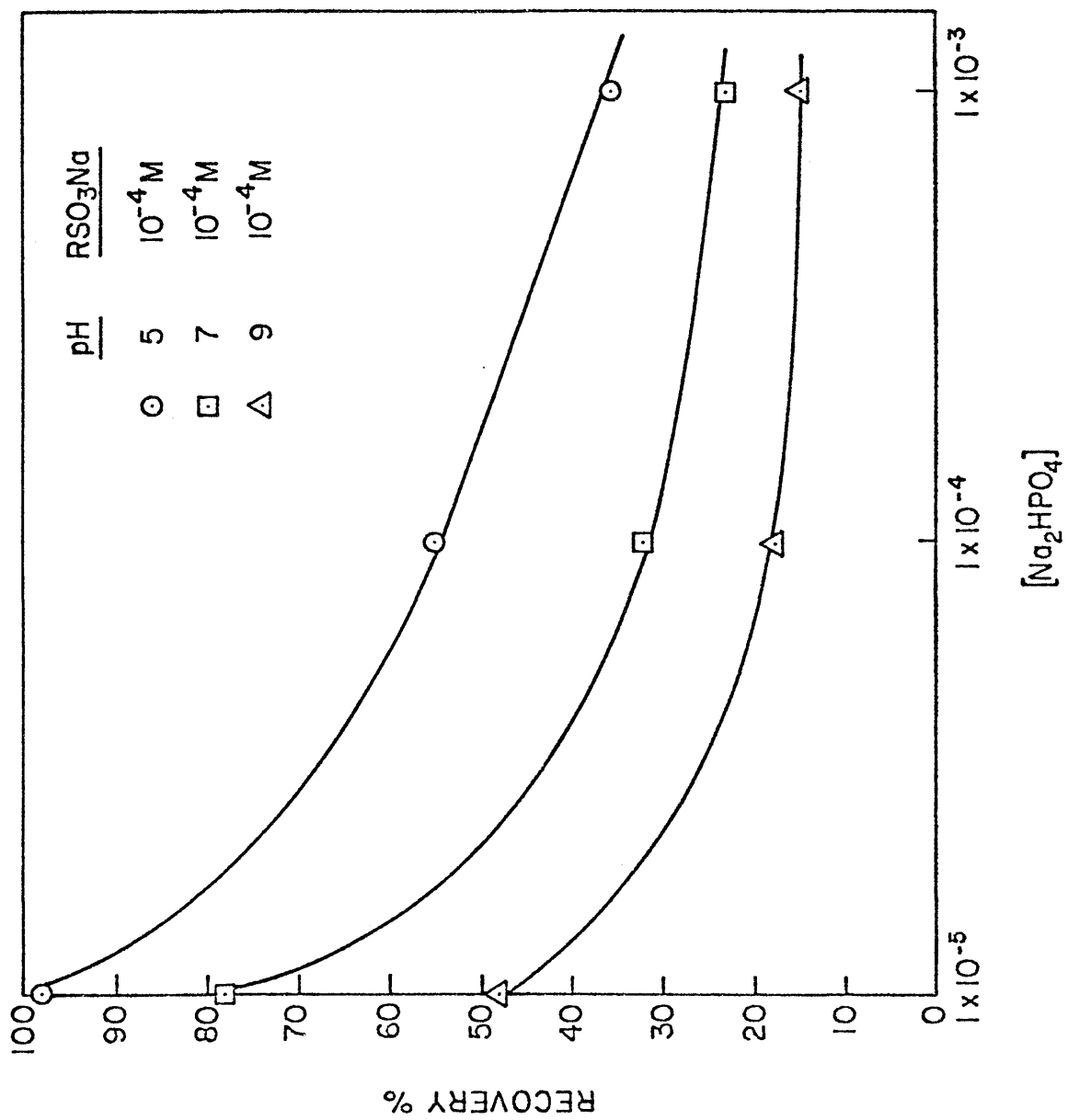
When the sulfonate and NaH_2PO_4 concentrations are both 10^{-4} M, 100% flotation is observed from pH 3.0 and below. Above this value the curve has a similar shape to the one discussed previously but is shifted to the right. Both curves become coincident at pH 11.

With the NaH_2PO_4 level decreased to 10^{-5} M and sulfonate concentration maintained at 10^{-4} M, the cassiterite flotation response curve takes on a similar shape to the first cassiterite-sulfonate- NaClO_4 curve discussed. Complete recovery is experienced for acid pH values up to 4.5. As the pH is increased the curve drops linearly and joins the other two NaH_2PO_4 curves, discussed previously, at a pH value of 12.

As shown in Figure 5 flotation is essentially completely inhibited when the sulfonate concentration is lowered to 10^{-5} M and NaH_2PO_4 solution strength is maintained at 10^{-3} M.

Cassiterite flotation recovery as a function of NaH_2PO_4 concentration for a fixed sulfonate addition of 10^{-4} M and for fixed pH values of 5, 7, and 9 is presented in Figure 6. As shown, these curves are generally colinear, with recovery at any chosen

Figure 6. Recovery of cassiterite vs concentration of NaH_2PO_4 for a fixed sodium dodecylsulfonate concentration at fixed pH values.



NaH_2PO_4 concentration, highest for pH 5 and decreasing with increasing pH.

For each pH value recovery drops rapidly when the NaH_2PO_4 concentration is increased from 10^{-5} M to 10^{-4} M. When increasing the electrolyte concentration from 10^{-4} M to 10^{-3} M the recovery for each curve begins to approach a constant value.

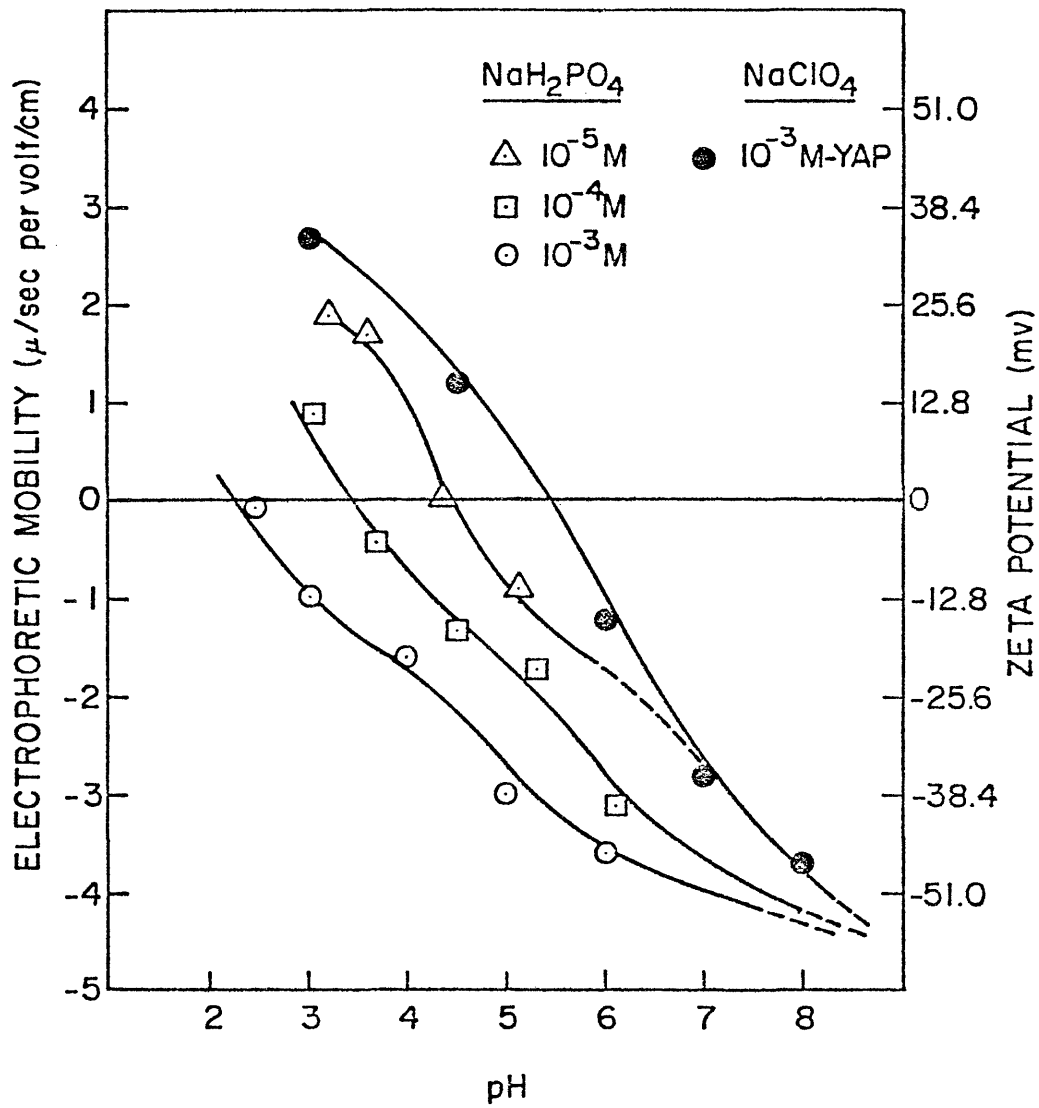
B) Electrokinetic Results

The effect of various concentrations of NaH_2PO_4 on the electrophoretic mobility or on the zeta potential of cassiterite is shown in Figure 7. These data were determined in the absence of sulfonate. Presented also in the figure are Yaps results of a cassiterite in the presence of 10^{-3} M NaClO_4 .

As depicted, a NaH_2PO_4 concentration of 10^{-3} M shifts the ZPC to a pH value of 2.3. For a concentration of 10^{-4} M the ZPC occurs at a pH of 3.4, and for 10^{-5} M the pH of the ZPC is 4.4.

The curve for 10^{-5} M NaH_2PO_4 appears to coincide with 10^{-3} M NaClO_4 curve at about pH 7. At this same pH, however, the 10^{-4} M and 10^{-3} M curves have much larger negative electrophoretic mobilities or negative zeta potential values. These two curves appear to join the 10^{-3} M NaClO_4 above pH 8.

Figure 7. Electrophoretic mobility and zeta potential of cassiterite vs pH in the presence of NaClO_4 and in the presence of various concentrations of NaH_2PO_4 .



