

FLOTATION BEHAVIOR OF GALENA AND LEAD-ACTIVATED
SPHALERITE IN THE PRESENCE OF ZINC SULFATE

by

Guillermo L. Serna

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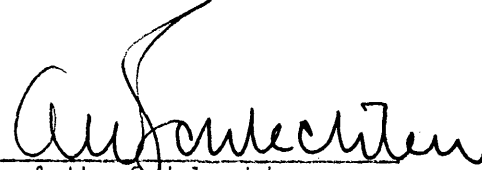
A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

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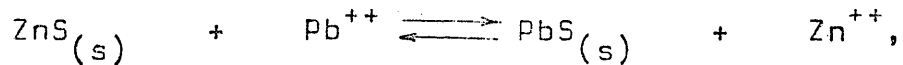

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ABSTRACT

Micro-flotation studies with galena and lead-activated sphalerite were performed to determine the depressing effect of zinc sulfate on the flotation behavior of these minerals. System depression is closely related to the formation of zinc hydroxide colloids.

Surface charge determinations of the minerals and the colloids indicate that electrical phenomena are involved to a minor extent in the depression of galena at low additions of zinc sulfate. An increase in the zinc sulfate addition causes a charge reversal of the zinc hydroxide colloids and practically no depression occurs under these circumstances.

The depressing effect of zinc sulfate on lead-activated sphalerite is governed by the reaction:



and by the equilibrium constant of that reaction:

$$K = (\text{Zn}^{++})/(\text{Pb}^{++}) = 1000.$$

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INTRODUCTION

Differential flotation of lead-zinc ores has been practiced over the years to obtain separate concentrates of each of the metal sulfides. Although several sequences have been used in this separation, the general trend today is towards the recovery of the more easily floatable galena, followed by flotation of the activated sphalerite.

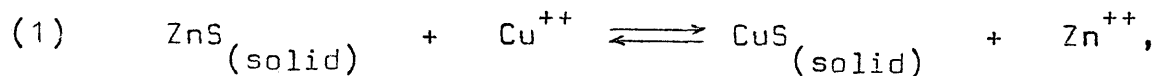
When the above sequence is used, two fundamental steps are involved in the separation:

1. Flotation of galena using a sulfhydryl collector such as potassium ethyl xanthate. Sphalerite is kept depressed by the addition of either zinc sulfate alone or a combination of zinc sulfate and sodium cyanide.
2. Flotation of activated sphalerite using copper sulfate and more potassium ethyl xanthate as activating and collecting agents, respectively.

The role of sodium cyanide as a depressing agent can be explained by its ability to form soluble cyanide complexes with

the different metal ions in solution that could activate sphalerite. The most common activating agent used for sphalerite flotation is copper sulfate, and the mechanism of this activation of zinc sulfide is now well established. Studies on copper activation of sphalerite performed by Gaudin, Fuerstenau, and Mao⁽¹⁾, confirmed the atom-for-atom exchange of copper for zinc, and indicated that the replacement can be predicted from thermodynamic data. It is probable that copper activation is not a true surface reaction for, given sufficient time and a thermodynamic driving force, copper ions will replace zinc throughout a solid piece of zinc sulfide, and the applicability of thermodynamic treatment is then possible.

The replacement reaction can be written as follows:



and the equilibrium expression as

$$(2) \quad K = (\text{Zn}^{++})/(\text{Cu}^{++}) = 9.0 \times 10^{10}$$

When copper sulfate is added to a flotation pulp in which the pH is in the normal range for zinc flotation, copper hydroxide or a basic copper salt is precipitated immediately. If the precipitate is copper hydroxide, the copper ion concentration is given by the solubility product expression

$$(3) \quad (\text{Cu}^{++}) (\text{OH}^-)^2 = 1.6 \times 10^{-19}.$$

If 10.0 is taken as a typical pH for sphalerite flotation,

$$(\text{OH}^-) = 10^{-4} \text{ M}, \text{ and therefore}$$

$$(4) \quad (\text{Cu}^{++}) = 1.6 \times 10^{-19} / (10^{-4})^2 = 1.6 \times 10^{-11}.$$

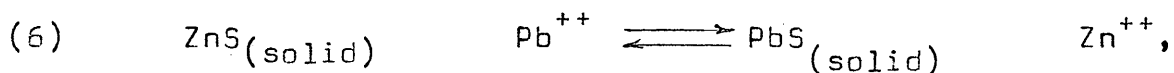
This copper ion concentration seems to be very low but it is large enough to permit copper to substitute for zinc in sphalerite. Precipitation of basic copper salts is also possible, but redissolution of these salts will also result in activation of the mineral.

According to equation 2, the substitution of copper for zinc at pH 10.0 can continue until

$$(5) \quad (Zn^{++}) = (9.0 \times 10^{10}) (1.6 \times 10^{-11}) \\ = 1.4 \underline{M}.$$

The zinc ion concentration will not reach this level because of the low solubility of zinc hydroxide ($K_{sp} = 4.5 \times 10^{-17}$). As a result, the best possible way to prevent copper activation of sphalerite is by adding a soluble cyanide to form copper cyanide complexes.

Lead activation of sphalerite takes place according to the following reaction:



and the corresponding equilibrium expression is

$$(7) \quad K = (Zn^{++}) / (Pb^{++}) = 10^3.$$

When the ratio of zinc to lead ions is equal to or greater than the equilibrium constant K, activation does not take place. The substitution of lead for zinc will continue until

$$(8) \quad (Zn^{++}) = 10^3 (Pb^{++}),$$

which means that there exists the possibility of controlling activation of sphalerite by lead by means of zinc salt additions.

Fuerstenau and Metzger⁽²⁾ corroborated this possibility experimentally.

The pH of the flotation pulp can be controlled by the addition of either sodium carbonate or lime, depending on the nature of the associated minerals. Tveter and McQuiston, Jr.⁽³⁾ reported that the use of lime as a pH regulating agent for lead and zinc flotation was apparently restricted to those plants treating ores with high pyrite or pyrrhotite content, and that its use had reduced cyanide requirements to a minimum. Fuerstenau and Metzger⁽²⁾ showed that the use of sodium carbonate for pH adjustment in lead-zinc separations is more effective because it forces the ratio $(Zn^{++})/(Pb^{++})$ to a value greater than 10^3 , due to the decrease in lead ion concentration caused by the increase in carbonate ion concentration.

Pryor⁽⁴⁾ considers that the effect of zinc sulfate in the depression of sphalerite is obscure but he suggests that the zinc ion can either react to form zinc cyanide, which concentrates near the surface of the mineral, or make a common ion concentration to the lattice, the wetting sulfate making the particle more hydrophilic. Klassen and Mokrousov⁽⁵⁾ refer to several experiments conducted on sphalerite with additions of zinc sulfate, and conclude that one of the causes for the depression of the mineral is the adsorption of zinc hydroxide colloids on the sphalerite surface. They mention that in the flotation of lead-zinc ores the zinc hydroxide is a considerably stronger depressant for sphalerite than for galena, although it is not yet clear what

causes the selective action of such colloids. However, the possibility that galena can still retain its ability to attach air bubbles after the zinc hydroxide is adsorbed on its surface, whereas the weakly-floating sphalerite is completely suppressed even by small quantities of adsorbed zinc hydroxide, is considered.

The objective of this investigation therefore is:

1. To determine the flotation behavior of galena and lead-activated sphalerite in the presence of zinc sulfate; and
2. To establish the mechanism involved in the depressing action of that modifying reagent on both minerals.

The experimental approach to this investigation covered micro-flotation studies with galena and sphalerite, surface charge determinations of the minerals and of the colloids, and calculation of zinc and lead ion concentrations in solution under flotation conditions.

EXPERIMENTAL MATERIALS AND METHODS

The following experimental materials and methods were used during this investigation:

Materials.

The materials used comprised mineral samples, water, and reagents.

Mineral Samples. High purity galena crystals from Kansas, and sphalerite from the Ballard Mine, Baxter Springs, Kansas, were the minerals used in the experimental work. Qualitative analysis of the mineral by emission spectroscopy showed the impurities listed in Table 1.

The preparation of the mineral samples involved hand grinding in a porcelain mortar and pestle, and size separation with Tyler sieves. The size fraction selected for the flotation experiments was 100x150 mesh; for the surface-charge determination experiments the minerals and the colloids were ground to approximately 5 microns.

Table 1. Emission spectroscopic analysis of galena and sphalerite.

<u>Galena</u>		<u>Sphalerite</u>	
Impurity	Relative abundance	Impurity	Relative abundance
Ag	Minor constituent	Cu	Minor
Fe	Trace	Cd	Trace
Mg	Faint trace	Pb	Faint trace
Al	Trace	Ag	Faint trace
Si	Trace	Fe	Minor constituent
		Mg	Faint trace
		Al	Faint trace
		Si	Trace
		Ge	Faint trace

Water. Conductivity water, prepared by passing distilled water through a column of anionic-cationic exchange resin (Amberlite MB-3), was used for the experimental work.

Reagents. Pure potassium ethyl xanthate (KEX) was used as collector. It was prepared and purified following the procedure described by Foster⁽⁶⁾. Ethyl alcohol and potassium hydroxide were reacted to form the corresponding alcoholate, and then excess carbon disulfide was added to form ethyl xanthate, which precipitated upon addition of ethyl ether; the xanthate formed was filtered and washed with ethyl ether; the precipitate was then dis-

solved in acetone, and ethyl xanthate was again precipitated with ethyl ether. Re-dissolution and re-precipitation of the product was repeated twice, and finally the xanthate was filtered and dried to obtain a high-purity product.

Reagent-grade hydrochloric acid and potassium hydroxide were used for pH adjustment. Lead chloride, zinc sulfate, and all of the other chemicals used were reagent-grade.

Methods.

The experimental methods used in the investigation involved a micro-flotation technique and surface charge determinations with a Zeta-Meter.

Micro-Flotation Technique. The flotation studies were conducted using the micro-flotation technique described by Fuerstenau⁽⁷⁾ using a modified Hallimond tube^(8, 9, 10) instead of the conventional micro-flotation cell.

Micro-Flotation Apparatus. The modified Hallimond tube has a fritted glass bottom (with a 60-micron average pore size) for gas entrance. The Hallimond cell used during the investigation was constructed to hold 150 ml pulp (Figure 1).

Nitrogen was purified by passing it through Ascarite to remove carbon dioxide before it entered the bottom of the tube through the glass frit. Admittance of the gas to the system was controlled with a regulating valve, a water manometer, a constant-head reservoir, and a gas-measuring burette (by water displacement).

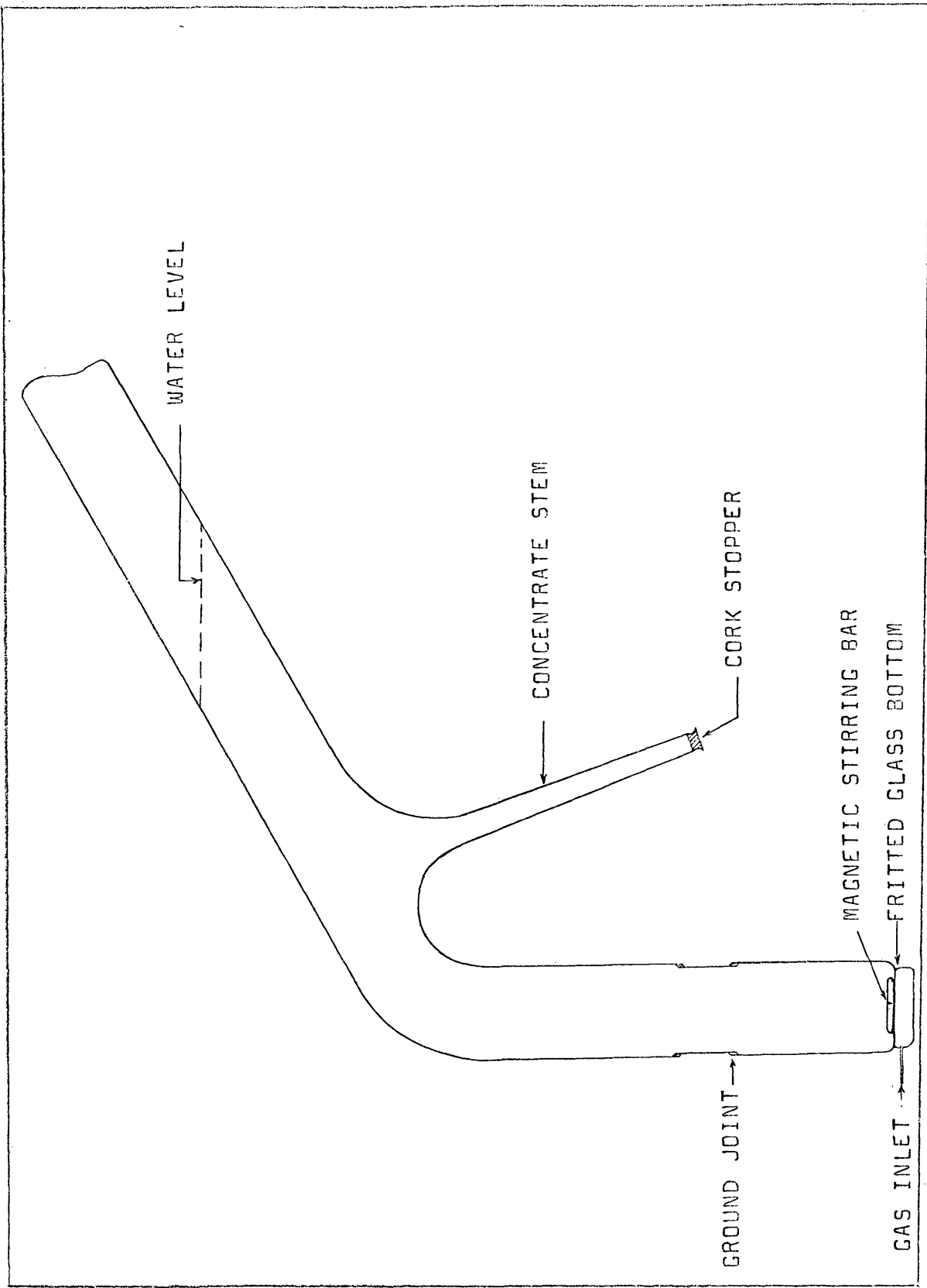


Figure 1. Schematic diagram of the modified Hallimond tube.

The main advantages of this type of equipment are: (a) operating variables such as flotation time, gas flow rate, and agitation rate can be accurately controlled; (b) samples of 1 to 3 grams can be floated; (c) reagent concentration and amount of liquid is kept constant during each test; and (d) contamination is nil for no metallic parts are involved in the flotation system. A schematic diagram of the micro-flotation apparatus appears in Figure 2.