Na₂HAsO₄ SystemA) Flotation Results

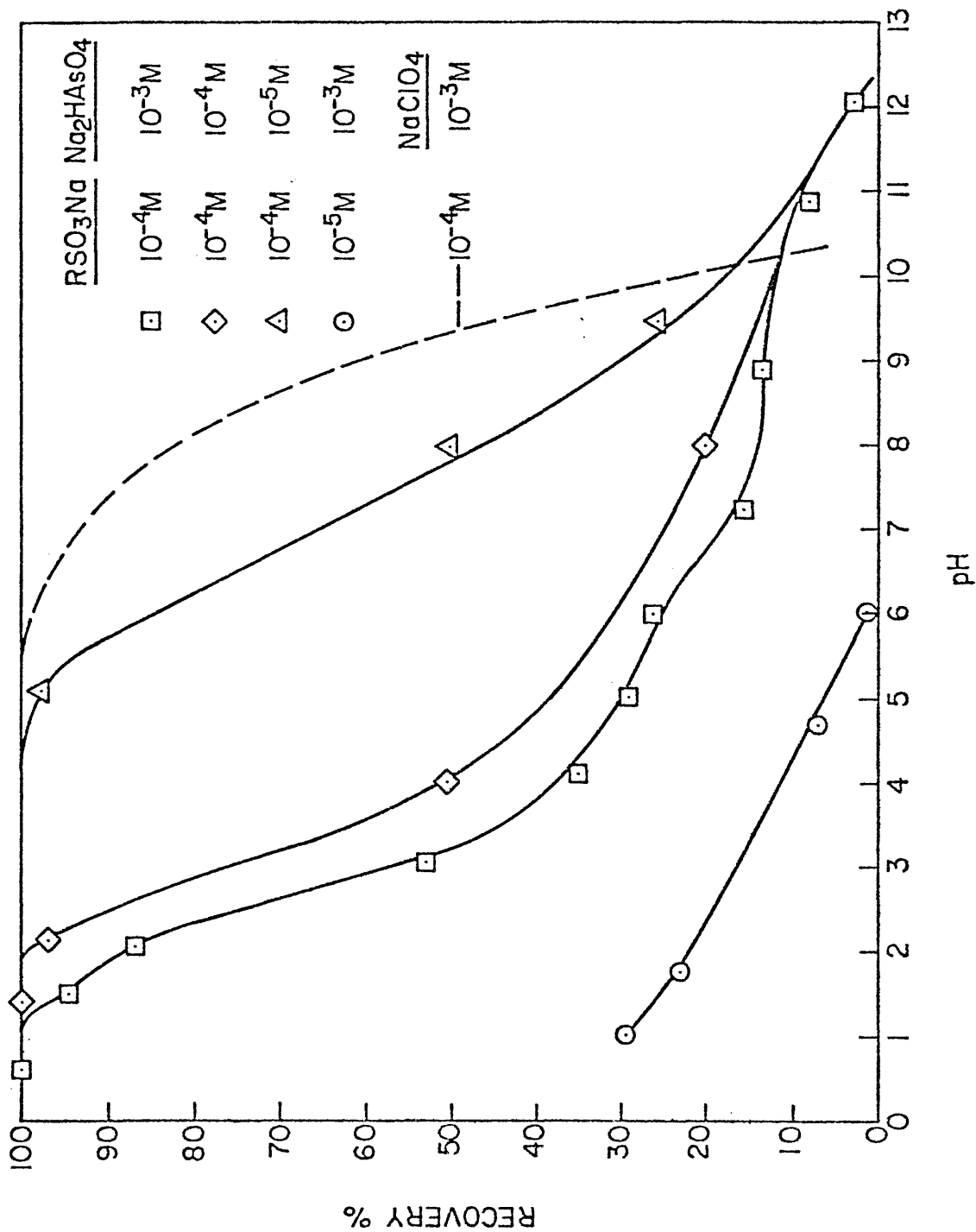
Flotation recovery curves of cassiterite as a function of pH, for 10^{-4} M sulfonate in the presence of 10^{-3} M, 10^{-4} M, 10^{-5} M Na₂HAsO₄ are presented in Figure 8. Shown also in the figure is the cassiterite recovery response for 10^{-5} M sulfonate when in the presence of 10^{-3} M Na₂HAsO₄.

For 10^{-4} M sulfonate with 10^{-3} M Na₂HAsO₄ complete flotation is not encountered until a pH of 1.5 or below is obtained. Above a pH of 1.5 the curve begins to drop and increases in slope after passing pH 2. It begins to flatten after pH 4 but experiences a slight downward inflexion between pH 6 and pH 7. Above neutral pH the recovery shows only a slight change until an approximate pH of 11 is reached, when flotation again decreases going to zero at pH 12.2.

When 10^{-4} M sulfonate and 10^{-4} M Na₂HAsO₄ are present, 100% flotation is observed for pH values up to 2.3. After passing this value the response is similar to the previously discussed Na₂HAsO₄ system with the curve shifted slightly to the right and coinciding at a pH of 10.

For a Na₂HAsO₄ concentration of 10^{-5} M and a maintained sulfonate level of 10^{-4} M complete cassiterite flotation is experienced for acid pH values of 4.1 and below. Above this pH point the curve drops linearly and joins the two curves discussed above at a pH

Figure 8. Recovery of cassiterite vs pH for 10^{-4} M and 10^{-5} M sodium dodecylsulfonate in the presence of various concentrations of Na_2HASO_4 .



value of 11.

With sulfonate concentration lowered to 10^{-5} M and the Na_2HAsO_4 level maintained at 10^{-3} M flotation is extremely depressed. At a pH of 1.0 a recovery of only 30% is realized. From this point the curve drops in a linear fashion to zero at pH 6.0.

Flotation recovery of cassiterite as a function of Na_2HAsO_4 concentration for a fixed sulfonate strength of 10^{-4} M and for fixed pH values of 5, 7, and 9 are presented as Figure 9. These curves show similar characteristics to the ones produced for NaH_2PO_4 . For the chosen sulfonate level recovery is highest at pH 5 decreasing when going toward pH 9. This is true for all the Na_2HAsO_4 concentration shown. As the Na_2HAsO_4 content is increased the three pH curves flatten in slope, tending toward a constant recovery value.

B) Electrokinetic Results

The effect of 10^{-5} M, 10^{-4} M and 10^{-3} M concentrations of Na_2HAsO_4 on the electrokinetic characteristics of cassiterite are presented in Figure 10. As in the NaH_2PO_4 system these electrophoretic mobility or zeta potential curves were determined in the absence of sulfonate. Yap's data for 10^{-3} M NaClO_4 are also presented.

The pH of the ZPC for 10^{-3} M Na_2HAsO_4 was not determined but extrapolation of the curve indicates an approximate value of 1.5. For 10^{-4} M Na_2HAsO_4 the ZPC occurs at a pH of 2.4 and for 10^{-5} M

Figure 9. Recovery of cassiterite vs concentration of Na_2HAsO_4 for a fixed sodium dodecylsulfonate concentration at fixed pH values.

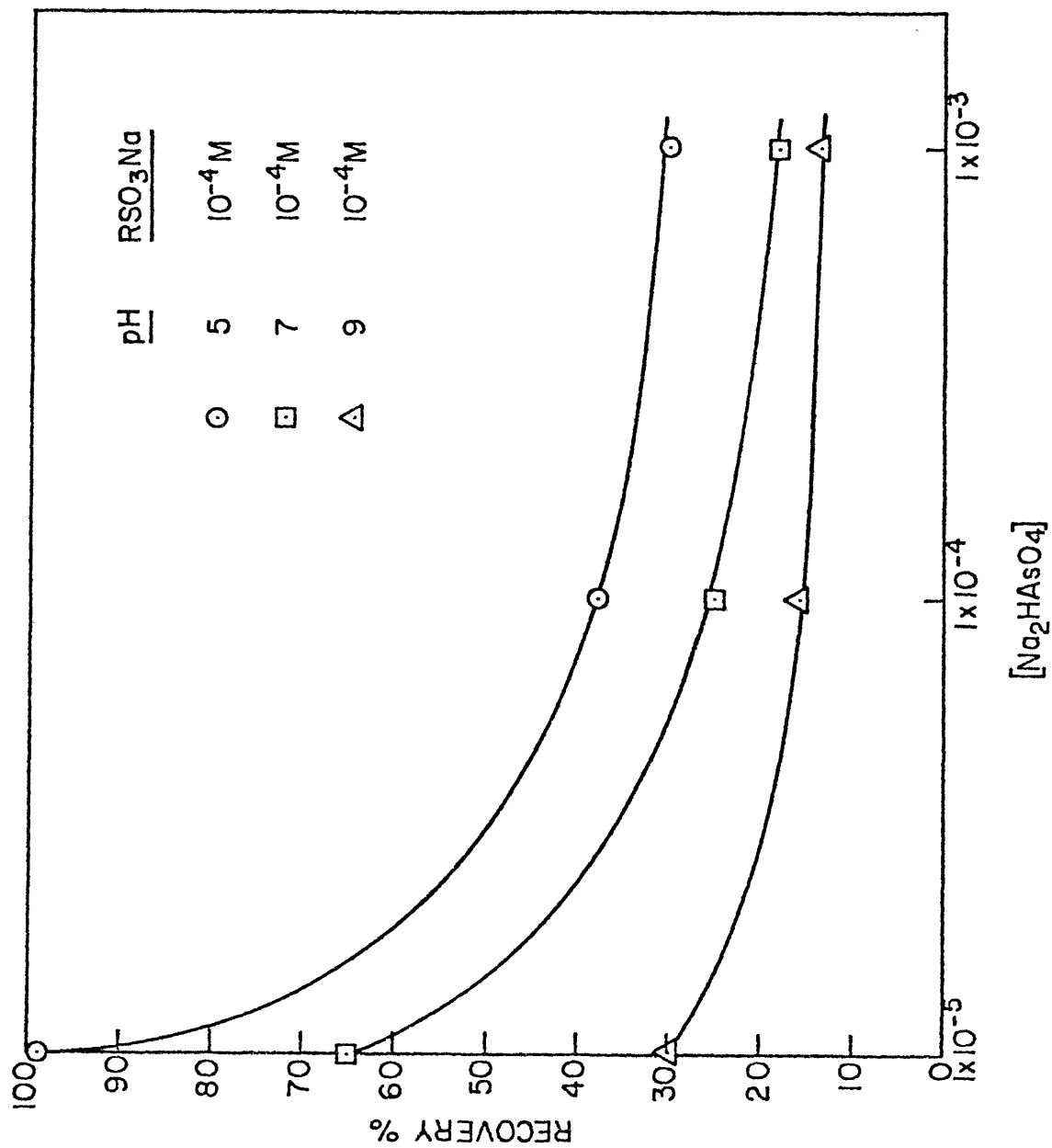
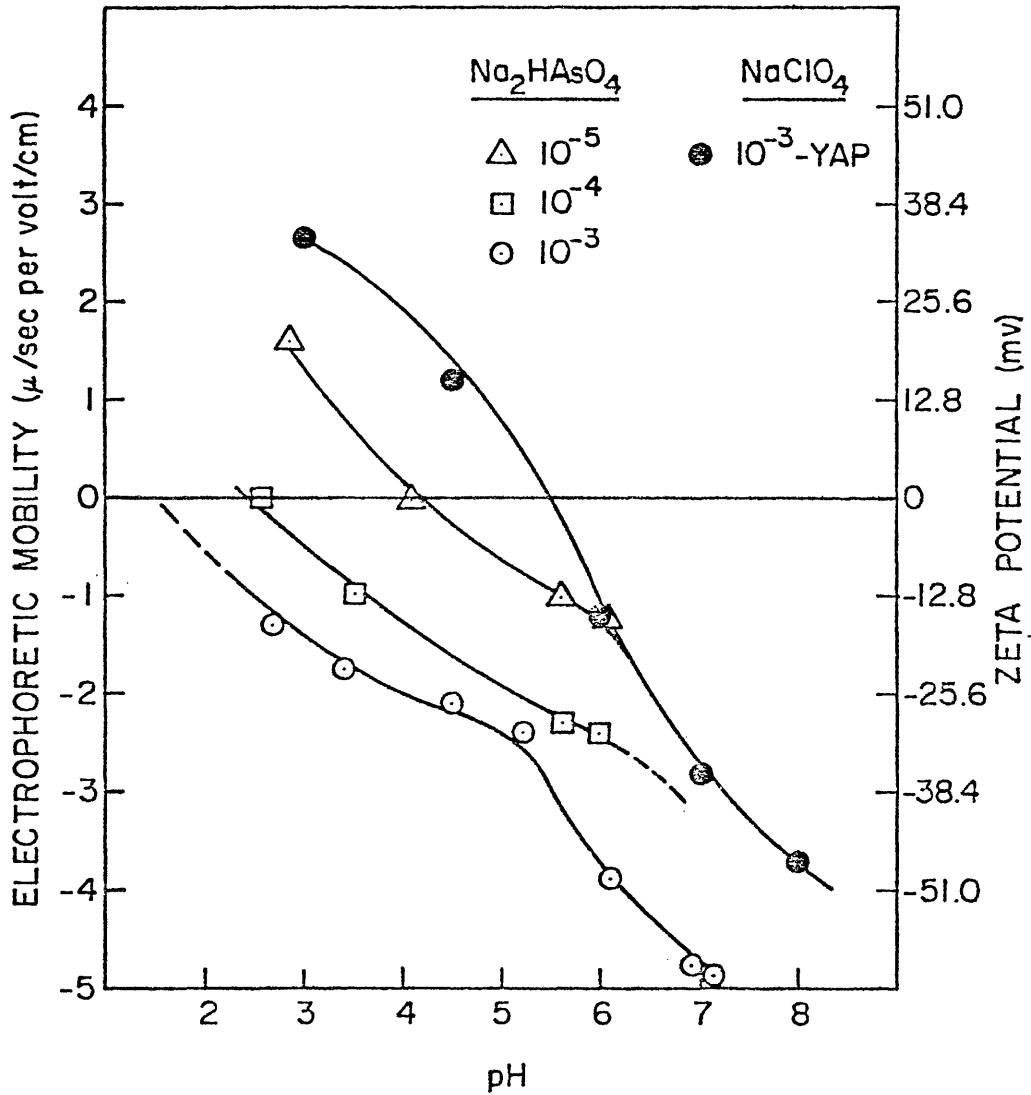


Figure 10. Electrophoretic mobility and zeta potential of cassiterite vs pH in the presence of NaClO_4 and in the presence of various concentrations of Na_2HAsO_4 .



the pH of the ZPC is 4.2.

The 10^{-5} M curve became coincident with Yap's 10^{-3} M NaClO_4 curve at pH 6. However at this pH value $\text{Na}_2\text{HA}_5\text{O}_4$ concentrations of 10^{-4} M and 10^{-3} M produced significantly larger negative mobilities or negative zeta potentials.

NaHSO₃ System

The flotation recovery versus pH curves for cassiterite in solution with 10^{-3} M NaHSO_3 with 10^{-4} M and with 10^{-5} M sulfonate are shown in Figure 11.

For an addition of 10^{-4} M sulfonate complete flotation ceases when the pH is increased above 3.8. Recovery drops rapidly after this value but shows a leveling in slope when going through pH 7. Above neutral pH the recovery again drops rapidly for increasing alkalinity, going to zero about pH 11.5.

When the sulfonate level is lowered to 10^{-5} M, while maintaining the NaHSO_3 concentration at 10^{-3} M, flotation is depressed but extends over a wide pH range.

Na₂SO₄ System

The flotation recovery characteristic of cassiterite in a solution of 10^{-4} M sulfonate and 10^{-3} M Na_2SO_4 is shown graphically in Figure 12.

Figure 11. Recovery of cassiterite vs pH for various concentrations of sodium dodecylsulfonate in the presence of NaHSO_3 .

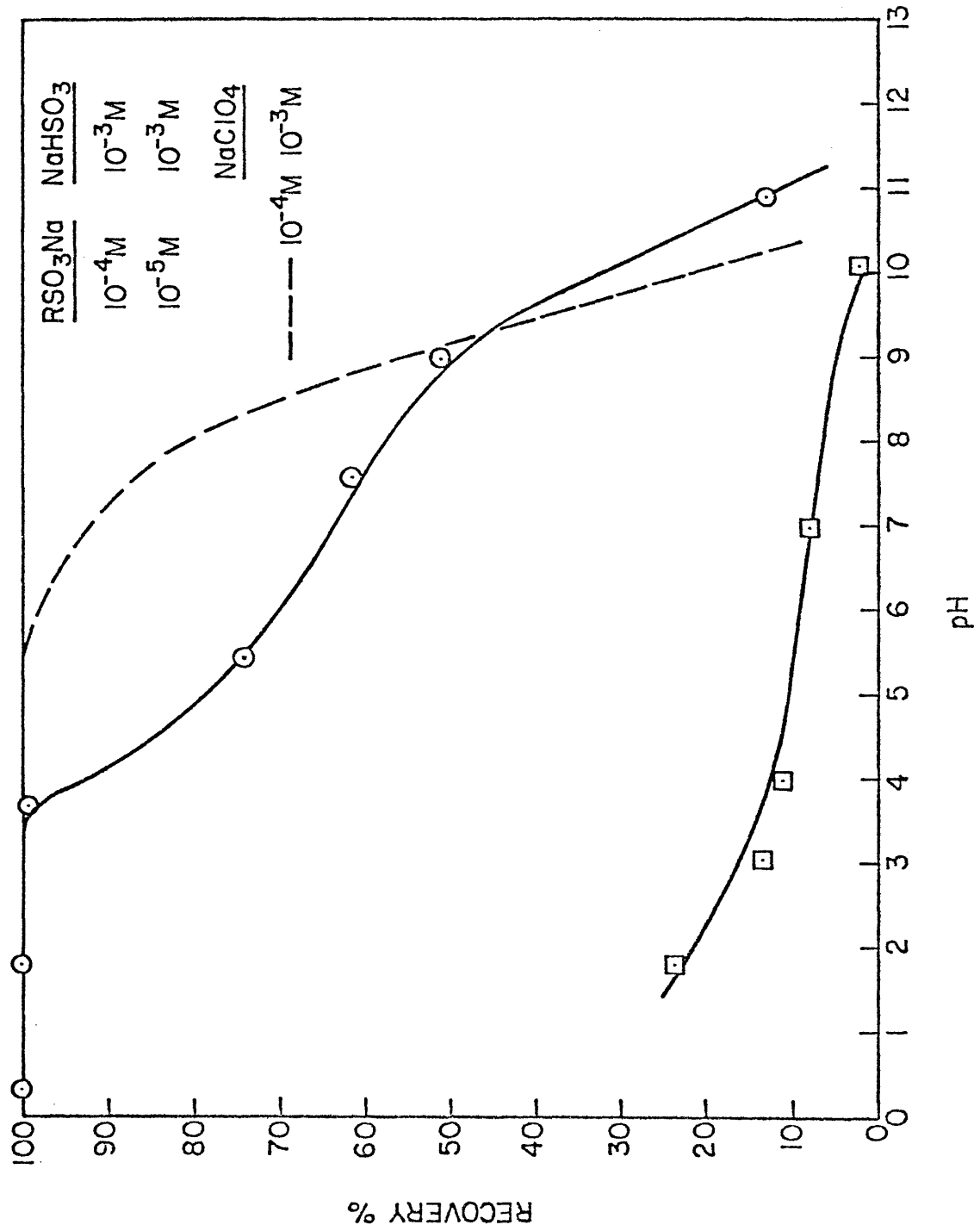
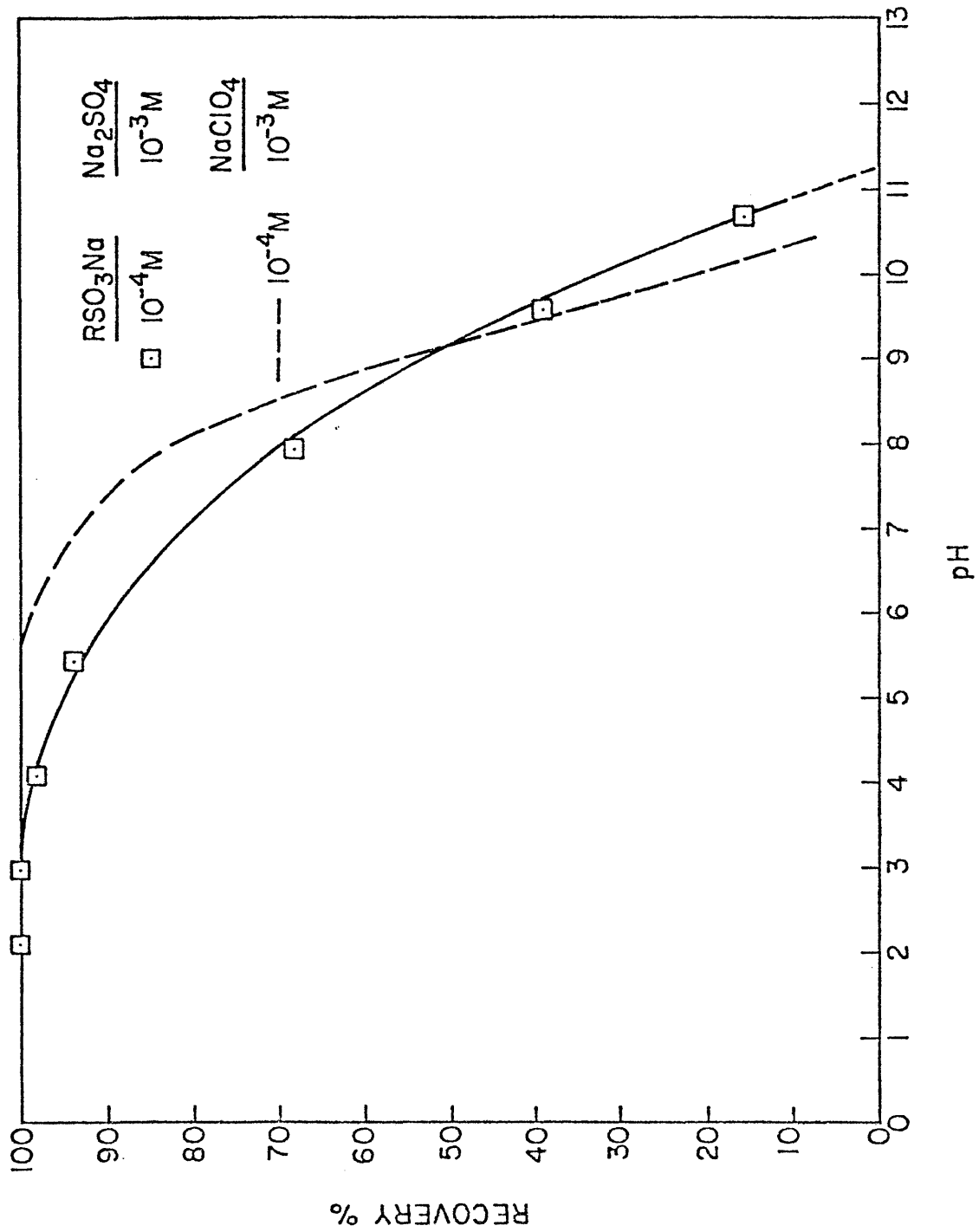


Figure 12. Recovery of cassiterite vs pH for sodium dodecylsulfonate in the presence of Na_2SO_4 .



Recovery of 100% is only found for pH values of 3 or below. Increasing pH above this causes decreased flotation with the curve going to zero about pH 11.4. It is important to note the difference in the shape of this curve as compared to those for the other inorganic electrolytes discussed previously.

Composite Recovery Versus pH Curves

Composite recovery versus pH curves of cassiterite flotation are presented as Figures 13 and 14. Figure 13 shows the response for 10^{-4} M sulfonate in the presence of 10^{-3} M sodium salts of ClO_4^- , H_2PO_4^- , HAsO_4^- , HSO_3^- , and SO_4^- . Figure 14 presents the cassiterite flotation response for 10^{-5} M sulfonate in conjunction with 10^{-3} M concentrations of the aforementioned sodium salts.

Figure 13. Recovery of cassiterite vs pH for 10^{-4} M sodium dodecylsulfonate in the presence of the various inorganic sodium salts.