Flotation Procedure. Flotation experiments were conducted at room temperature in the following manner:

1. A predetermined volume of conductivity water was combined with the necessary volumes of collector solution and modifying reagents in a 250-ml beaker.
2. The pH of the system was adjusted to the desired value with hydrochloric acid or potassium hydroxide solutions.
3. One gram of the sized mineral was deslimed and then added to the solution.
4. The conditioning times and the sequence of addition of modifying reagents and collector solution were as follows:
 - (a). For the galena experiments, the pulp was conditioned for 2 min with zinc sulfate, followed by a 3-min conditioning with the collector, KEX.
 - (b). For the lead-activated sphalerite experiments, the pulp was conditioned for 2 min with lead chloride, followed by a 2-min conditioning period with zinc sulfate, and then a 3-min conditioning with the collector, KEX.

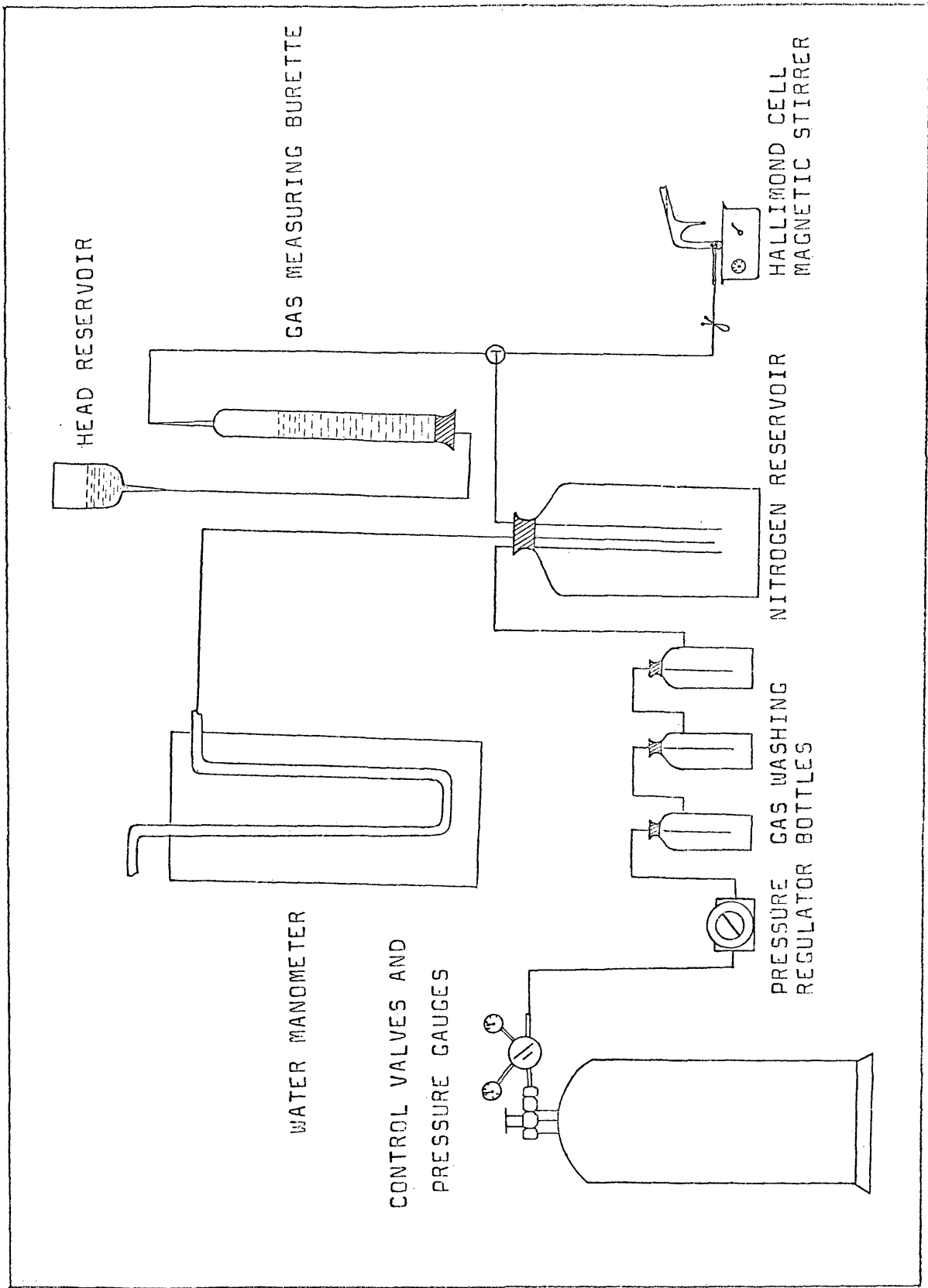


Figure 2. Schematic diagram of the micro-flotation apparatus.

5. The pH of the system was measured at the end of the conditioning time. This was considered the flotation pH.
6. The pulp was then transferred to the Hallimond cell, and 60 ml of purified nitrogen were passed in 30 sec.
7. The pH of the remaining suspension after flotation was measured to check for pH stability.
8. The flotation products were dried and weighed, and the recovery was calculated.

Surface Charge Determinations. For the determination of the electrical charge on the surface of the minerals and the colloids, a Zeta-Meter was used.

The Riddick Zeta Meter⁽¹¹⁾. This equipment enables the determination of the electrophoretic mobility of the suspended mineral and colloid particles at different pH values. The electrodes are immersed in a suspension of the solid particles, and the velocity of separate particles along the appropriate counting line is determined. The surface charge (actually the zeta potential) of the particles is then determined by the use of the Helmholtz-Smoluchovsky equation, as follows:

$$\zeta = \frac{4\pi\mu E \rho}{D_t} \quad , \text{ where}$$

- ζ = zeta potential in volts;
 μ = viscosity of the fluid in dyne-sec/cm²
 D_t = dielectric constant of the fluid in coul/volt-cm
 = $80 \times 1.12 \times 10^{-12}$ for water;

E.M. = electrophoretic mobility in $\text{cm}^2/\text{sec. volt}$
= v/V

v = velocity of the suspended particle, in cm/sec ;

V = voltage per cm length of fluid.

Electrophoresis Experiments. These experiments were conducted with the Zeta-Meter according to the following procedure:

1. A 50-mg sample of minus 5-micron particles was placed in a 250-ml beaker with 150 ml of water.
2. The pH of the suspension was measured and adjusted to the desired value.
3. The pulp was conditioned for 15 min by controlled agitation with a magnetic stirrer, and at the end of the conditioning period the pH was measured again.
4. The Zeta-Meter cell was filled with an aliquot of the suspension. Care was taken during this operation to remove all air bubbles from the system.
5. The cell was placed on its holder, and the 6X objective of the microscope was focused on the solid particles.
6. Ten separate particles traveling along the 6X objective were then timed in their traverse of one micrometer division (160 microns) when a determined emf was applied.
7. The polarity switch was reversed and ten more particles were timed during movement in the opposite direction.
8. The pH of the suspension was measured again, and an average of the initial and final readings was taken as the experimental

value.

9. Direct application of the Helmholtz-Smoluchovsky formula gives the values for the zeta potentials. Standard charts based on this formula are also available for the determination of the electrophoretic mobilities and zeta potential values.

EXPERIMENTAL RESULTS

The experimental work has been divided into two principal sections:

1. Flotation studies with galena and sphalerite using potassium ethyl xanthate as collector, lead chloride as activating agent for sphalerite, and zinc sulfate as depressing agent.
2. Zeta potential measurements of the minerals and of the colloids with and without the addition of sodium sulfate.

Flotation Experiments.

Flotation experiments were conducted with each of the minerals at a constant collector concentration to establish the effects upon flotation response of pH and modifying reagents.

Galena Flotation. Figure 3 depicts the flotation response of galena as a function of pH at a constant collector addition of 1×10^{-4} mole per liter KEX. Galena responded well to flotation over a wide pH range; two regions of depression were encountered,

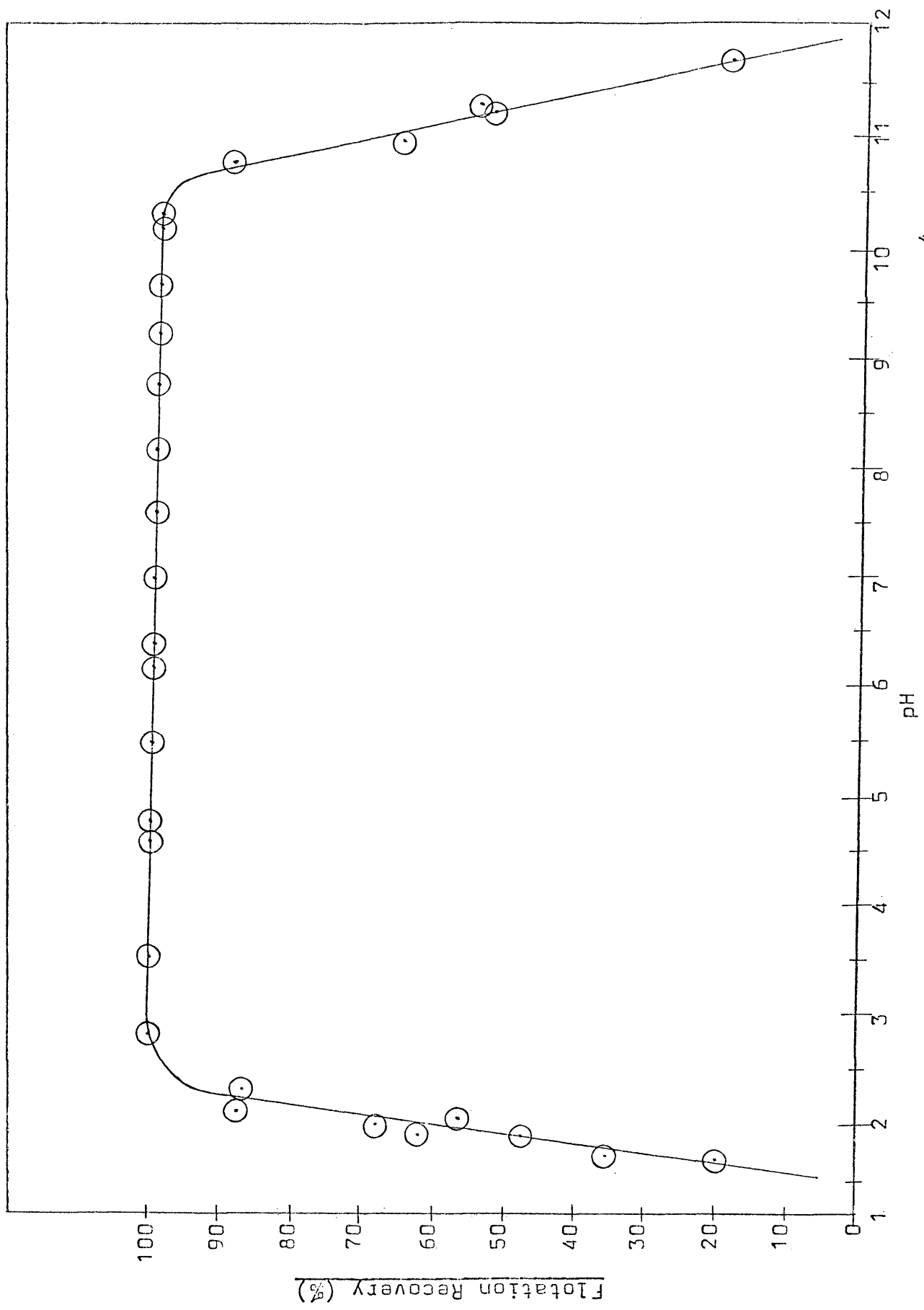


Figure 3. Flotation recovery of galena as a function of pH. KEX 1×10^{-4} mole per liter.

one below pH 2.5, and the other one above pH 10.5.

In the next series of experiments, galena flotation recovery was measured as a function of both pH and zinc sulfate addition, for a collector addition of 1×10^{-4} mole per liter KEX. Depression of the mineral occurred at low levels of addition of zinc sulfate as it is shown in Figures 4, 5, and 6. At pH 8.5 the system was depressed for additions of 1×10^{-4} and 5×10^{-4} mole per liter modifying reagent. When 1×10^{-3} mole per liter zinc sulfate was added, the depression region appeared at pH 9.5.

The depressing effect was minimized when high additions of zinc sulfate were involved in the flotation system. In Figure 7 the flotation recovery of galena is presented as a function of pH for three different levels of zinc sulfate addition. Depression was practically nil under these conditions.

In another series of experiments, the effects of decreasing the collector concentration were studied. Figure 8 depicts the flotation response of galena as a function of pH for a collector concentration of 1×10^{-5} mole per liter KEX and an addition of 1×10^{-3} mole per liter zinc sulfate. A region of depression between two areas of flotation appeared under these conditions. Complete flotation was obtained up to pH 7.5, with the depression region at about pH 8.1. The maximum flotation response between pH 8.0 and 10.9 was 61 percent at pH 8.5.

In Figures 9 and 10 the flotation recoveries of the mineral for a collector addition of 1×10^{-5} mole per liter potassium ethyl xanthate and higher levels of zinc sulfate addition are shown.

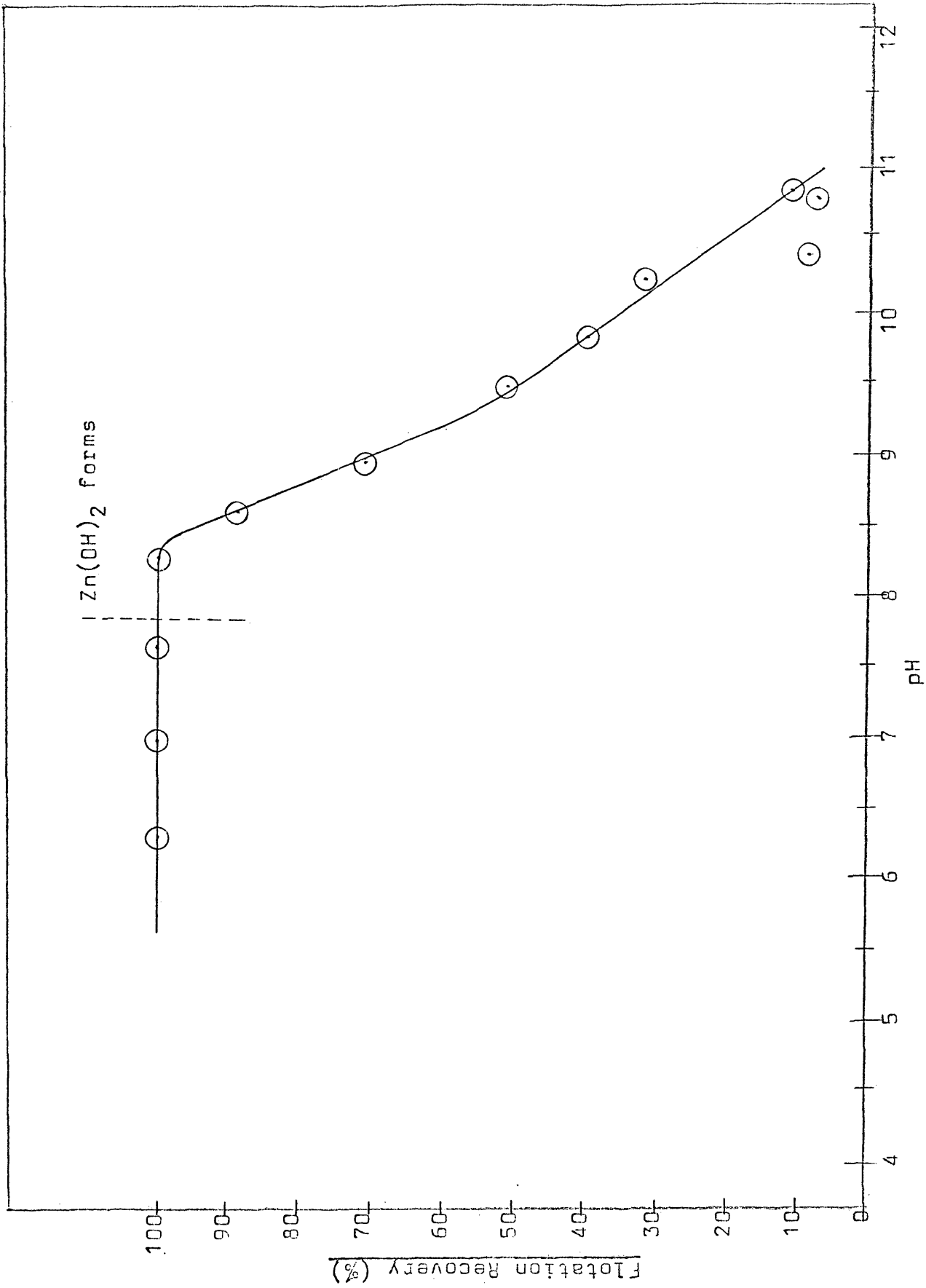


Figure 4. Flotation recovery of galena as a function of pH for additions of 1×10^{-4} mole per liter zinc sulfate and 1×10^{-4} mole per liter KEX.