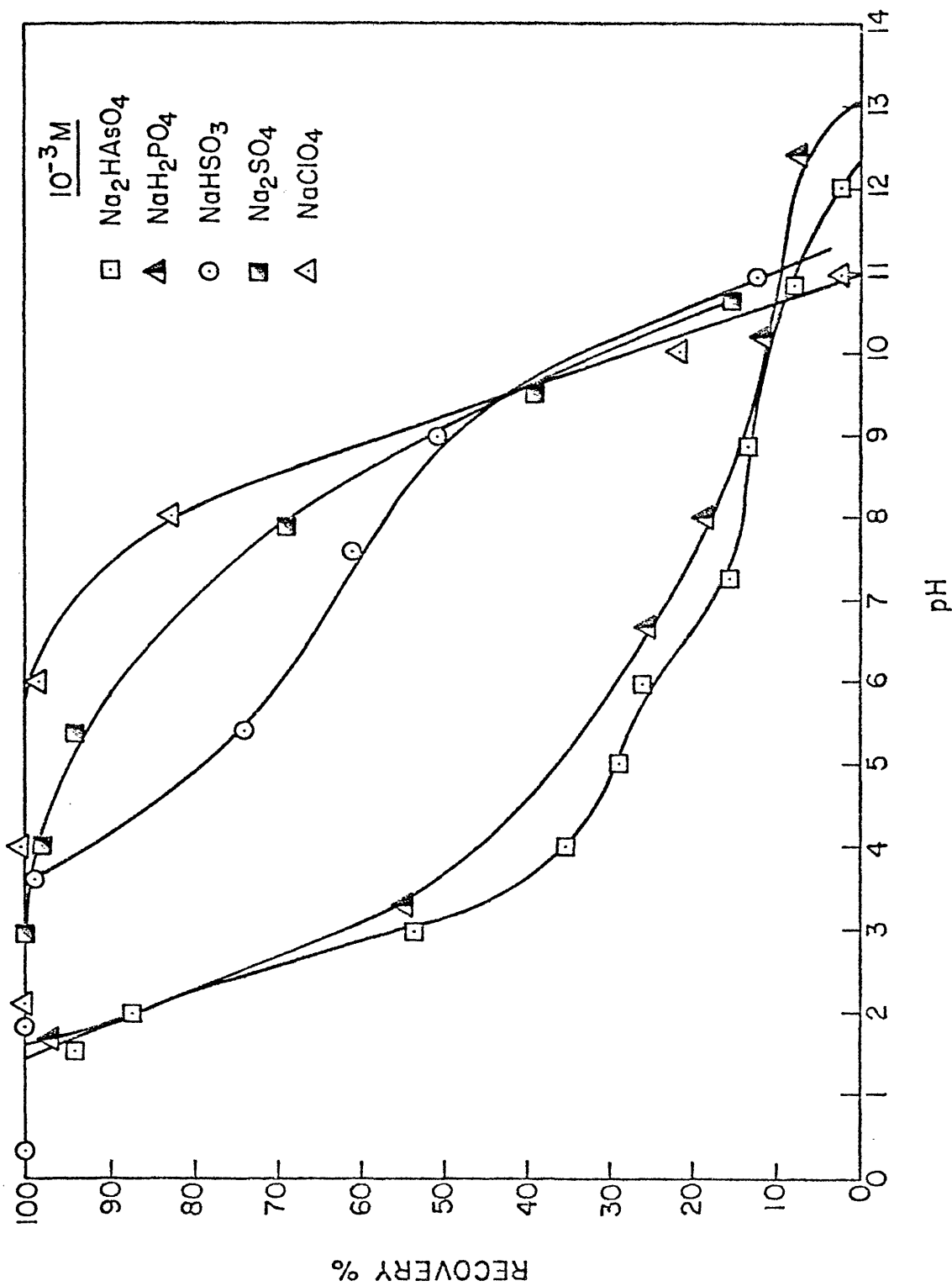
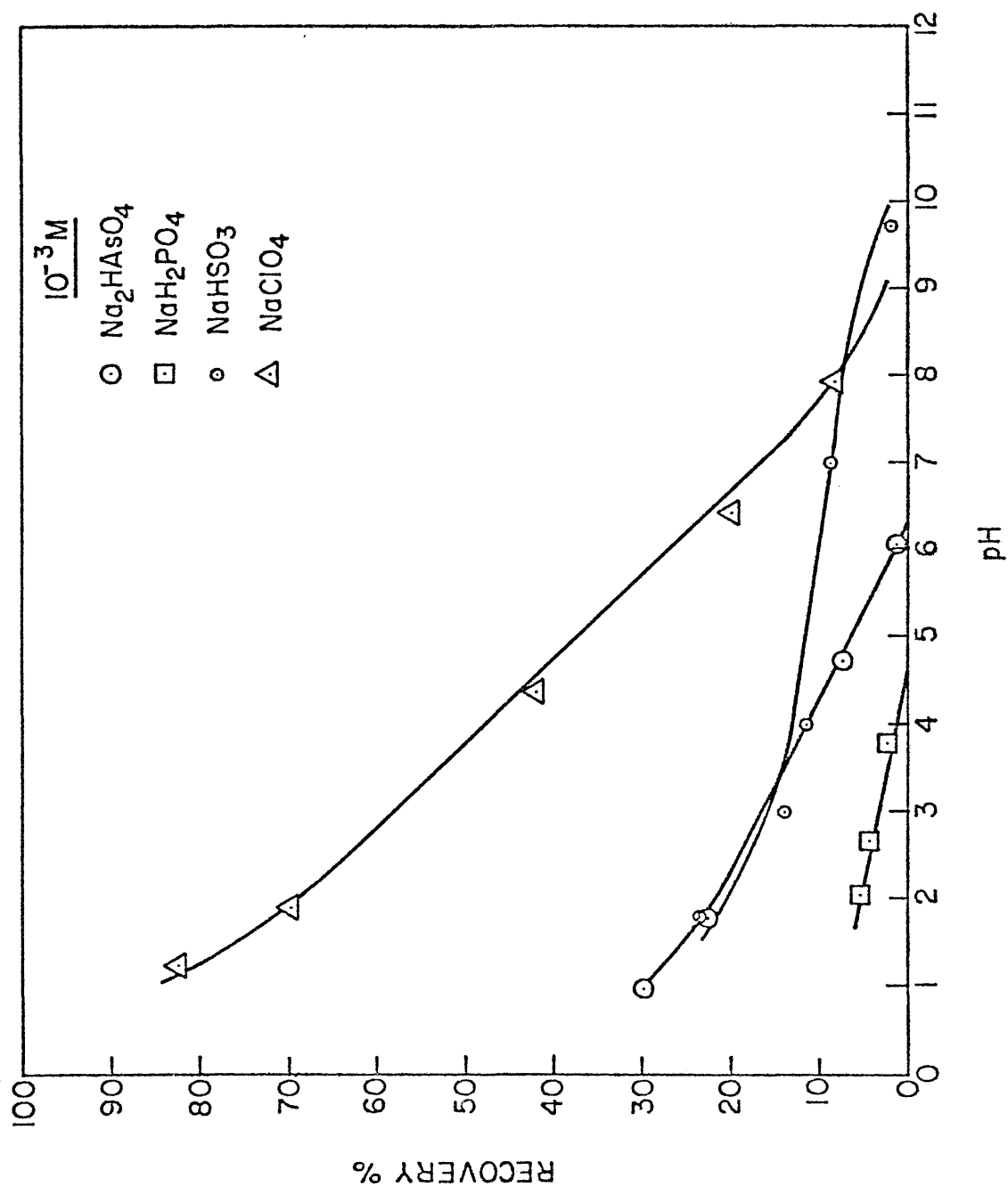


Figure 14. Recovery of cassiterite vs pH for 10^{-5} M sodium dodecylsulfonate in the presence of the various inorganic sodium salts.



GENERAL DISCUSSION

To understand the effect of the inorganic sodium salts on the flotation of cassiterite by sodium dodecylsulfonate a discussion of the mineral's crystalline structure and the mineral's surface characteristic in a water medium is warranted.

Cassiterite Crystal Structure

The cassiterite form of tin and oxygen atoms is considered to have a rutile-type structure. For this mineral the oxygen atoms are arranged octahedrally, entering in coordinate bonding with the tin (IV) cation.

In this lattice each atom of tin is surrounded by 6 atoms of oxygen (coordination number 6) and each atom of oxygen is surrounded by 3 atoms of tin. A schematic of this arrangement is shown in the following figure.

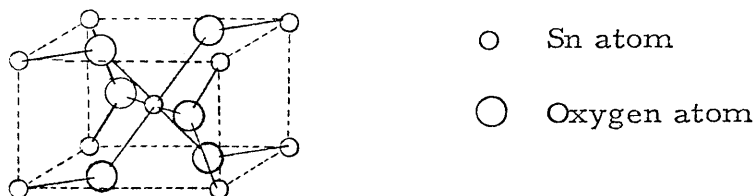


Figure 15. Crystal structure of cassiterite

Cassiterite Surface Characteristics in a Water Medium

When an oxide mineral is placed in an aqueous medium a charge distribution is established in the form of an electrochemical double layer (25). The creation of an electrical bias on the surface of cassiterite, and its characteristics, will be the subject of this section of the thesis.

Generally, the charge of an oxide surface is dictated by the aqueous concentrations of hydrogen and hydroxyl ions. Parks and DeBruyn (25) suggested that the charge property of an oxide-aqueous interface is established by a two step mechanism;

1. Surface hydration, followed by
2. Dissociation of the surface hydroxide.

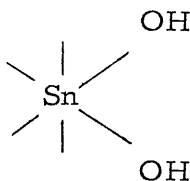
This surface hydration is due to the attempt of exposed surface atoms to stabilize their charge balance by completing their

coordination requirements. For a cation this is accomplished by attracting an OH^- ion or H_2O molecule. For an exposed anion pulling of a H^+ proton fulfills its coordination requirements. In either case the net result is that the surface is covered by a hydroxyl layer with the cation buried below.

Following this argument it can be concluded that surface charge is established by adsorption of H^+ or OH^- ions. This approach can find support in the cassiterite-water system.

When cassiterite is ground, the newly fractured surfaces will show tin and oxygen atoms with incomplete coordination. According to their polarity these unstable sites will be saturated with hydroxyl ions or with protons. The net result, again, is that the cassiterite surface is covered by a hydroxide layer.

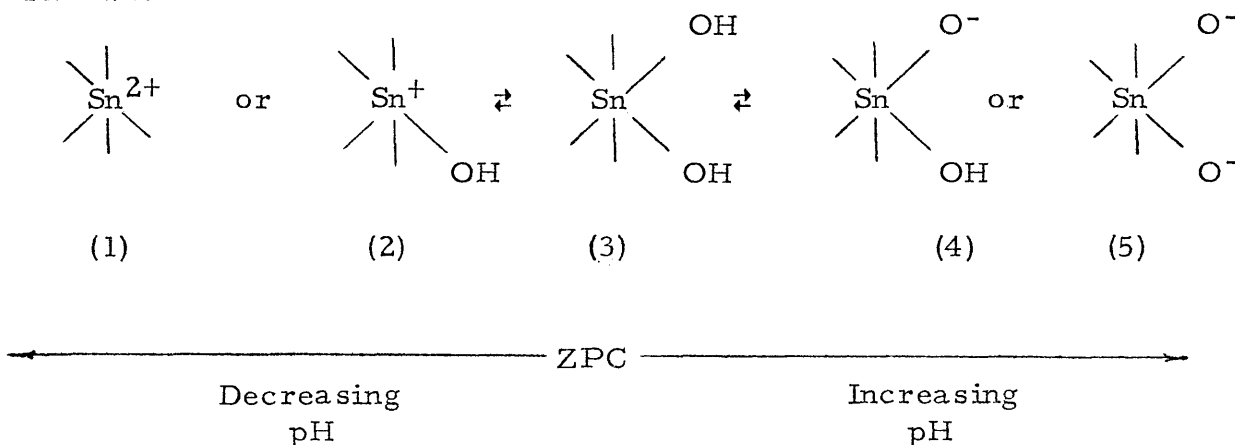
Cibulka and Dobias (26) suggested that the crystal surface of cassiterite, when in the presence of water, has the following structure.



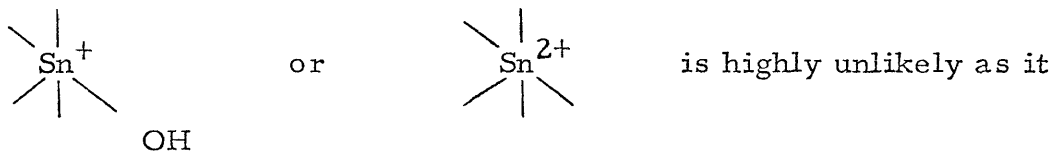
The infrared spectra of water-wetted cassiterite shows the presence of an OH band which supports the above hypothesis.

Studies by Edward and Ewers (27) also proposed the existence

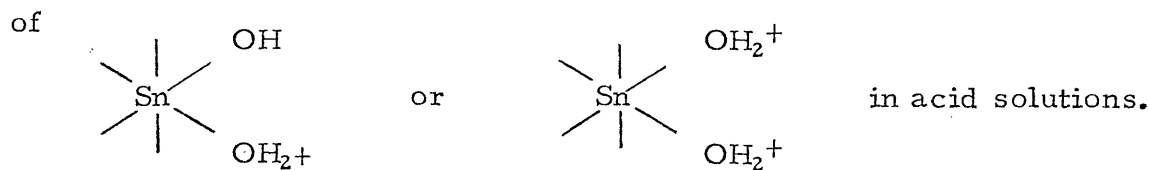
of the above surface scheme, with the amphoteric dissociation of this unit giving rise to the charge character of the exposed portion of the cassiterite. This dissociation is expressed schematically as follows:



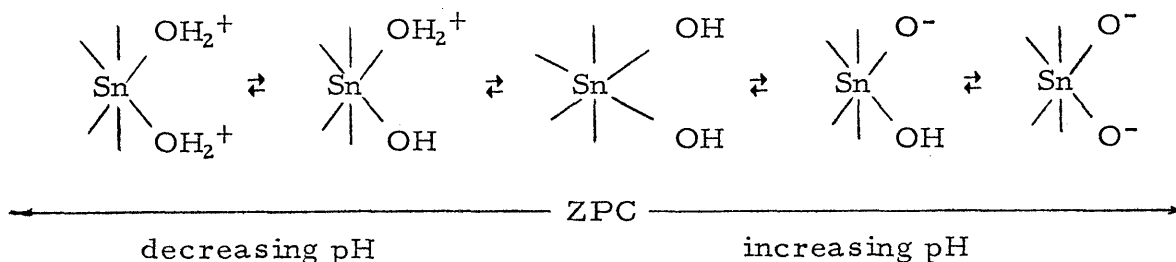
This approach is consistent with the electrokinetic properties of cassiterite and has been accepted by many investigating the same area. However, Yap (21) has suggested that the existence of structures 1 and 2 in an aqueous phase is suspect. The existence of 5-coordinated tin is not supported even in a solution where stabilization by structure transformation is possible. This transformation of the tin's structure to



would involve too much bond distortion requiring a very high activation energy. Therefore it is more credible that surface structure consist



For different pH values then, the cassiterite-water interfacial equilibrium can be written as follows:



This scheme has been proposed by both Yap (21) and Blazy, DeGoul, and Houot (28).

A common equation used to express the surface potential (Ψ_0) in terms of the concentration or activity of the positive potential determining ion (a_{H^+}) is shown below

$$\Psi_0 = \frac{RT}{F} \ln \left[\frac{a_{\text{H}^+}}{(a_{\text{H}^+})_{\text{ZPC}}} \right]$$

where R, T, and F are the gas constant, absolute temperature, and the Faraday constant, respectively and $(a_{\text{H}^+})_{\text{ZPC}}$ is the activity of H^+ at the zero point of charge.

The corresponding expression for the surface charge (σ_s) is

$$\sigma_s = F (\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-})$$

where Γ denotes adsorption densities.

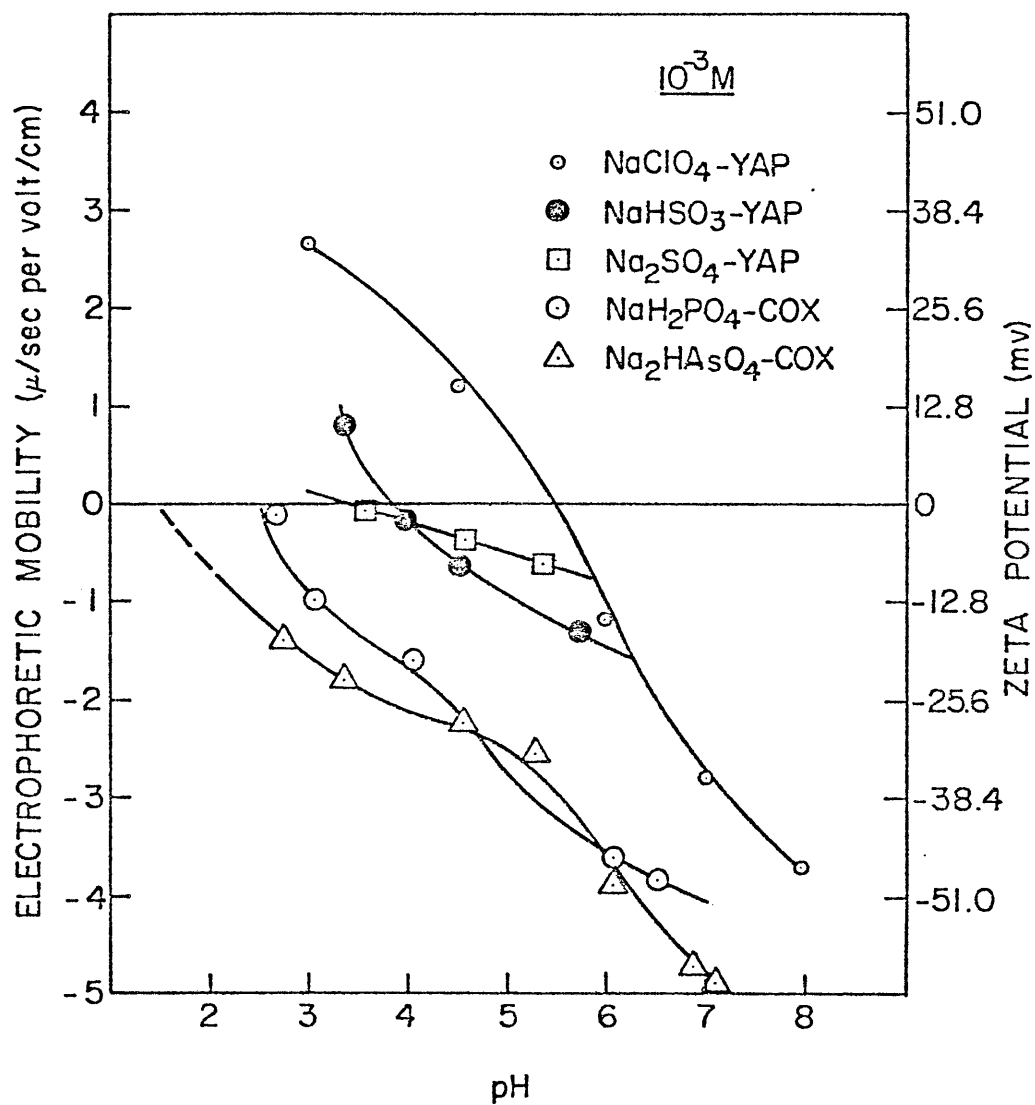
Effect of Inorganic Sodium Salts on the
Surface Electrical Properties of Cassiterite

Hingston, et al (30) have shown that minerals which experience specific adsorption of anions have their ZPC shifted to lower pH values. Investigations dealing with cassiterite have shown similar results.

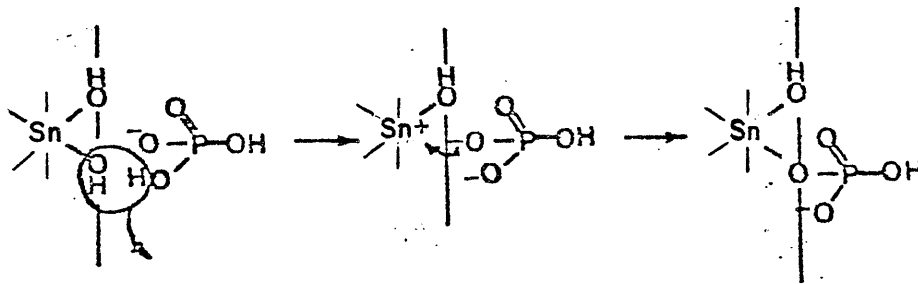
Yap (21) studied the electrophoretic mobility of cassiterite as a function of pH in the presence of 10^{-3} M NaCl, NaClO₄, NaNO₃, NaH₂PO₄, Na₂HAsO₄, NaHSO₃, and Na₂SO₄. Test results showed NaCl, NaClO₄ and NaNO₃ to be indifferent electrolytes having no effect on the mineral's ZPC. However the presence of NaH₂PO₄, Na₂HAsO₄, Na₂SO₄ and NaHSO₃ produced an obvious decrease in the pH of the ZPC, indicating some type of specific adsorption mechanism. Yap's results for 10^{-3} M concentrations of NaClO₄, NaHSO₃ and of Na₂SO₄ are shown in Figure 16, also shown are the 10^{-3} M curves for NaH₂PO₄ and Na₂HAsO₄ taken from Figures 7 and 10. The latter two curves will be discussed in the following thesis section. The results shown in Figure 16 indicate the effect of the inorganic salts on the pH of the ZPC in Na₂HAsO₄ > NaH₂PO₄ > NaHSO₃ and Na₂SO₄.

Both Hingston (30) and Yap (21) have proposed mechanisms of anion adsorption onto oxide mineral surfaces. Hingston's approach involves ligand exchange of surface groups with anions in solution, while Yap's method deals with an acid-base reaction

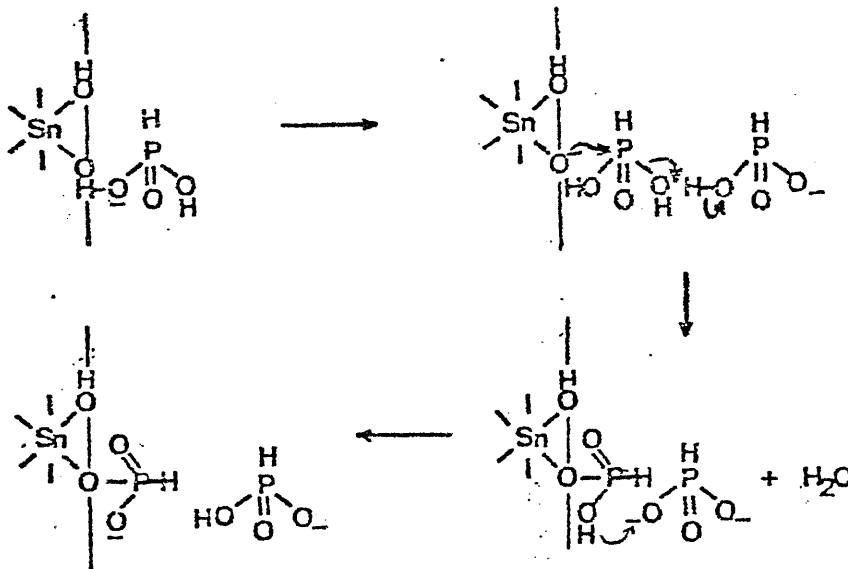
Figure 16. Electrophoretic mobility and zeta potential of cassiterite vs pH in the presence of the various inorganic sodium salts.



between the surface protons and anion species. An example of Hingston's mechanistic approach using H_2PO_4^- adsorption onto cassiterite is shown as follows.



A schematic of Yap's method using H_2PO_3^- as the adsorbed specie is shown here.



Both mechanisms, however, agree that this adsorption of anions take place in the Stern layer.

DISCUSSION OF RESULTS

This portion of the thesis will discuss both the flotation and the electrokinetic results produced in the different salt systems. Each system will be discussed independently as follows:

NaClO₄ System

Study of cassiterite's zeta potential with 10^{-3} M NaClO₄ by Yap (21) indicated that the anion has essentially no effect on the mineral's ZPC. The flotation curve in Figure 4, page 16, shows that deviation from 100% flotation occurs at an approximate pH of 5.5. The ZPC of the cassiterite used in this experimental work was not determined. However, in Figure 4 the results of Zambrana's (7) study of cassiterite in an almost identical system are overlaid and show deviation from complete flotation at about pH 6.

Zambrana (7) determined the ZPC of his cassiterite to be approximately pH 6 by electrophoretic measurements. Since the cassiterite used in this study gave identical results, with the flotation curve shifted slightly to the left, it was felt justified to assume the ZPC of this sample to be around pH 5.5.

Following this argument it can be seen from Figure 4 that

flotation recovery of cassiterite above the ZPC in this system is steadily reduced with increasing pH. However, it should be noted from Figure 4, that significant flotation recovery is observed for 10^{-4} M sulfonate at pH values considerably above the ZPC. Slight recoveries are observed even for 10^{-5} M. Similar behavior was found by Blazy et al (28) for 10^{-5} M and other concentrations when studying different samples of cassiterite.