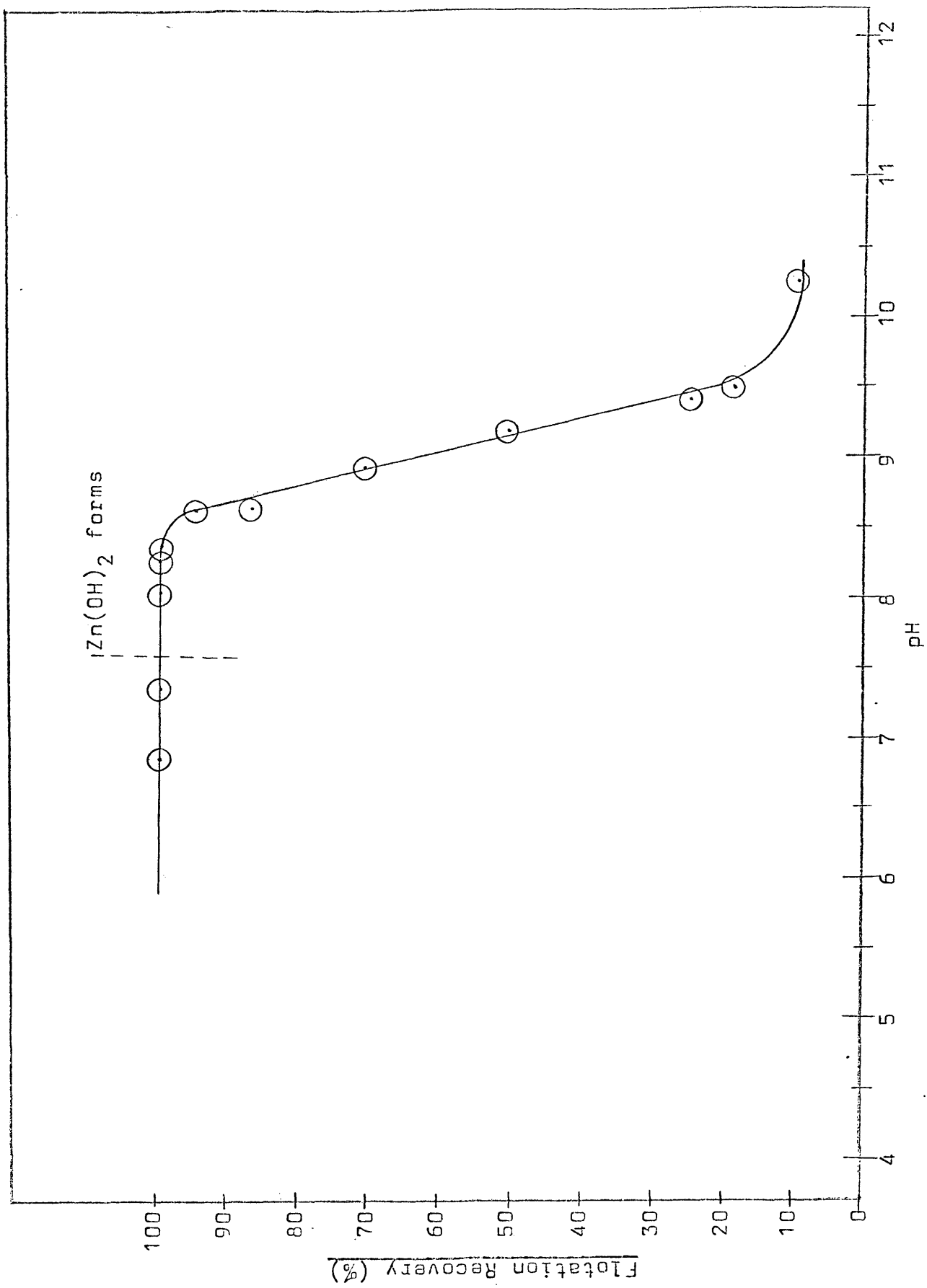


Figure 5. Galena flotation recovery as a function of pH for an addition of 5×10^{-4} mole per liter zinc sulfate. $KEX 1 \times 10^{-4}$ mole per liter.

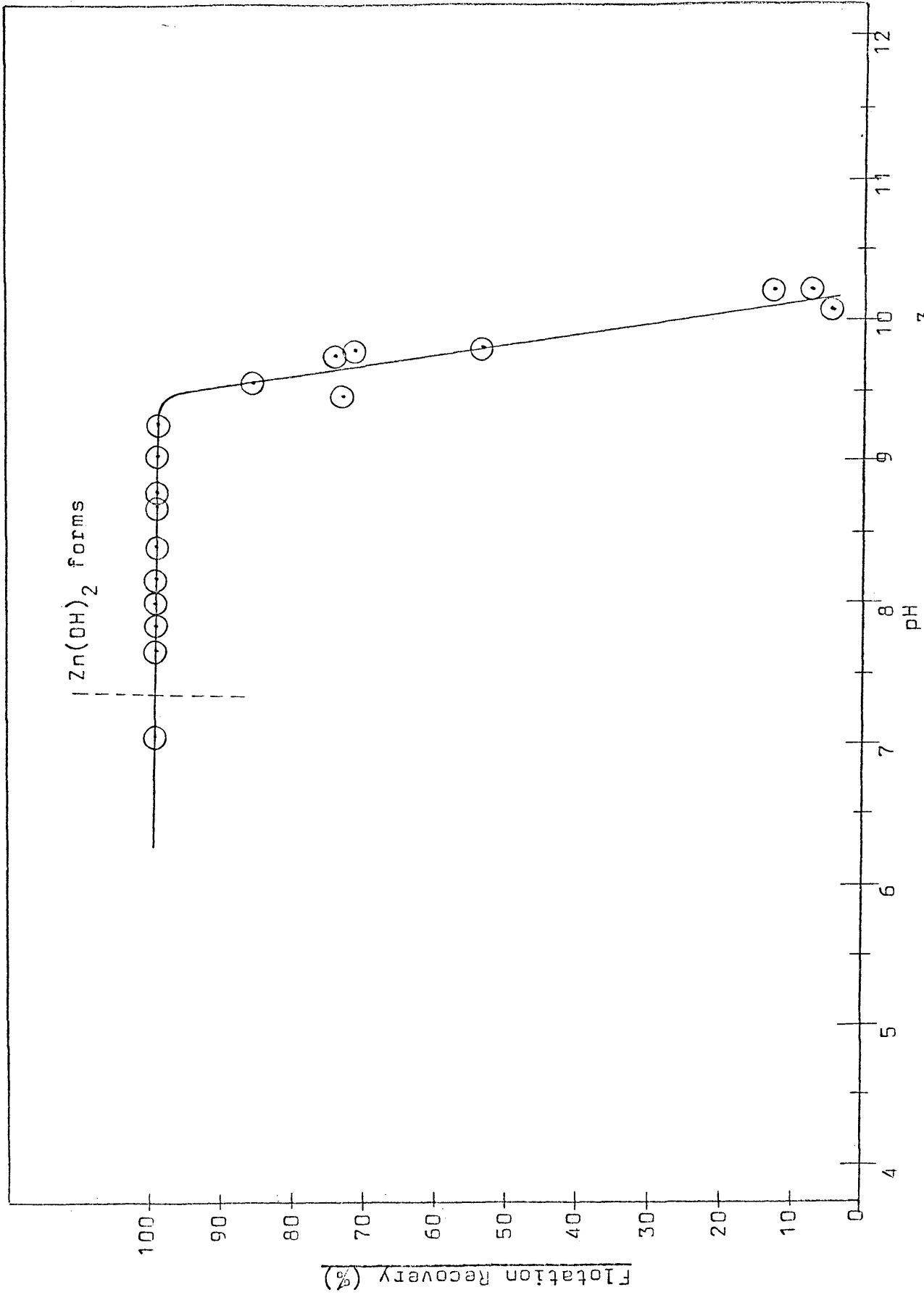


Figure 6. Flotation response of galena in the presence of 1×10^{-3} mole per liter zinc sulfate and 1×10^{-4} mole per liter KEX.

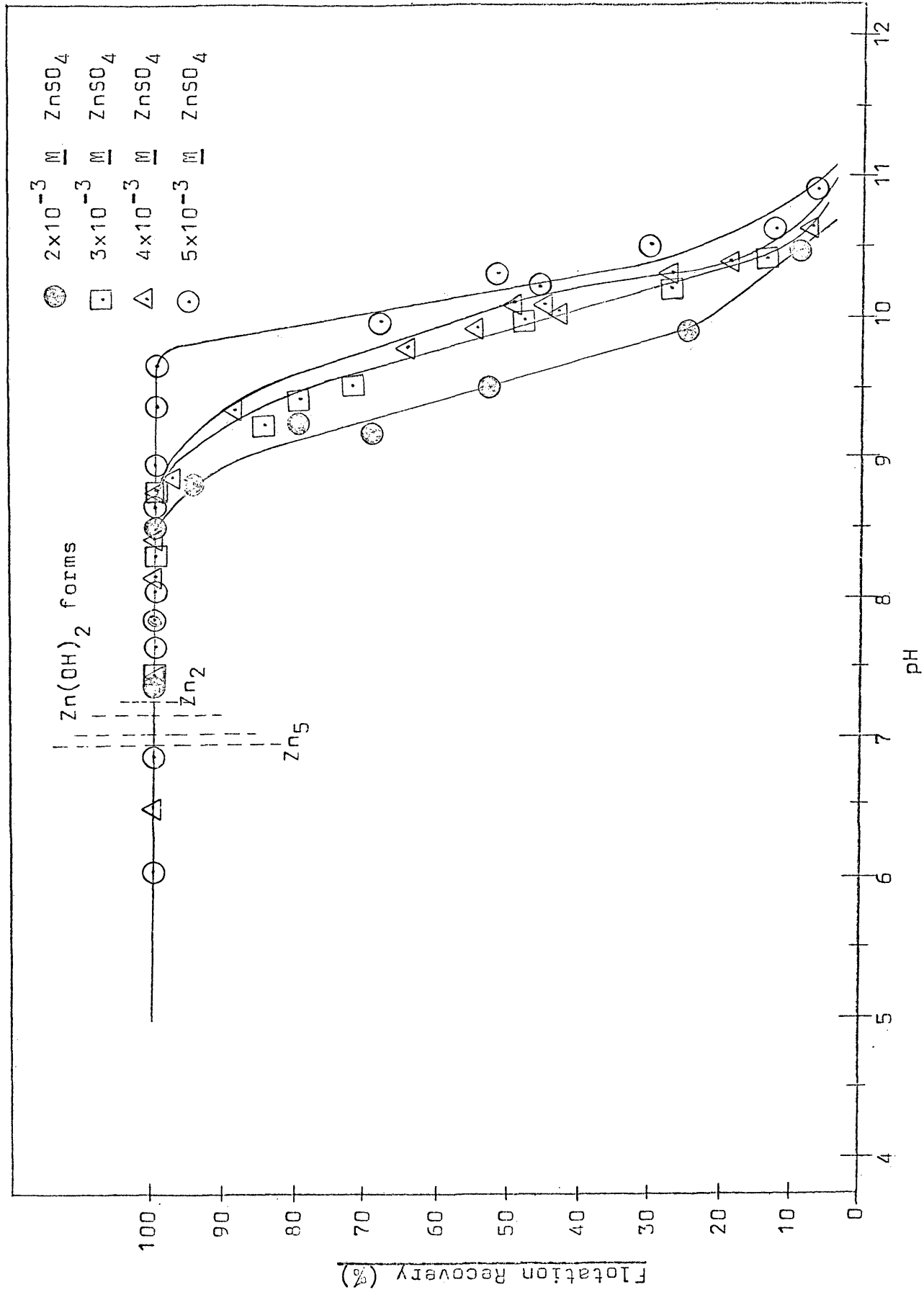


Figure 7. Flotation recovery of galena as a function of pH at four different levels of addition of zinc sulfate and a constant collector addition of 1x10⁻⁴ mole per liter KEX.