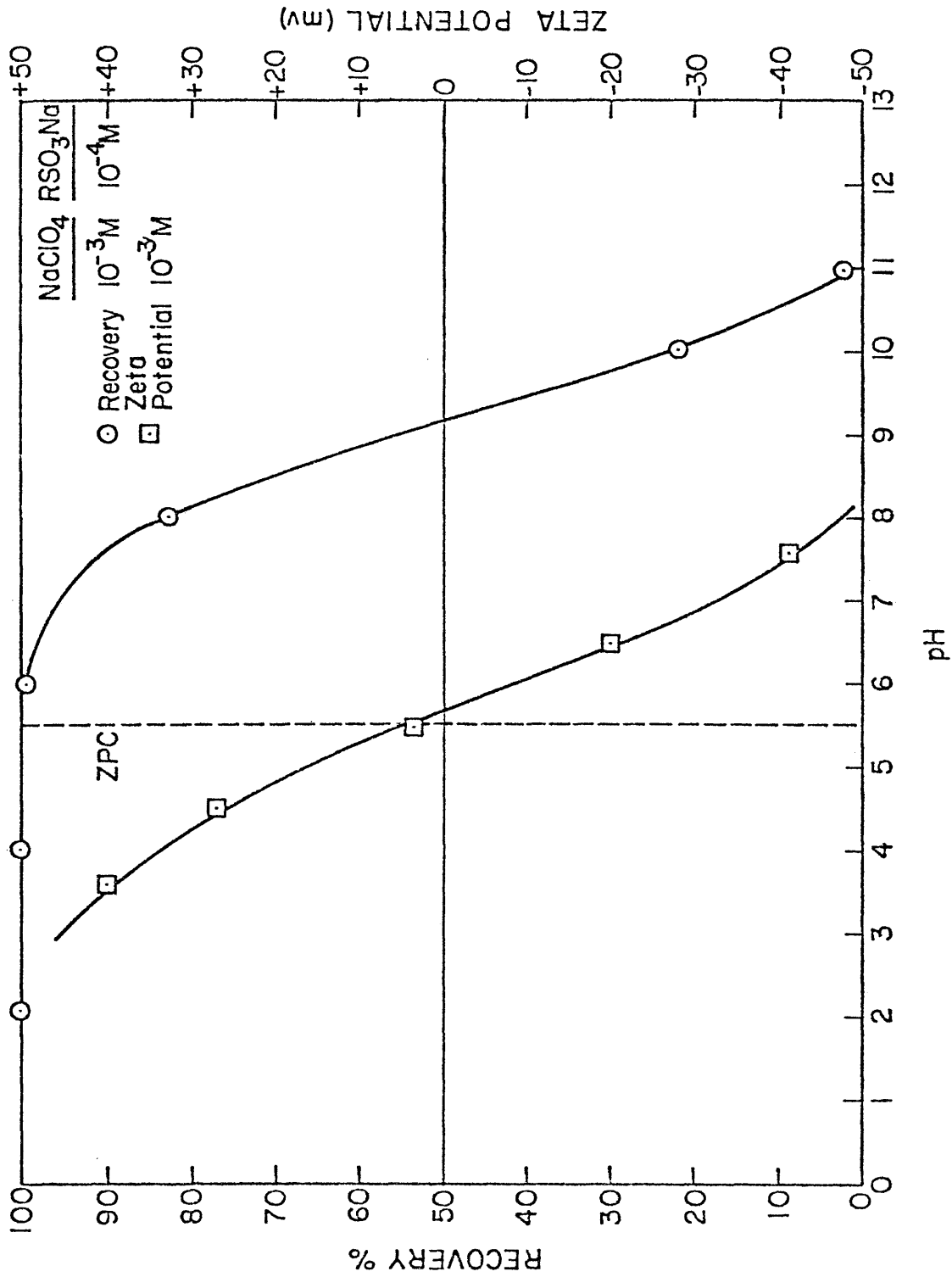
If these results are compared to others, for example, Iwasaki et al's data on goethite (31), then one is forced to conclude that adsorption of sulfonate onto cassiterite is not governed solely by electrostatic forces, as was also postulated by Blazy et al (28).

The effect of the surface potential on the flotation of cassiterite with the sulfonate may be better expressed by a figure showing both the zeta potential vs pH curve and the recovery vs pH curve. Such a diagram for the 10^{-3} M in NaClO_4 system is presented in Figure 17. It can be seen from Figure 17 that, 100% flotation recovery is only achieved when positive values of the zeta potential are obtained. Immediately the zeta potential becomes negative, the flotation recovery is reduced.

NaH_2PO_4 System

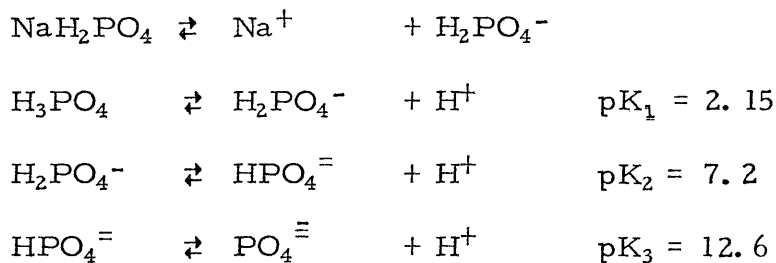
The flotation recoveries shown in Figure 5 for different concentrations of sulfonate and sodium hydrogen phosphate have been

Figure 17. Recovery of cassiterite vs pH for sodium dodecylsulfonate in the presence of NaClO_4 and zeta potential of cassiterite vs pH in the presence of NaClO_4 .



described in a previous section.

For the phosphate in aqueous solution the following equilibria apply.



Thus, in the pH range $2.15 < \text{pH} < 7.2$ the predominant phosphate species is H_2PO_4^- and $\text{HPO}_4^{=}$ in the range $7.2 < \text{pH} < 12.6$. In Hingston's (30) work on orthophosphate adsorption onto goethite as a function of pH, a discontinuity in the amount adsorbed was observed at each pK value.

The results in Figure 5 show a differently shaped curve for 10^{-4}M and 10^{-3}M compared to 10^{-3}M NaClO_4 . The flattening of the curves seems to occur at $\text{pH} = \text{pK}_2$, indicating a change from H_2PO_4^- to $\text{HPO}_4^{=}$ as the predominant species.

In Hingston's work the adsorption of phosphate was continually increasing with decreasing pH, and was independent of ionic strength.

This ionic strength effect is in general agreement with the plots shown in Figures 5 and 6, where the flotation recovery became independent of phosphate concentration above 10^{-4}M and above $\text{pH} \cong 8$. It can also be seen from the electrokinetic data in Figure 7 that the zeta potential became independent of concentration for $>10^{-4}\text{M}$ at $\text{pH} > 8$.

The effect of the electrokinetic properties on the flotation recovery can be clearly shown in Figure 18 where both recovery and zeta potential are plotted as a function of pH. The zeta potential at pH 7 for 10^{-5} M NaH_2PO_4 is shown to have a negative value of 29.4 mv. However, at this same pH the 10^{-4} M and 10^{-3} M curves show significantly larger negative zeta potential values. This large difference is also manifested in the flotation recovery curves.

As shown the 10^{-5} M NaH_2PO_4 flotation curve is of a similar shape to the 10^{-3} M NaClO_4 with deviation from complete flotation occurring at pH 4.5. At pH 7 the 10^{-5} M NaH_2PO_4 curve indicates a recovery of 75%. For 10^{-4} M and 10^{-3} M NaH_2PO_4 at this same pH recoveries are shown to be only 30% and 23%, respectively. Yet, regardless of the depressed condition of flotation as the zeta potential becomes less negative, recovery is enhanced, going to 100% as the surface becomes positive, as was seen in the perchlorate system.

Thus, even though Hingstons results indicate stronger adsorption of phosphate at lower pH values, the flotation appears to be governed solely by the charge characteristics of the interface.

It was seen in Figure 5 that maintaining the NaH_2PO_4 concentration at 10^{-3} M and decreasing the collector concentration to 10^{-5} M inhibited flotation almost completely. Thus it appears that with a starvation quantity of collector (often used for maximum selectivity) that is below the concentration at which hemi-micelles form (32)

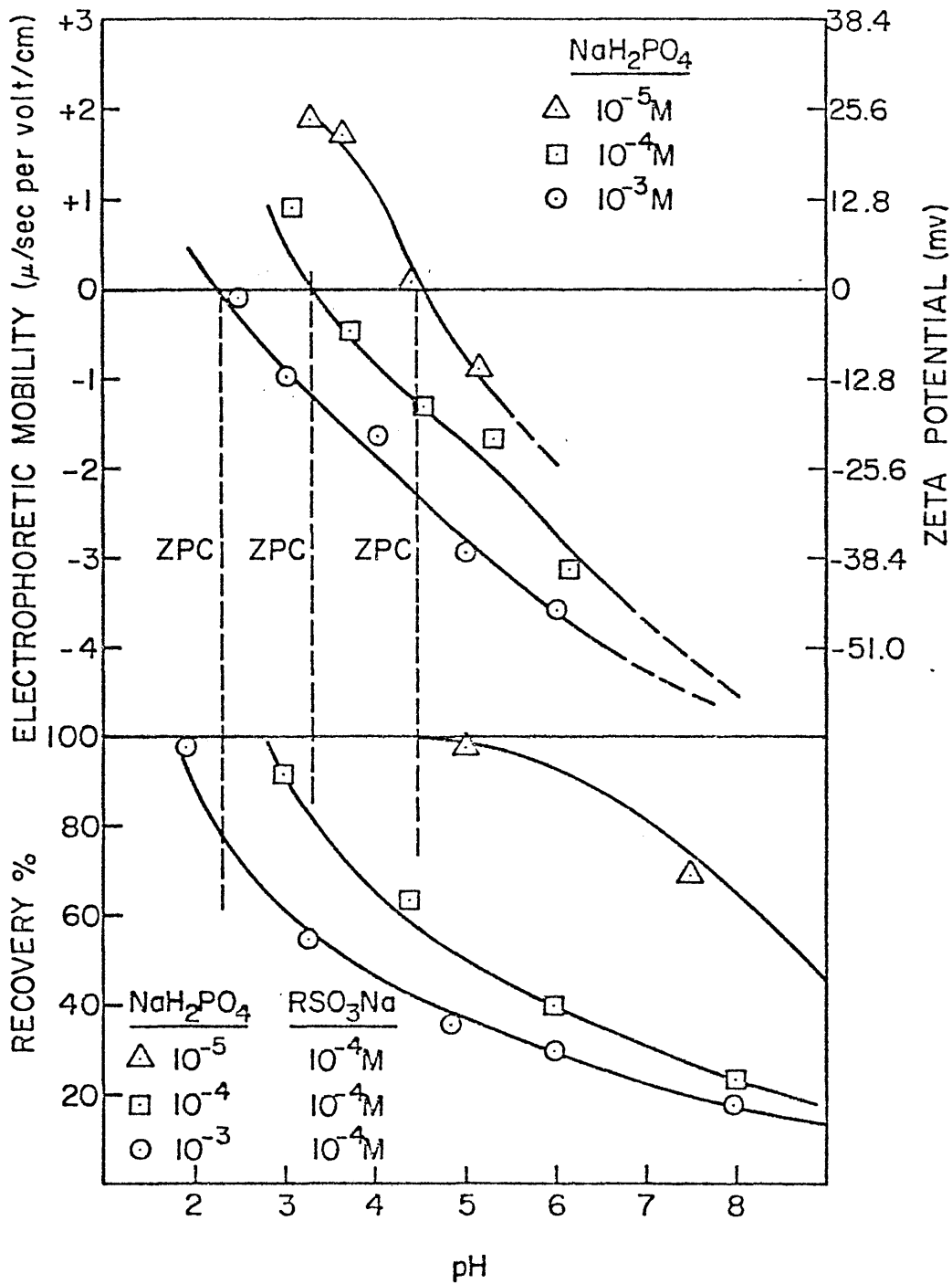


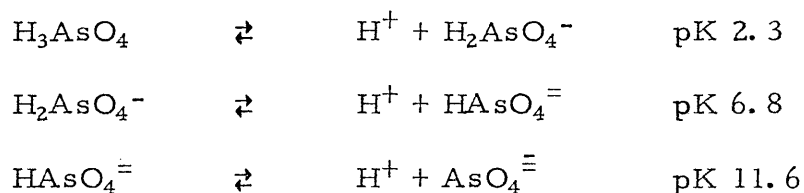
Figure 18. Recovery of cassiterite vs pH for sodium dodecylsulfonate in the presence of various concentrations of NaH₂PO₄ and zeta potential of cassiterite vs pH in the presence of various concentrations of NaH₂PO₄.

and thus governed solely by electrostatic forces, the small amount of collector adsorbed does not produce a sufficiently hydrophobic surface for flotation to occur.

Na₂HAsO₄ System

The flotation recoveries for different concentrations of Na₂HAsO₄ and sulfonate have been discussed in this experimental results section and are shown in Figure 8.

The following equilibria apply for arsenate in an aqueous solution:



In this system then, in the pH range $2.3 < \text{pH} < 6.8$ the predominant species is H_2AsO_4^- and $\text{HAsO}_4^{=}$ in the range $6.8 < \text{pH} < 11.6$.

As in the NaH_2PO_4 system, the results for 10^{-3}M and 10^{-4}M Na_2HAsO_4 , presented in Figure 8, show a differently shaped curve when compared to 10^{-3}M NaClO_4 . The curves appear to flatten at the pH corresponding to arsenate's second pK, suggesting a transfer of the predominant species from H_2AsO_4^- to $\text{HAsO}_4^{=}$.

Recovery curves shown in Figures 8 and 9 exhibit the same ionic strength independence as the NaH_2PO_4 curves. As depicted, the flotation recovery becomes independent of arsenate concentration

above 10^{-4} M and $\text{pH} \approx 8.0$.

A plot of both zeta potential and flotation recovery are shown in Figure 19. As in the NaH_2PO_4 system correlations are seen between the zeta potential curves and the flotation recovery curves. For this system, Figure 10 shows that the 10^{-5} M Na_2HAsO_4 curve coincides with 10^{-3} M NaClO_4 curve at pH 6, which corresponds to a negative zeta potential of 16.6 mv. At this same pH the 10^{-4} M and 10^{-3} M Na_2HAsO_4 curves have negative values of 30.7 and 47.4, respectively. Inspection of the flotation recovery curves also shows large recovery difference between the 10^{-5} M curve and the 10^{-4} M and 10^{-3} M curves at the pH value of 6.

For 10^{-5} M Na_2HAsO_4 the recovery at the subject pH was is 85%. At this same pH the 10^{-4} M and 10^{-3} M curves experience recoveries of only 33% and 25%, respectively.

However, as in the two previously discussed systems, regardless of the studied electrolyte strength, complete flotation is realized only when positive zeta potential values are obtained. These data suggested that even though the cassiterite was experiencing adsorption of arsenate species, as its surface charge became less negative recovery was enhanced.

As shown in Figure 8, flotation is severely depressed when the sulfonate concentration is lowered to 10^{-5} M and the Na_2HAsO_4 is maintained at 10^{-3} M. As discussed for the similar situation in the

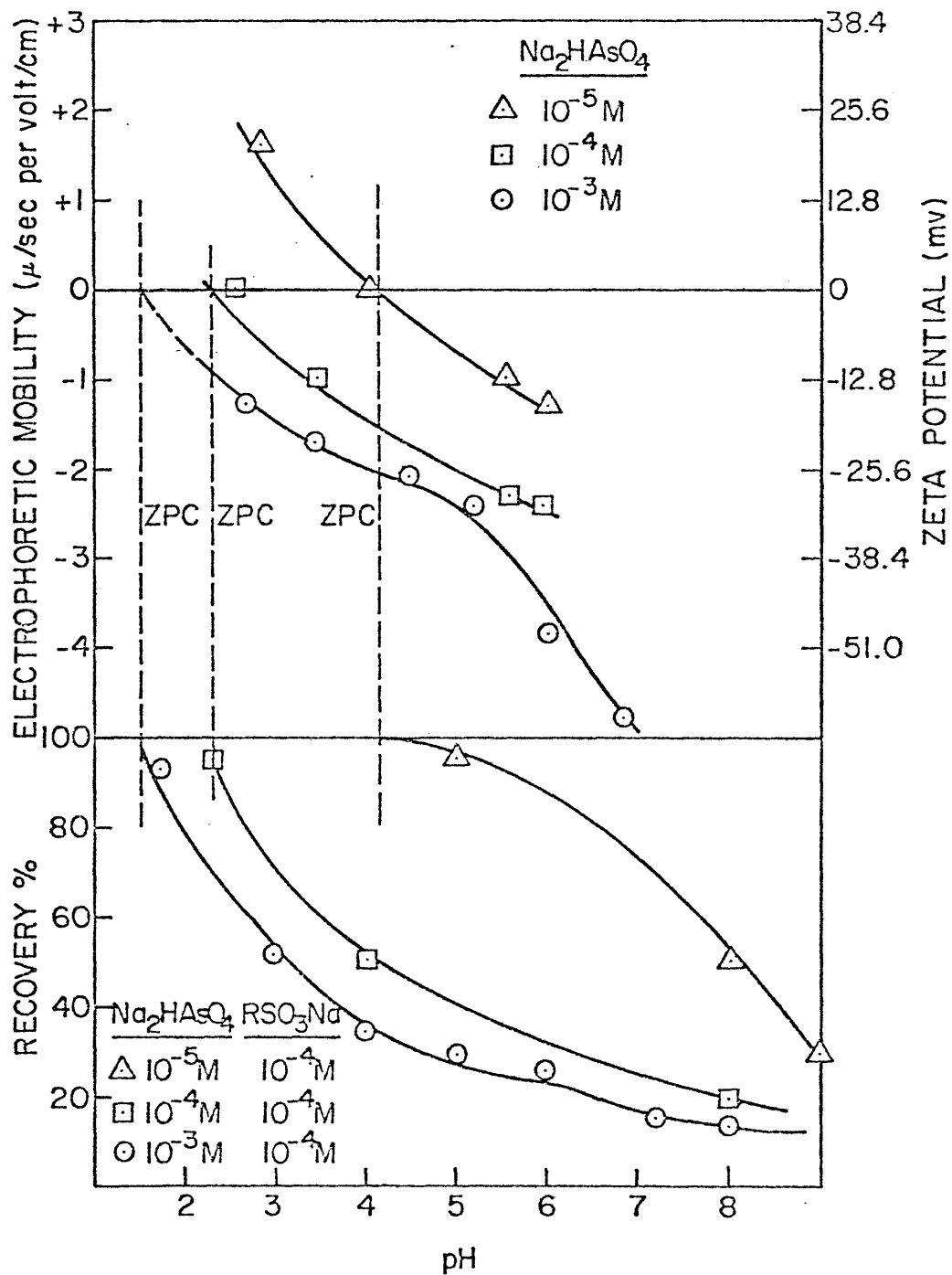
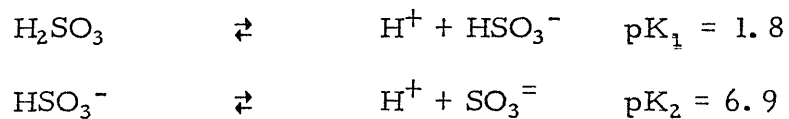


Figure 19. Recovery of cassiterite vs pH for sodium dodecylsulfonate in the presence of various concentrations of Na_2HAsO_4 and zeta potential of cassiterite vs pH in the presence of various concentrations of Na_2HAsO_4 .

NaH₂PO₄ system, it appears that this low dosage of collector does not produce sulfonate adsorption to the extent sufficient for flotation.

NaHSO₃ System

Figure 11, on page 29 shows the effect of HSO₃⁻ on flotation recovery. For HSO₃⁻ in an aqueous solution the following equilibria apply.



Thus in the pH range 1.8 < pH < 6.9 the main species is HSO₃⁻.

Above pH 6.9 the species SO₃⁼ predominates.

Inspection of curve for 10⁻⁴M sulfonate shows a different shape than the curve produced in the NaClO₄ system under similar conditions. The recovery experiences a flattening as the curve passes through the pH corresponding approximately to pK₂. At this pK species predominance is transferred from HSO₃⁻ to SO₃⁼.

The effect of electrokinetic properties on the flotation recovery is shown in Figure 20. These plots of zeta potential and flotation recovery demonstrate a similar behavior to the two previously discussed salt systems. As the surface potential becomes less negative recovery improves. As the potential passes into the positive region 100% flotation recovery is obtained.

Thus even though in the acid range where the cassiterite is

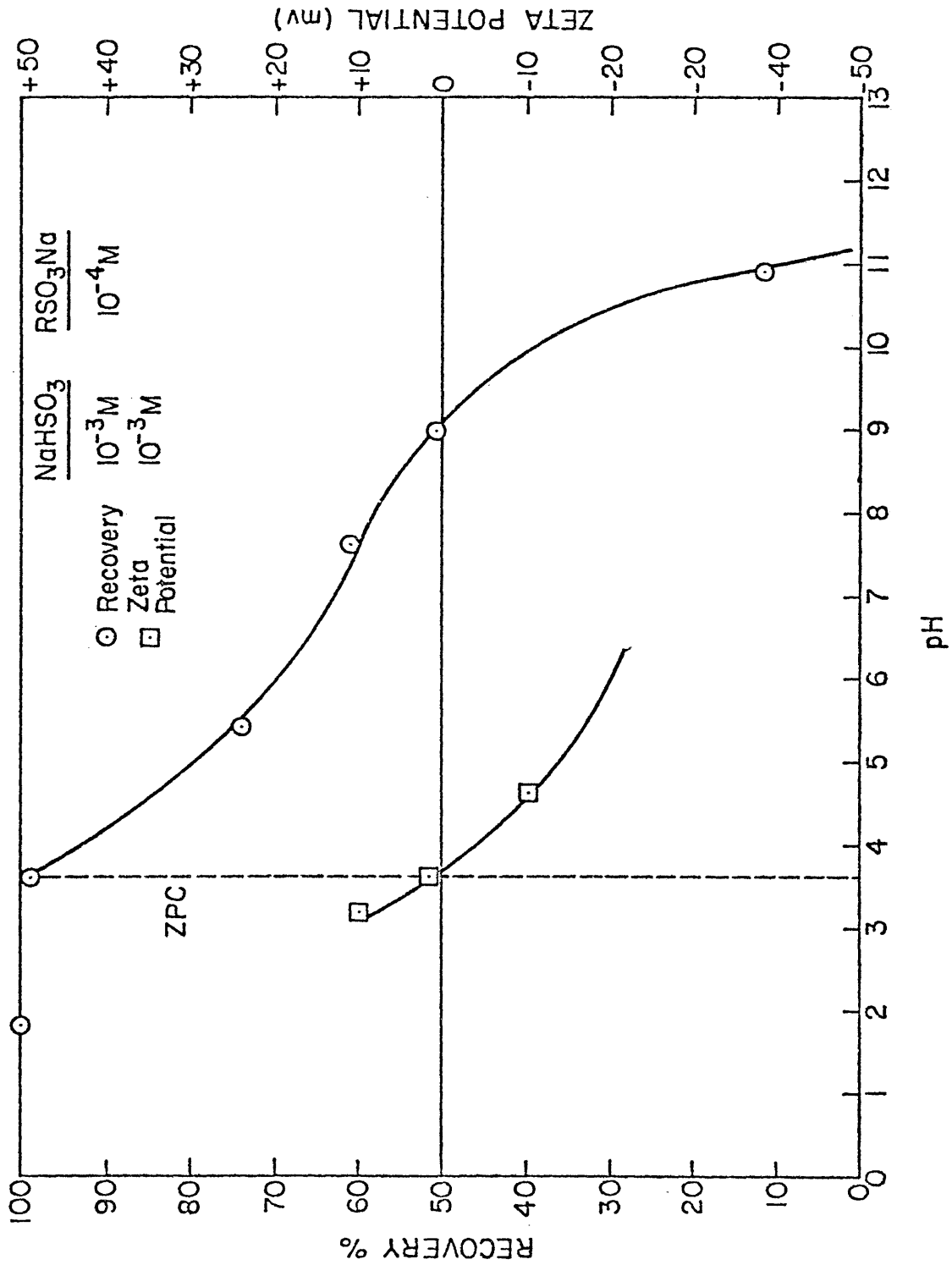


Figure 20. Recovery of cassiterite vs pH for sodium dodecylsulfonate in the presence of NaHSO_3 and zeta potential of cassiterite vs pH in the presence of NaHSO_3 .

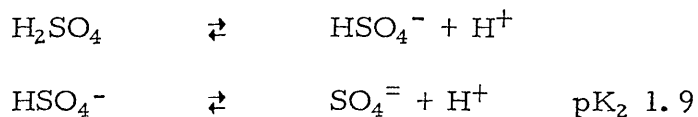
probably experiencing HSO_3^- adsorption, flotation recovery appears to be primarily a function of surface potential.