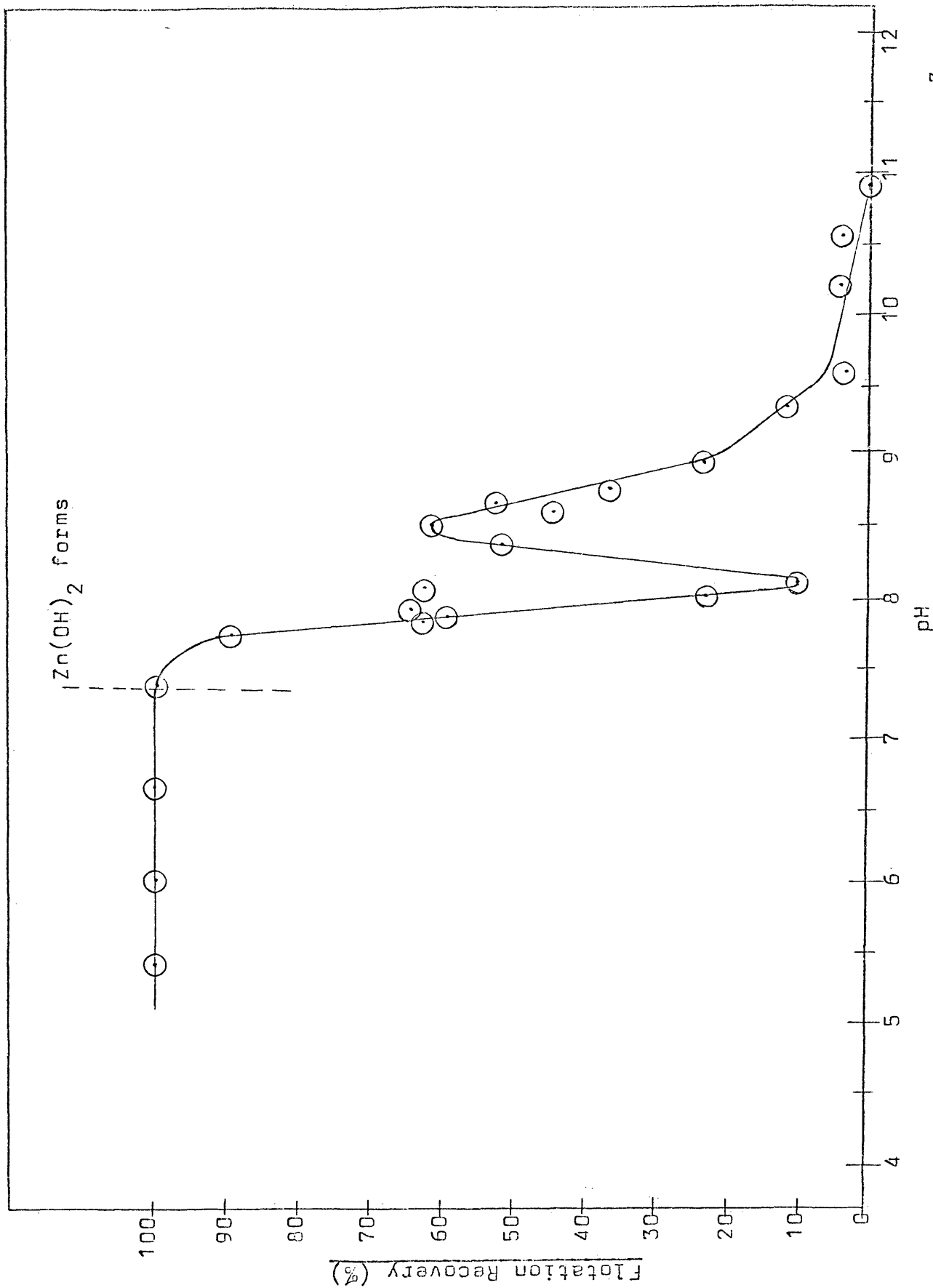


Figure 8. Galena flotation recovery as a function of pH for an addition of 1×10^{-3} mole per liter zinc sulfate. KEX 1×10^{-5} mole per liter.

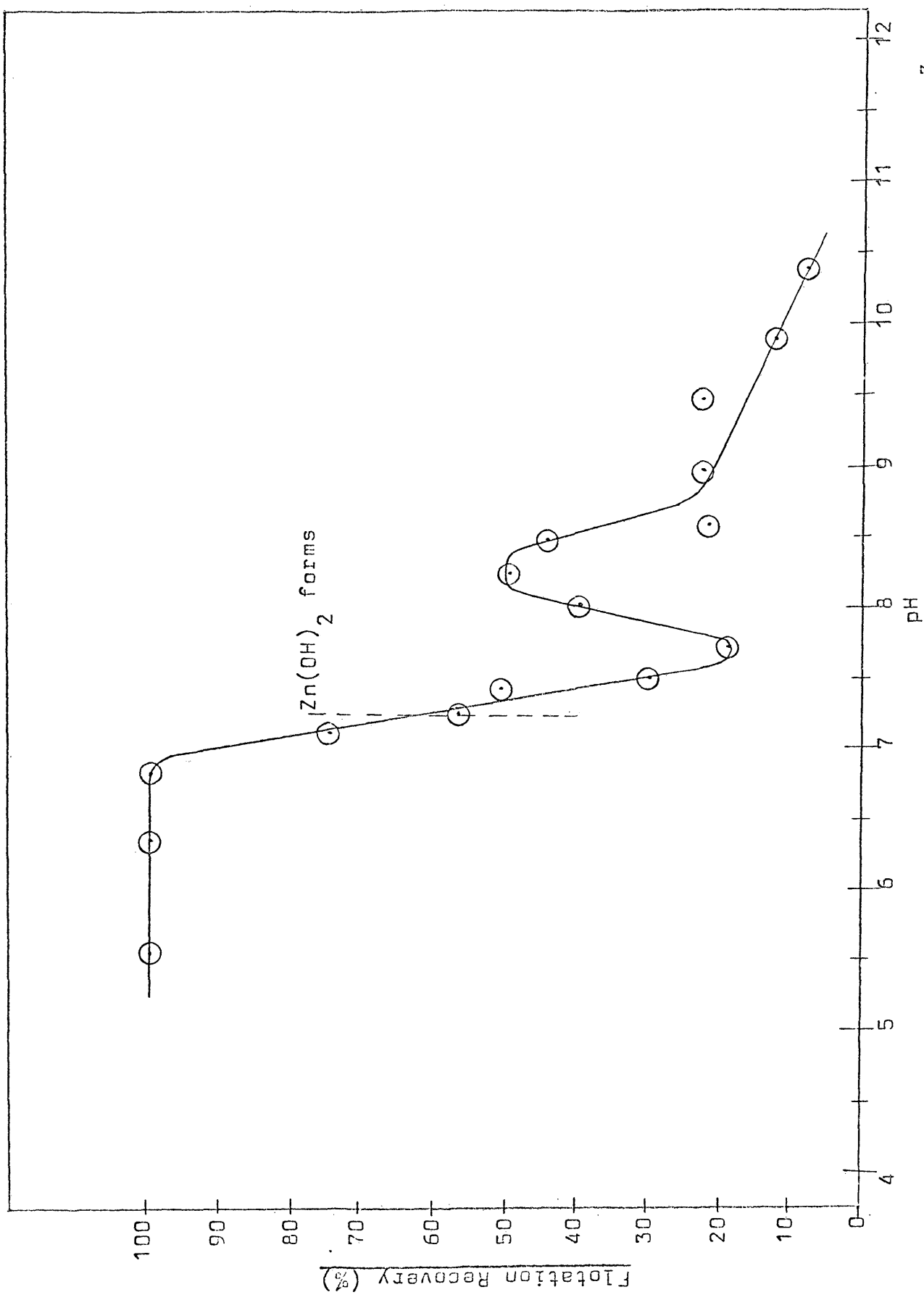


Figure 9. Flotation recovery of galena as a function of pH for additions of 2×10^{-3} mole per liter zinc sulfate and 1×10^{-5} mole per liter KEX.

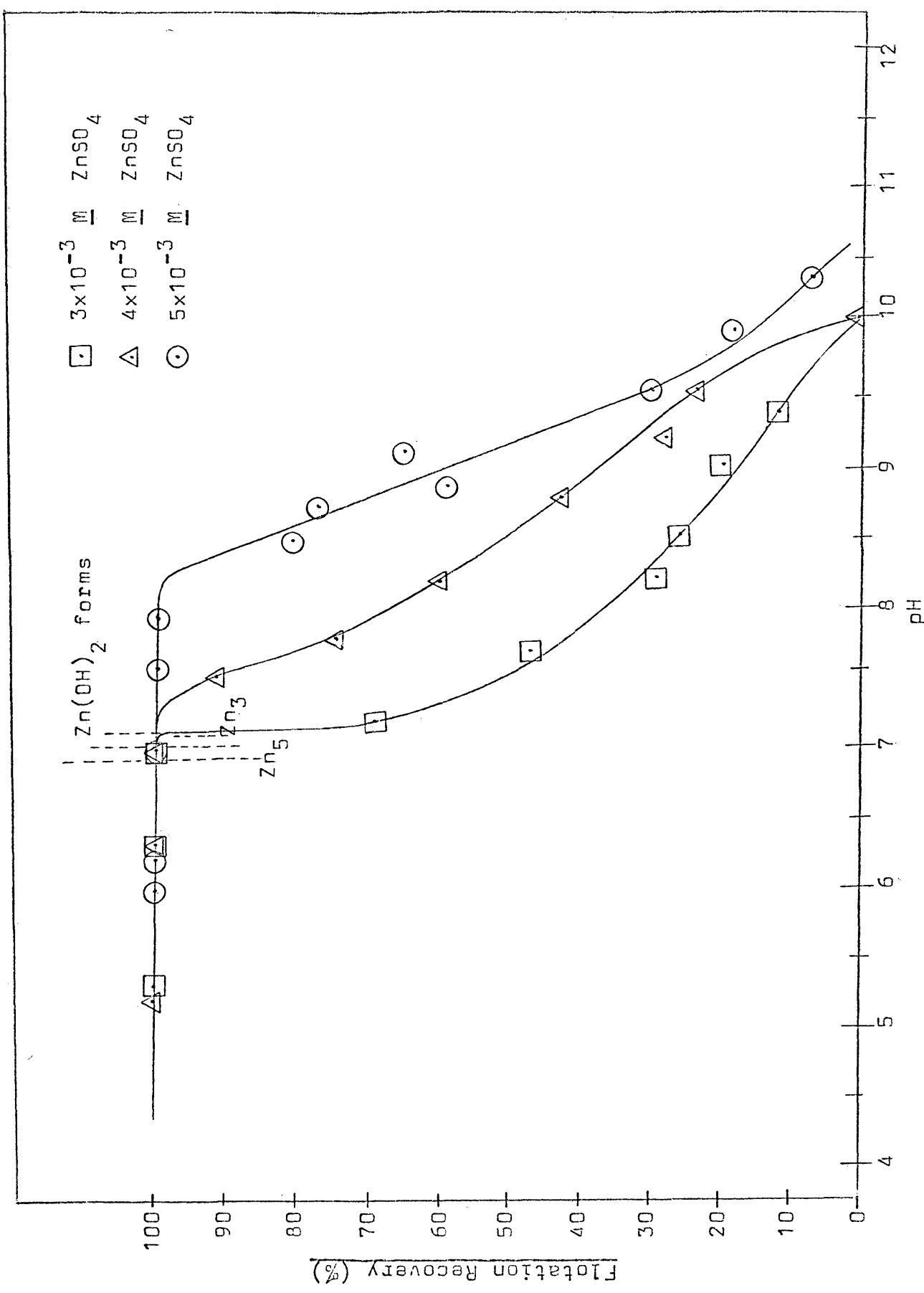


Figure 10. Galena flotation recovery as a function of pH at three different levels of zinc sulfate addition. KEX 1×10^{-5} mole per liter.

The net effect caused by a decrease in collector addition was the shift of the depression regions to lower pH values.

Sphalerite Flotation. The flotation recovery of sphalerite as a function of pH for a collector addition of 1×10^{-4} mole per liter KEX is depicted in Figure 11. The flotation response of the mineral is very poor when it has not been activated. Two regions of maximum flotation recovery were noted at approximately pH 4.5 and pH 7.0, with a depression region at about pH 6.0. Better flotation recoveries of sphalerite were achieved with potassium amyl xanthate (KAX), and the results obtained with this collector appear in Figure 12. For a collector addition of 1×10^{-4} mole per liter KAX, two regions of maximum flotation were observed at pH 3.0 and from pH 7.0 to pH 8.0; a region of depression appeared at about pH 6.0.

In another series of experiments, the flotation behavior of lead-activated sphalerite was considered as a function of pH for a constant collector addition of 1×10^{-4} mole per liter KEX (Figure 13). The activated mineral responded well to flotation under these conditions; two regions of depression were noted at pH 3.0 and pH 10.5. and complete flotation occurred over the pH range from 3.5 to 10.0.

The effect of zinc sulfate addition on the flotation recovery of lead-activated sphalerite was studied in another series of experiments, using a constant addition of 1×10^{-5} mole per liter lead chloride as activating agent.

Figure 14 depicts the flotation response of lead-activated

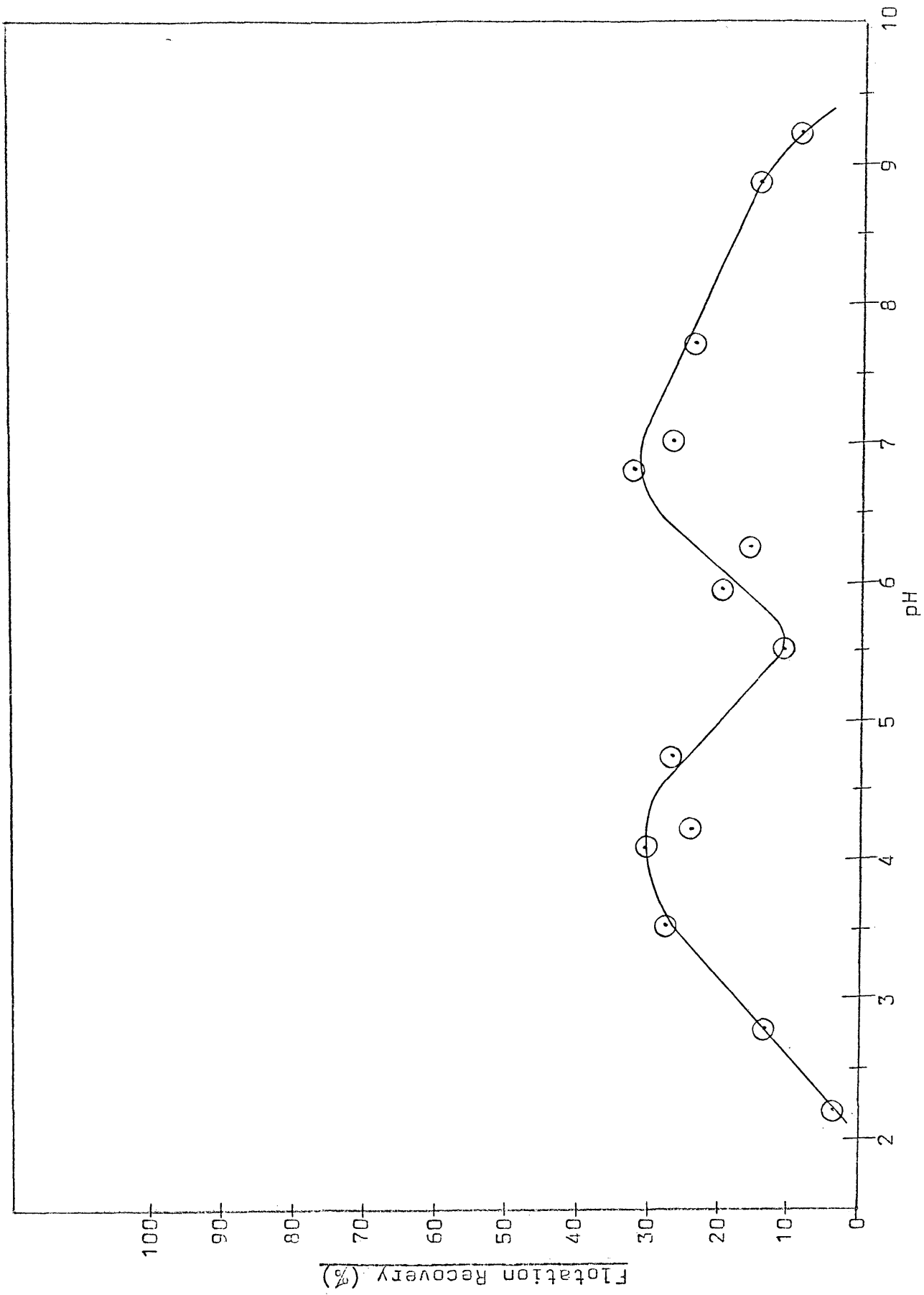


Figure 11. Sphalerite flotation recovery as a function of pH for a collector addition of 1×10^{-4} mole per liter potassium ethyl xanthate (KEX).