Recovery for 10^{-5} M sulfonate in the presence of 10^{-3} M NaHSO_3 is shown in Figure 11. Flotation is depressed but extends over a wider pH range than the similar situations in the NaH_2PO_4 and the Na_2HAsO_4 systems. Study of the effect of NaHSO_3 on the zeta potential in Figure 16 shows that this anion produces a less negative surface in the acid pH range than either NaH_2PO_4 or a Na_2HAsO_4 . This lower negative zeta potential seems to permit more adsorption of collector over a wider pH range, thus producing higher recovery with flotation extended to about pH 10.5.

Na_2SO_4 System

Flotation in the Na_2SO_4 system has been discussed in a previous section with the recovery curve shown in Figure 12.

For an aqueous solution of sulfate the following equilibria are in effect:



Therefore above pH 2.0 the predominate sulfate species is $\text{SO}_4^{=}$.

Study of the curve produced in the presence of 10^{-3} M Na_2SO_4 shows that is similar in shape to the NaClO_4 curve. No flattening of the curve is observed as in the previously discussed

NaH_2PO_4 , Na_2HAsO_4 , and NaHSO_3 systems.

This fact suggests that the conjugate acid's pK has some effect on the adsorption of the anion and thus a subsequent effect on flotation.

However the flotation behavior with respect to electrokinetic characteristics is similar to the other salt systems. As shown in Figure 21 recovery is dependent upon surface charge with complete flotation realized only when the cassiterite takes on a positive potential.

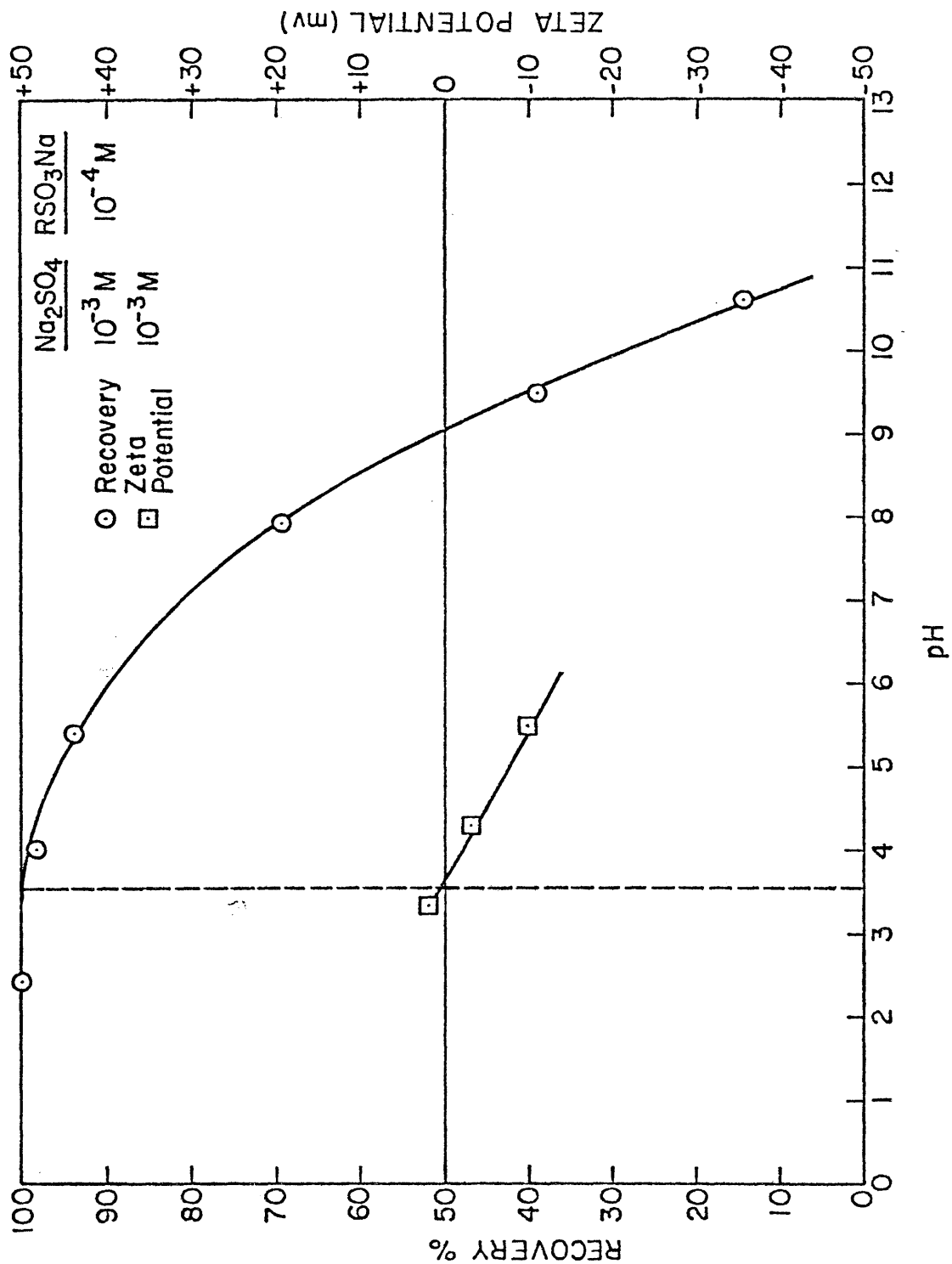


Figure 21. Recovery of cassiterite vs pH for sodium dodecylsulfonate in the presence of Na_2SO_4 and zeta potential of cassiterite vs pH in the presence of Na_2SO_4 .

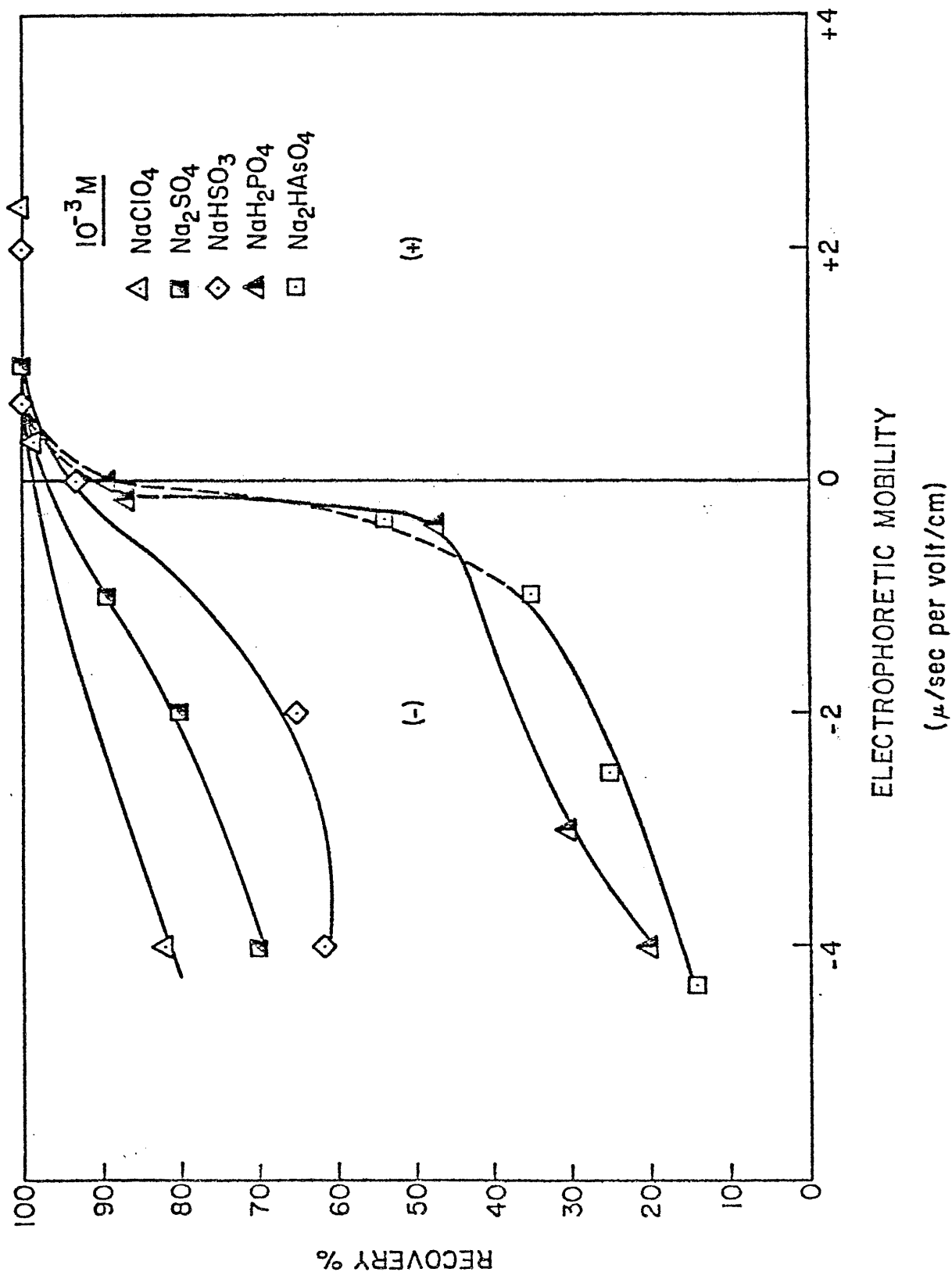
SUMMARY AND CONCLUSIONS

The test results presented for all discussed systems indicate that flotation recovery of cassiterite by sodium dodecylsulfonate is extremely dependent upon electrokinetic characteristics. This dependency is shown dramatically in Figure 22 where recovery is plotted as a function of electrophoretic mobility for 10^{-3} M concentrations of the various electrolytes. As depicted complete flotation is not realized in each system until the cassiterite surface takes on a positive mobility. Figure 22 also suggests that the relative depressive effect of the different sodium salts is $\text{Na}_2\text{HAsO}_4 > \text{NaH}_2\text{PO}_4 > \text{NaHSO}_3 > \text{Na}_2\text{SO}_4$.

It is also interesting to note that 10^{-5} M concentration of NaH_2PO_4 and Na_2HAsO_4 have about the same depressing effect as 10^{-3} M concentrations of NaHSO_3 and Na_2SO_4 . This indicates that phosphate and arsenate anions have a very strong affinity for cassiterite which supports the fact that phosphonic and arsonic acids have been considered the best collectors for this mineral.

Studies in the NaH_2PO_4 and in the Na_2HAsO_4 systems showed that increasing the salt solution strength from 10^{-5} M to 10^{-4} M

Figure 22. Recovery of cassiterite vs electrophoretic mobility for the various inorganic salt systems (electrophoretic data determined in the absence of sodium dodecylsulfonate, recovery data for 10^{-4} M sodium dodecylsulfonate in the presence of 10^{-3} M concentrations of the various inorganic sodium salts).



produced a significant depressive effect upon flotation recovery in the neutral pH range. Results in these two systems also indicated that recovery became independent of electrolyte concentration $>10^{-4}$ M at pH values approximately >8 .

Flotation curves for 10^{-3} M concentrations for all of the subject salts, except Na_2SO_4 , exhibited a different shape than the curve developed for 10^{-3} M NaClO_4 . Curves for NaH_2PO_4 , Na_2HAsO_4 and NaHSO_3 all experienced a flattening when passing through the pH value approximately corresponding to their conjugate acids second pK.

This curve flattening suggested that the pK of the anion's acid has a strong influence on the anions adsorption, and thus a subsequent effect on flotation. This proposal is supported by inspection of the 10^{-3} M Na_2SO_4 curve. In the pH range of departure from 100% flotation the plot does not pass through any pH values corresponding to a pK for Na_2SO_4 's conjugate acid. The curve shows no flattening in slope, deviating from complete flotation in a manner similar to 10^{-3} M NaClO_4 system.

When collector additions are of starvation quantities (10^{-5} M or less), below the concentrations at which hemi-micells form, collection appears to be govern solely by electrostatic forces. The small amount of adsorbed collector does not produce a sufficiently hydrophobic surface for significant flotation to occur. For higher

collector dosages (10^{-4} M or greater) the adsorption of sulfonate onto cassiterite does not appear to be a function of only electrostatic interactions.

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