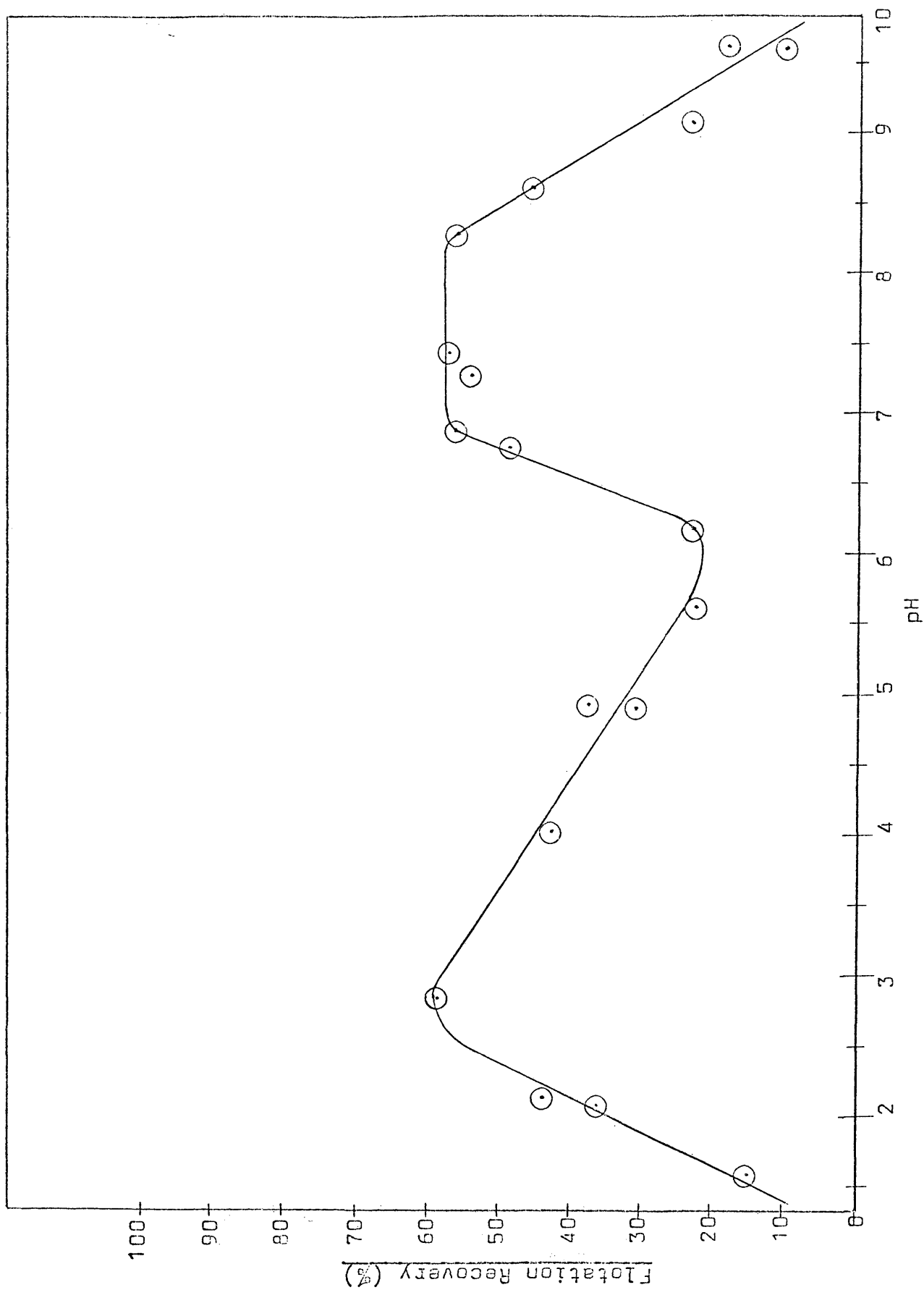


Figure 12. Sphalerite flotation recovery as a function of pH for a collector addition of 1×10^{-4} mole per liter potassium amyl xanthate (KAX).

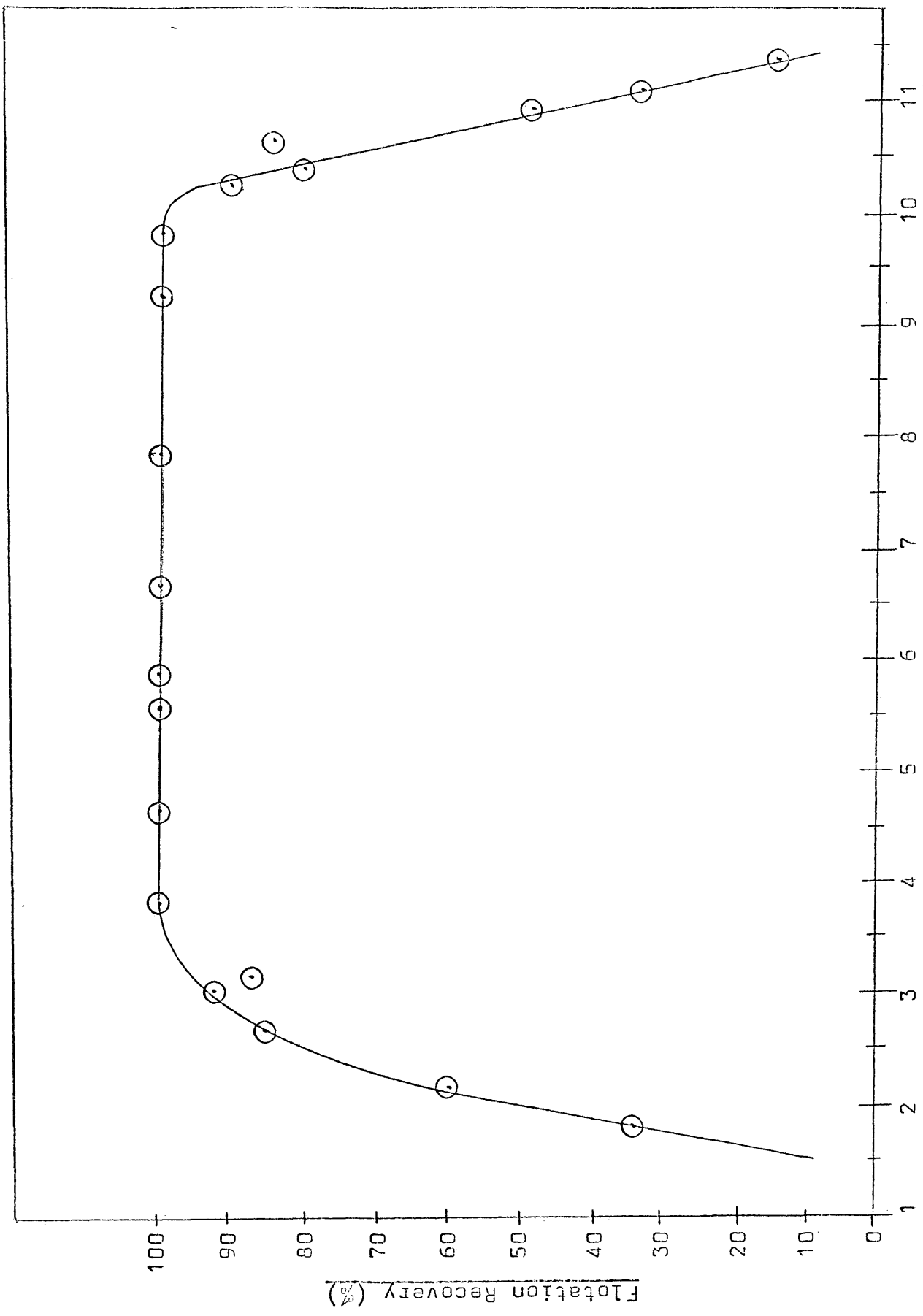


Figure 13. Flotation response of lead-activated sphalerite as a function of pH at a collector addition of 1×10^{-4} mole per liter KEX. Lead chloride 1×10^{-5} mole per liter.

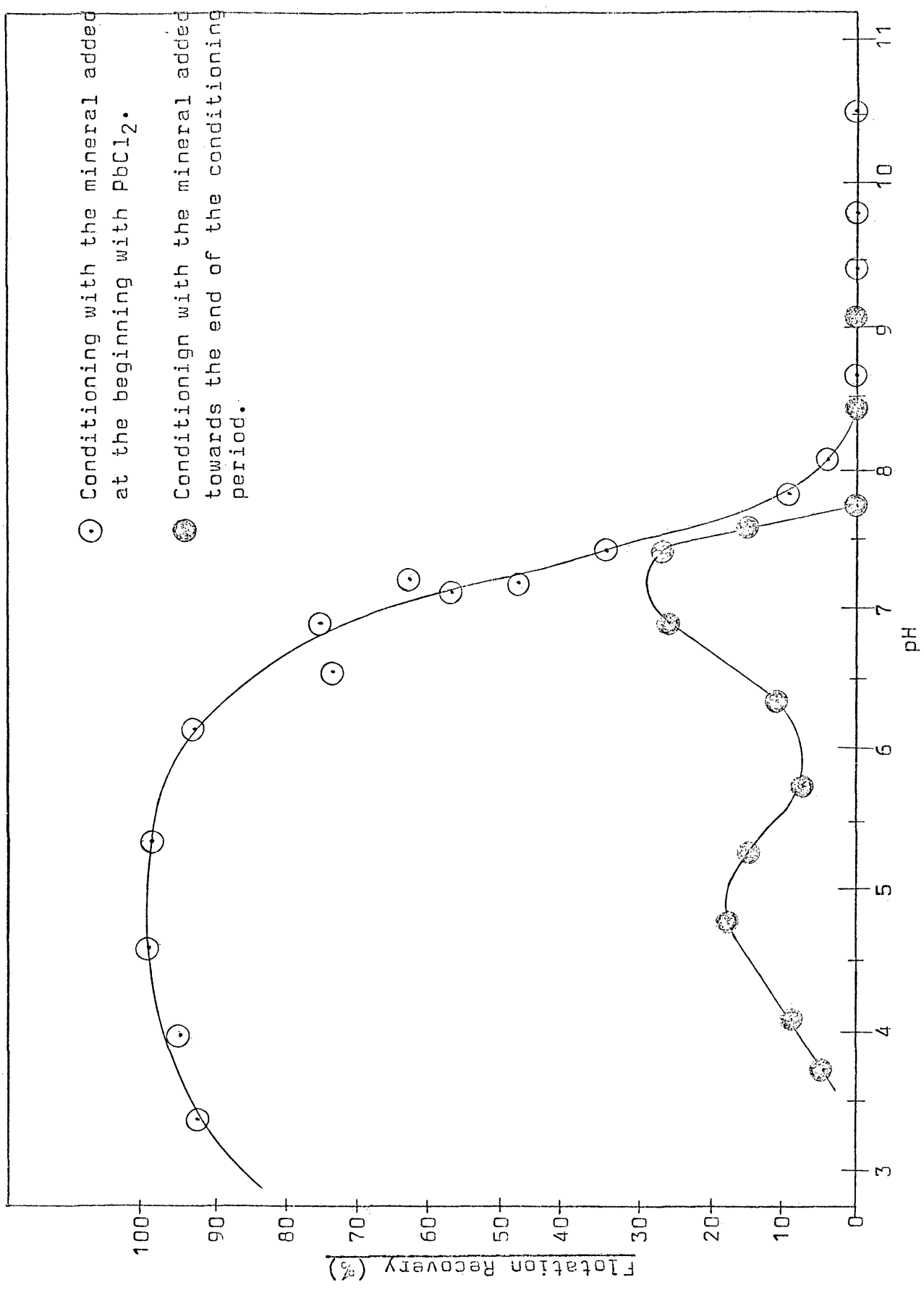


Figure 14. Flotation recovery of lead-activated sphalerite as a function of pH for additions of 1×10^{-4} mole per liter zinc sulfate and 1×10^{-4} mole per liter KEX.

sphalerite as a function of pH for a collector addition of 1×10^{-4} mole per liter KEX and an addition of 1×10^{-4} mole per liter zinc sulfate. Maximum flotation recovery was obtained from pH 4.0 to pH 6.0; depression started at pH 6.1, and at pH 8.0 the system was completely depressed. An increase in the zinc sulfate addition to 5×10^{-4} mole per liter (Figure 15) caused complete depression of the system at pH 7.3. At an addition of 1×10^{-3} mole per liter zinc sulfate complete depression of sphalerite occurred at pH 7.5 (Figure 16).

Further increase in the addition of modifying reagent caused a decrease in the maximum flotation recovery, and complete system depression was noted at pH 7.0 for zinc sulfate additions of 2×10^{-3} , 3×10^{-3} , 4×10^{-3} , and 5×10^{-3} mole per liter (Figures 17 and 18). In all cases the total depression of the system was closely related to the pH values at which zinc hydroxide colloids had precipitated.

A separate series of experiments were undertaken to ascertain the effect of the sequence of addition of reagents and mineral upon the flotation response of sphalerite. In these experiments the activating agent, lead chloride, and the regulating agent, zinc sulfate, were added both at the same time, and the solution was conditioned for 2 min, followed by a 2-min conditioning period with the mineral. The results obtained are indicated by black circles in the corresponding pH-recovery curves in Figures 14, 15, 16, and 17.

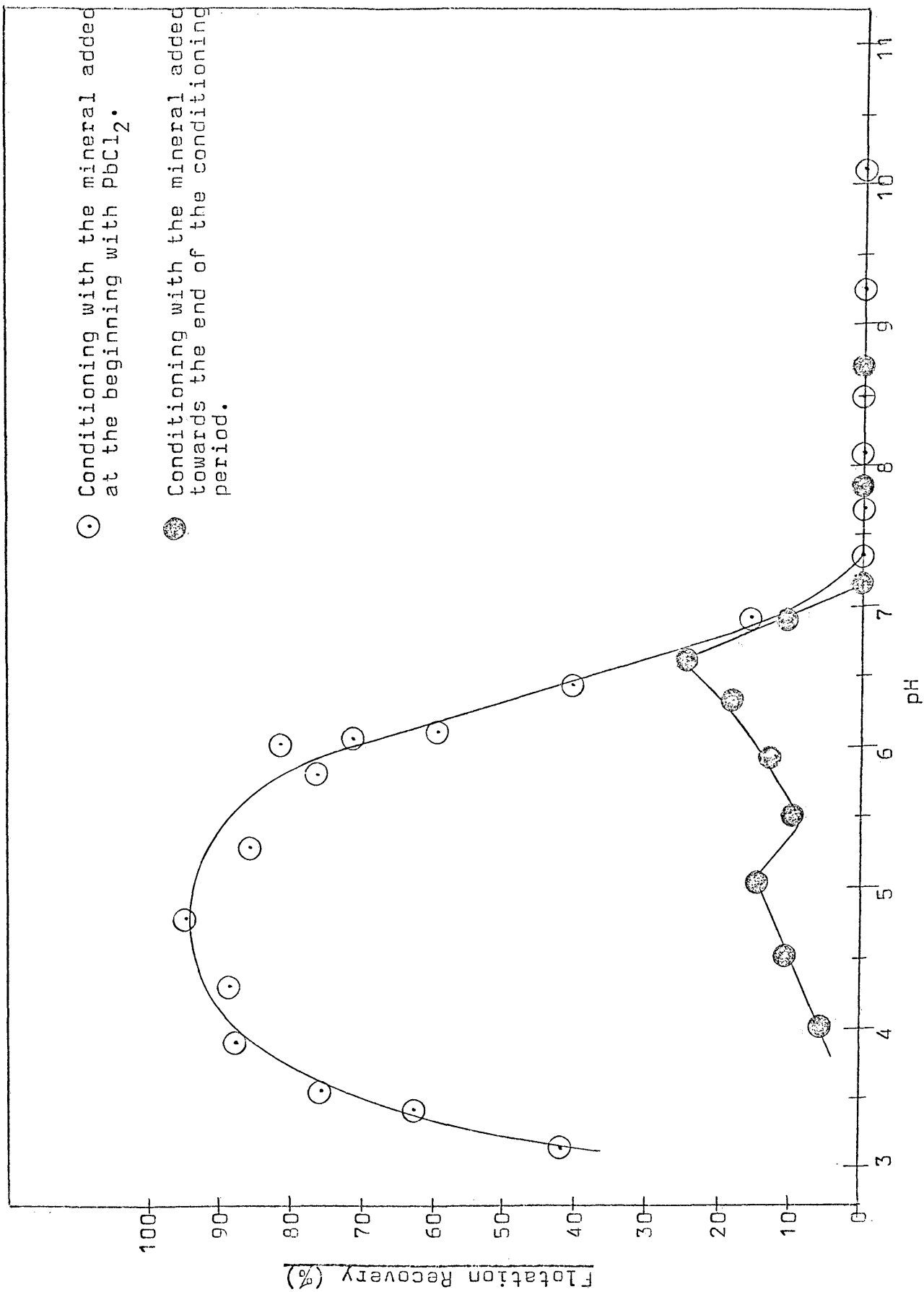


Figure 15. Lead-activated sphalerite flotation recovery as a function of pH in the presence of 5×10^{-4} mole per liter zinc sulfate. $KEX \ 1 \times 10^{-4}$ mole per liter.

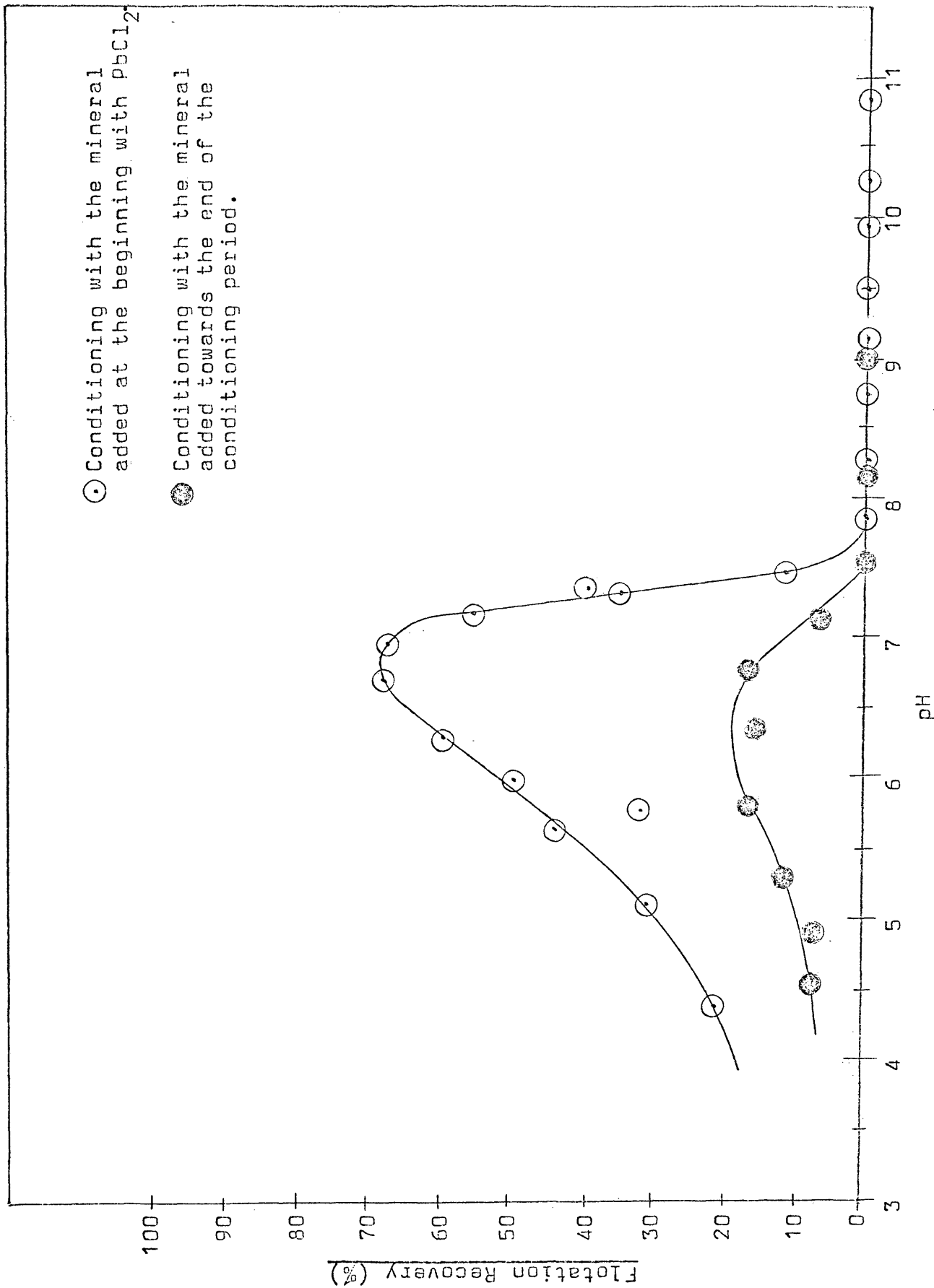


Figure 16. Flotation response of lead-activated sphalerite as a function of pH at an addition of 1×10^{-3} mole per liter zinc sulfate. $KEX 1 \times 10^{-4}$ mole per liter.

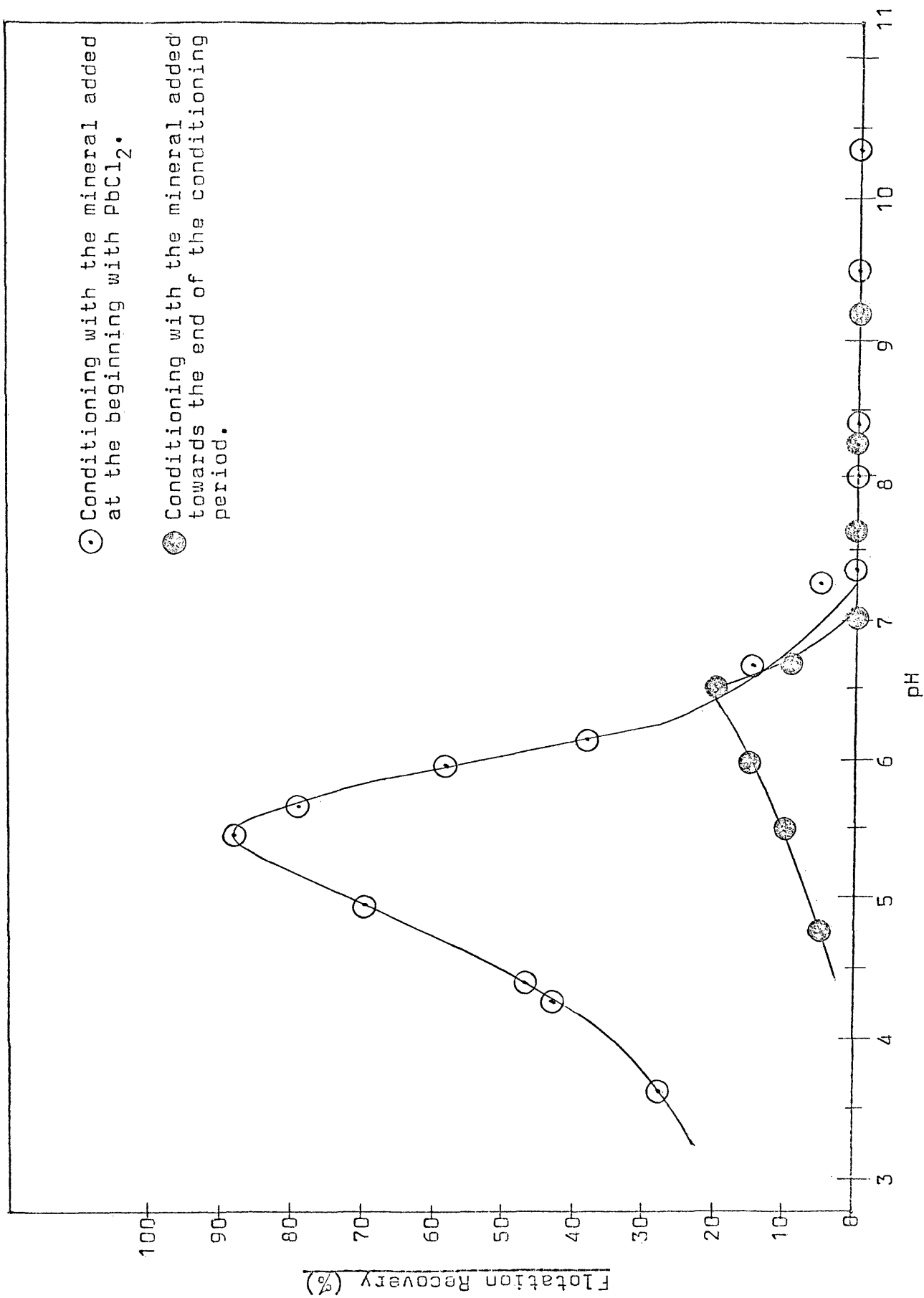


Figure 17. Flotation recovery of lead-activated sphalerite as a function of pH at an addition of 2×10^{-3} mole per liter zinc sulfate. $KEX 1 \times 10^{-4}$ mole per liter.

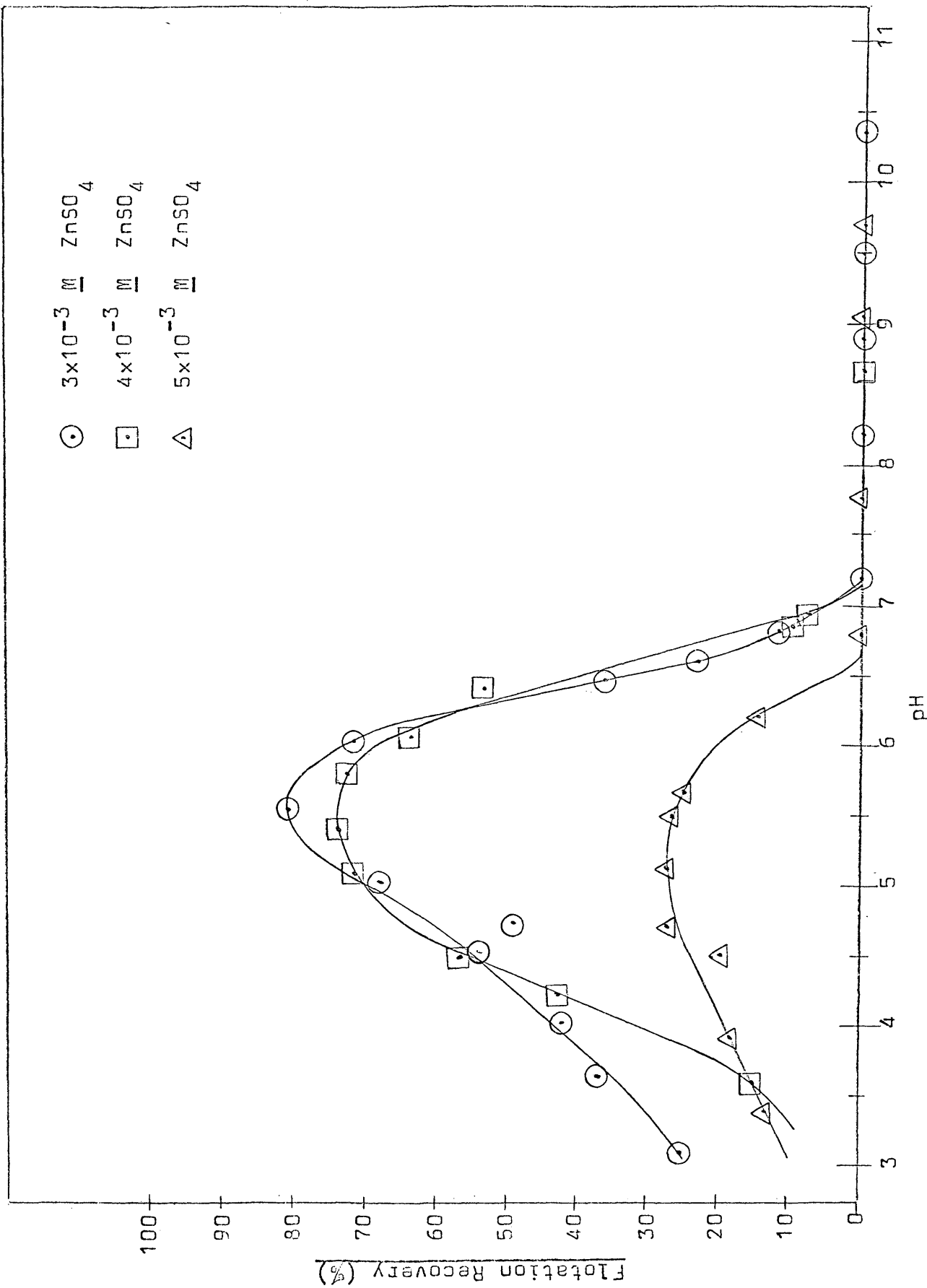


Figure 18. Flotation recovery of lead-activated sphalerite as a function of pH at three levels of zinc sulfate addition. KEX 1×10^{-4} mole per liter.

Electrophoresis Experiments. The presence of zinc hydroxide colloids in the flotation systems when the minerals were depressed, suggested some kind of interaction between the solid phases present. Zeta potential measurements were conducted with a Zeta-Meter to determine the electrical charge on the surface of the minerals and the colloids.

Galena. The zeta potential of galena is depicted as a function of pH in Figure 19. The zero-point-of-charge (ZPC) of the mineral was found to be pH 6.7.

Sphalerite. The zeta potential of sphalerite as a function of pH appears in Figure 20. The zero-point-of-charge of the mineral is pH 5.9. The corresponding values for lead-activated sphalerite are shown in Figure 21 (ZPC is pH 6.1).

Zinc Hydroxide Colloids. The electrophoresis data for zinc hydroxide colloids are recorded in Figure 22. The effects of sodium sulfate additions upon the surface charge of the colloids are shown in Figures 23 and 24. The colloids became more negatively charged as the addition of sodium sulfate increased, and at salt additions higher than 3×10^{-3} mole per liter they are negatively charged over the pH range from 7.0 to 11.0.

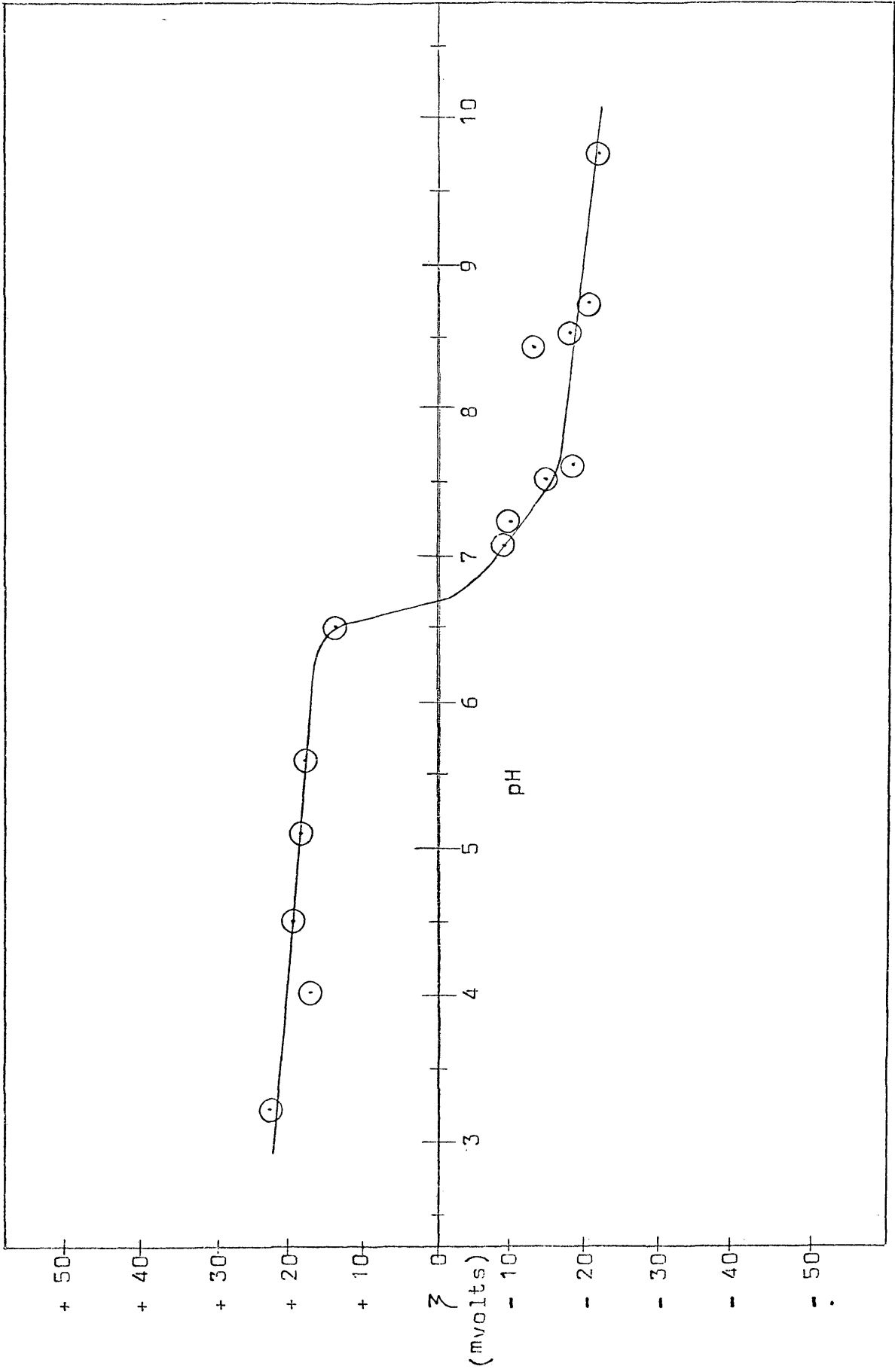


Figure 19. Zeta potential of galena as a function of pH.

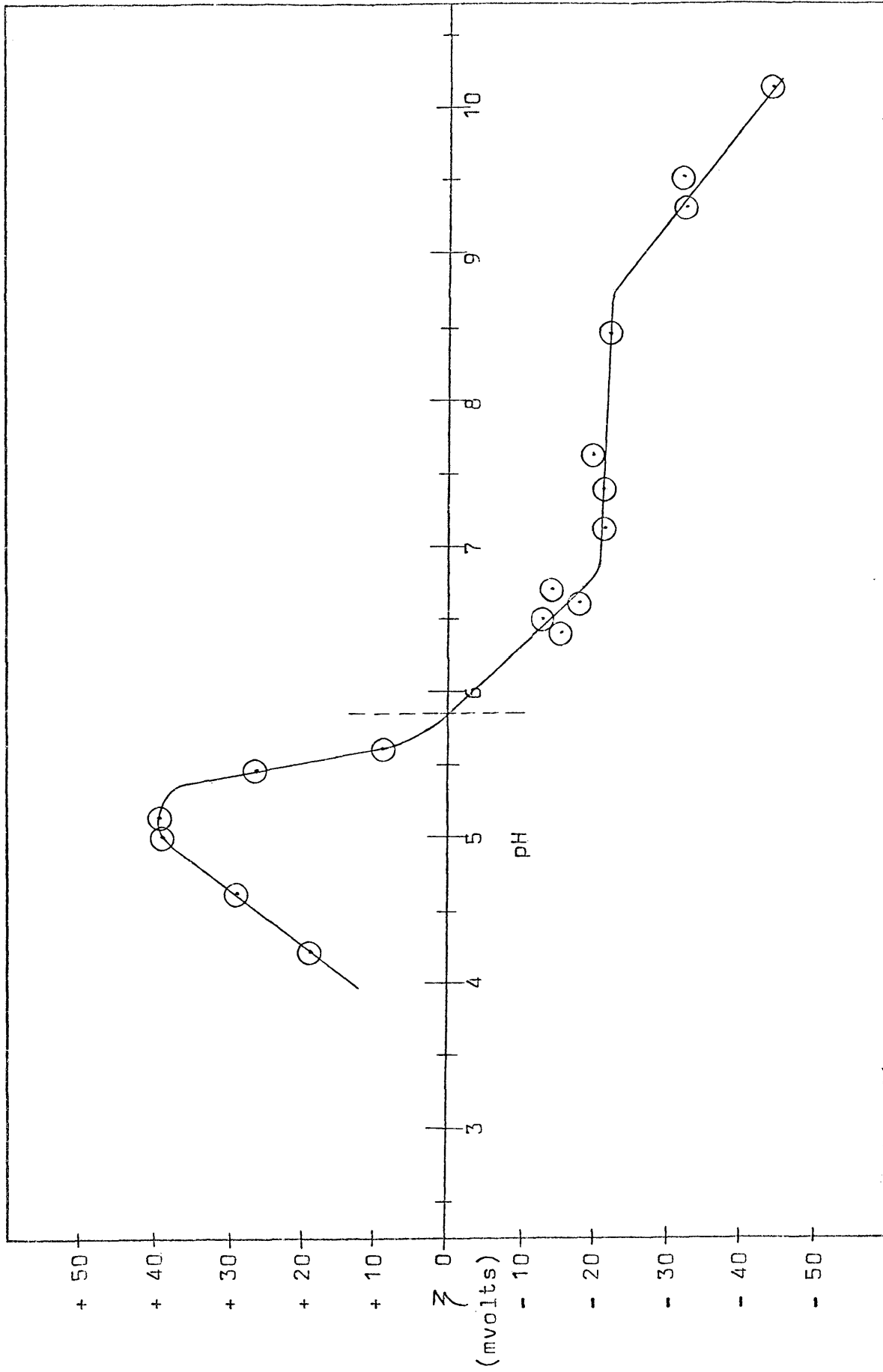


Figure 20. Zeta potential of sphalerite as a function of pH.

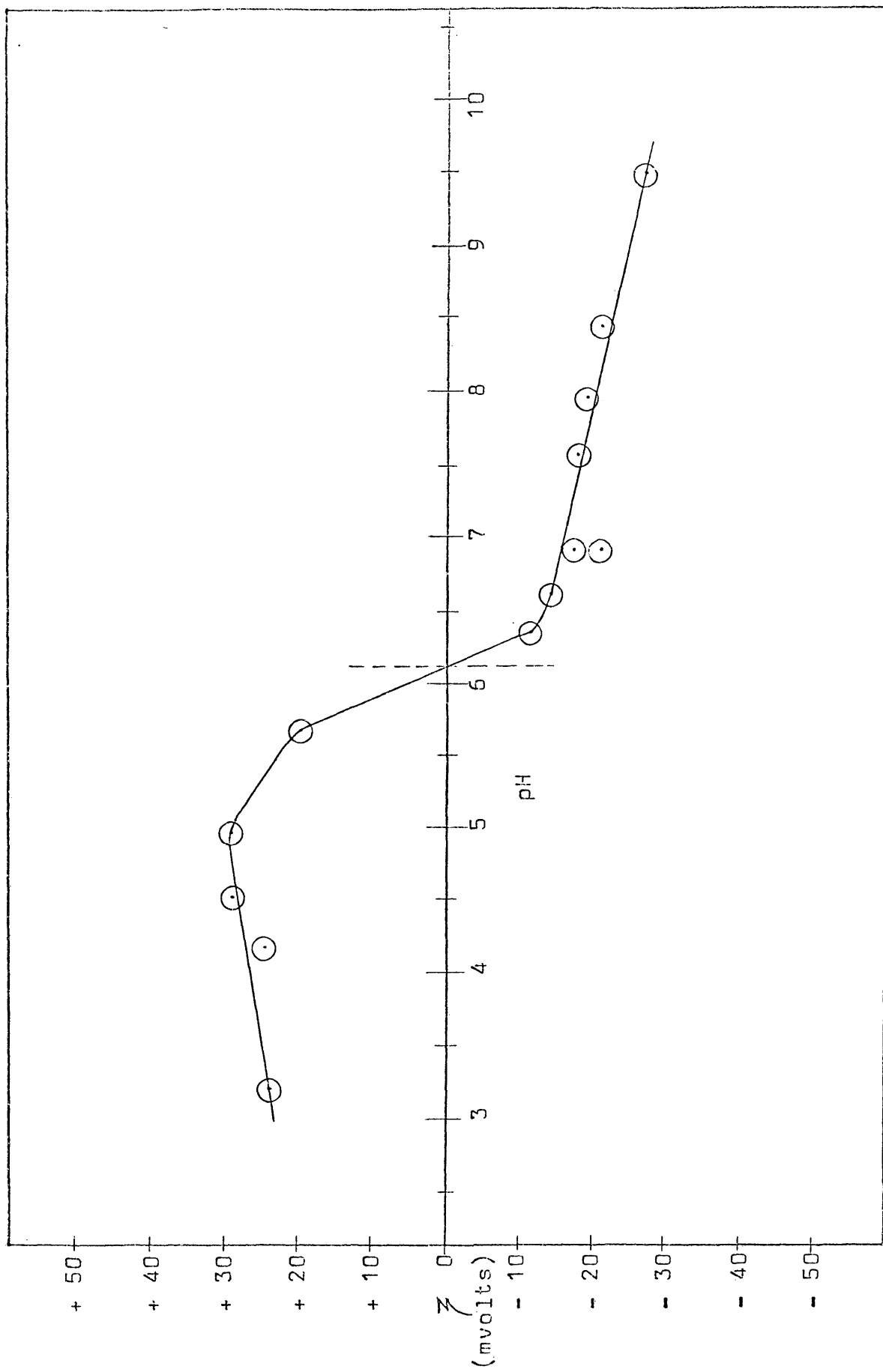


Figure 21. Zeta potential of lead-activated sphalerite as a function of pH.

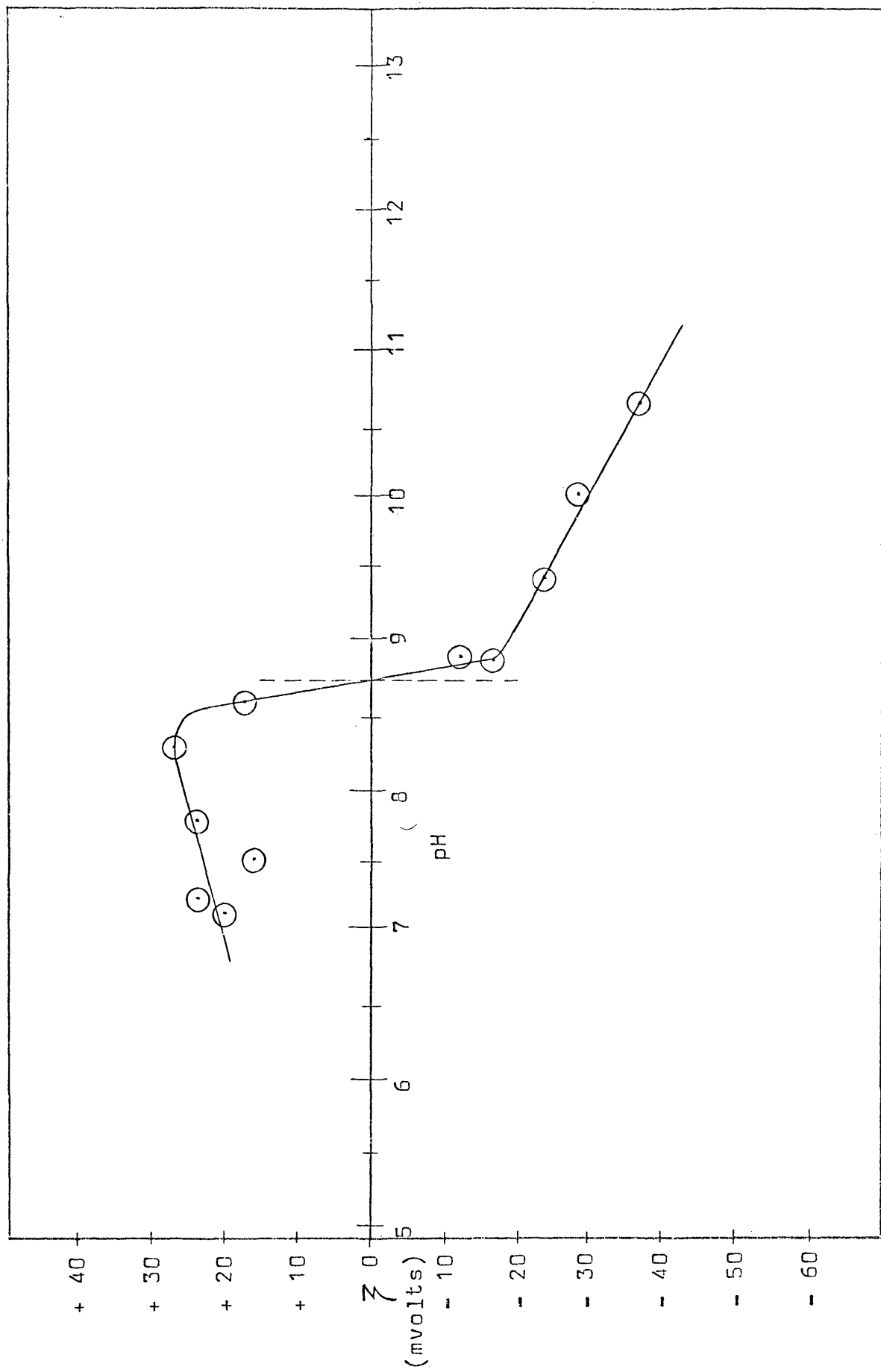


Figure 22. Zeta potential of zinc hydroxide colloids as a function of pH.

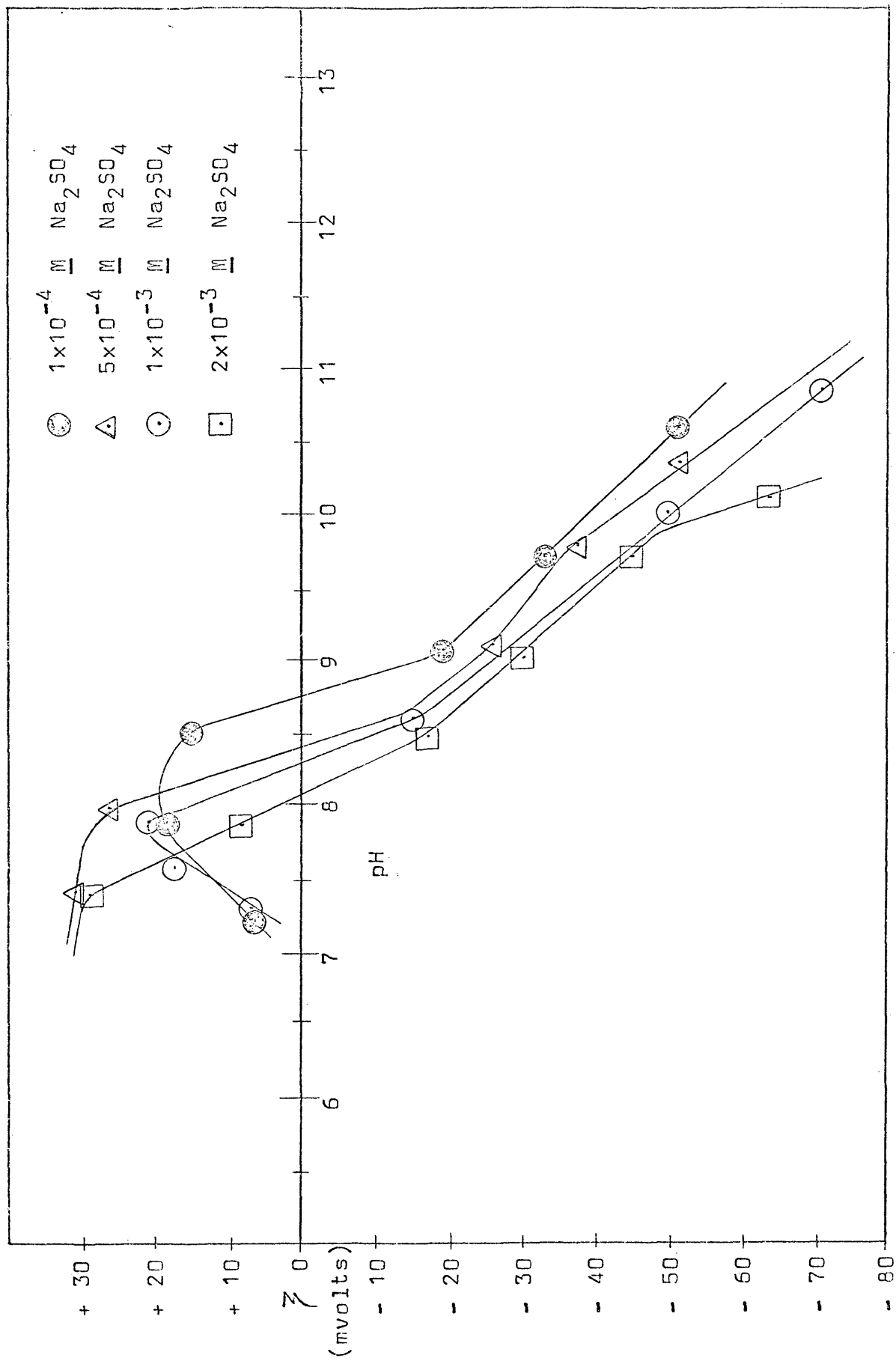


Figure 23. Zeta potential of zinc hydroxide colloids as a function of pH at three levels of sodium sulfate addition.

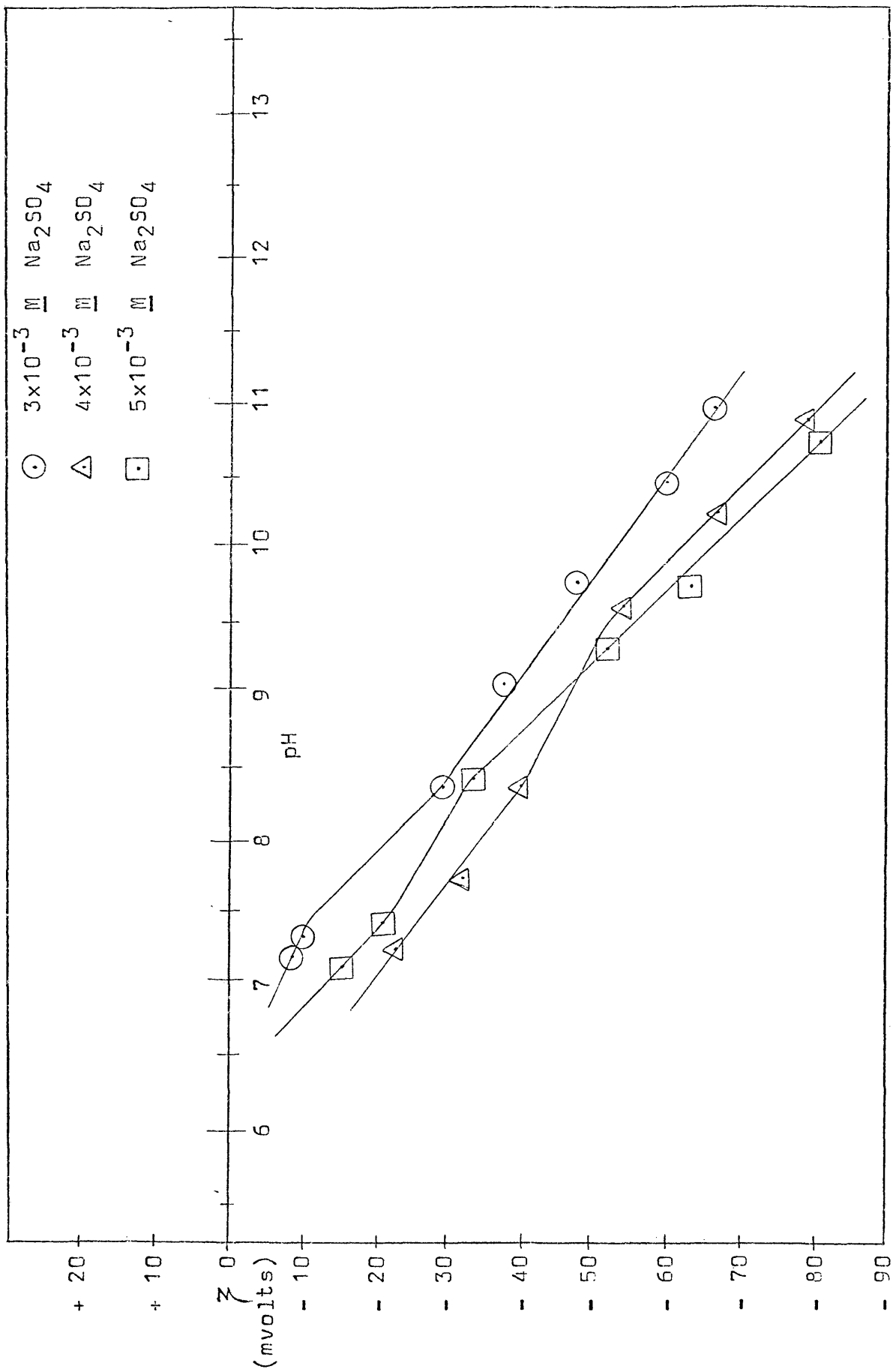
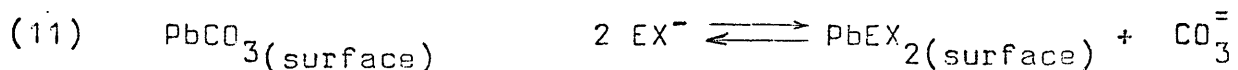
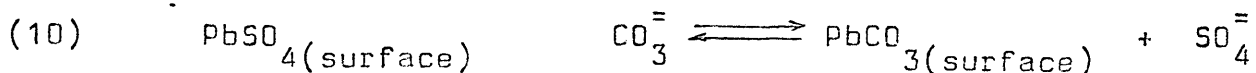
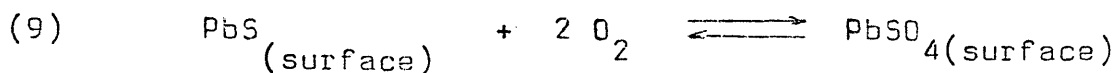


Figure 24. Zeta potential of zinc hydroxide colloids as a function of pH at three different levels of sodium sulfate addition.

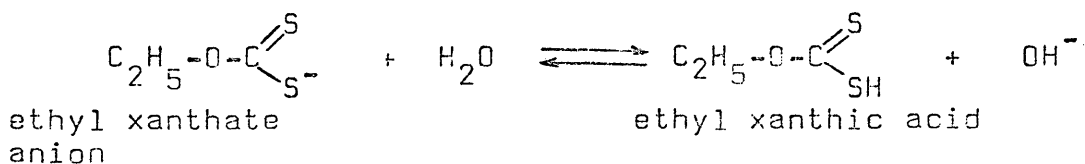
DISCUSSION OF RESULTS

The flotation behavior of galena with potassium ethyl xanthate substantiated the generally accepted mechanism of collector adsorption on the mineral surface to form an insoluble film of lead xanthate. Oxidation of the galena surface by dissolved oxygen occurs first, followed by carbonate replacement of sulfate ions, and then xanthate ion adsorption occurs, according to the following reactions:

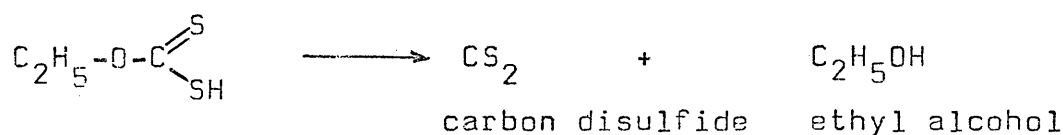


The two regions of depression that appeared in the flotation response of galena, below pH 2.5 and above pH 10.5, can be explained by decomposition of the collector in the low pH region, and by the formation of surface lead hydroxide or plumbite in the region of high pH values.

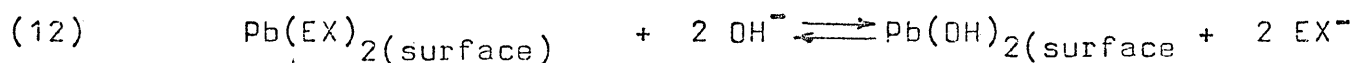
Xanthate anions are stable in water but hydrolyze to form xanthic acid in acid media⁽⁵⁾:



Xanthic acids are very unstable compounds and rapidly decompose into carbon disulfide and the corresponding alcohol:

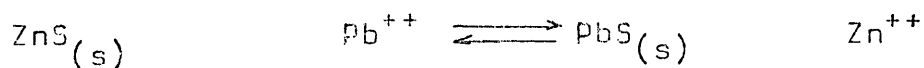


At high pH values surface lead ions will hydrolyze to lead hydroxide or perhaps to plumbite, $\text{Pb}(\text{OH})_3^-$:



Depression of the mineral at low levels of zinc sulfate addition and for a collector addition of 1×10^{-4} mole per liter KEX, was related to the pH values at which zinc hydroxide precipitated. These pH values are indicated with vertical lines in the pH-recovery curves.

For an addition of 1×10^{-4} mole per liter zinc sulfate to the galena-xanthate system (Figure 4), galena was depressed at about pH 8.0, and zinc hydroxide colloids started forming at about pH 7.8. It has been considered by Diaz⁽¹²⁾ that if the equilibrium constant of the reaction



given by the ratio $(\text{Zn}^{++})/(\text{Pb}^{++}) = 1000$ is exceeded, depression of galena would occur by the formation of a zinc sulfide coating on the mineral surface. If that were the case, depression of the system should occur at all the pH values lower than 8.0 where the above ratio reaches values much higher than 1000, as given by the Pb^{++} ion concentration determined by the solubility product of $\text{Pb}(\text{EX})_2$ and by the Zn^{++} ion concentration determined by the particular addition to the flotation system. Depression did start at pH 8.0 for an addition of 1×10^{-4} mole per liter zinc sulfate, and at this pH value zinc hydroxide colloids had formed. As a result, it would be more reasonable to consider that depression might be caused by adsorption of the colloids on the galena surface and not by a zinc sulfide coating on the surface of the mineral.

The depressing effect of zinc sulfate on galena diminished with the addition of modifying reagent (Figures 5 and 6), and upon additions of 4×10^{-3} and 5×10^{-3} mole per liter zinc sulfate practically no depression occurred (Figure 7). Under these conditions the colloids appeared at lower pH values, but the mineral floated through the colloids after they had precipitated. This flotation behavior of galena with high additions of zinc sulfate might be interpreted on the basis of electrical interaction between the phases present in the flotation system.

A schematic diagram of the zeta potential based on the Stern model of the electric double layer⁽¹³⁾ appears in Figure 25. It

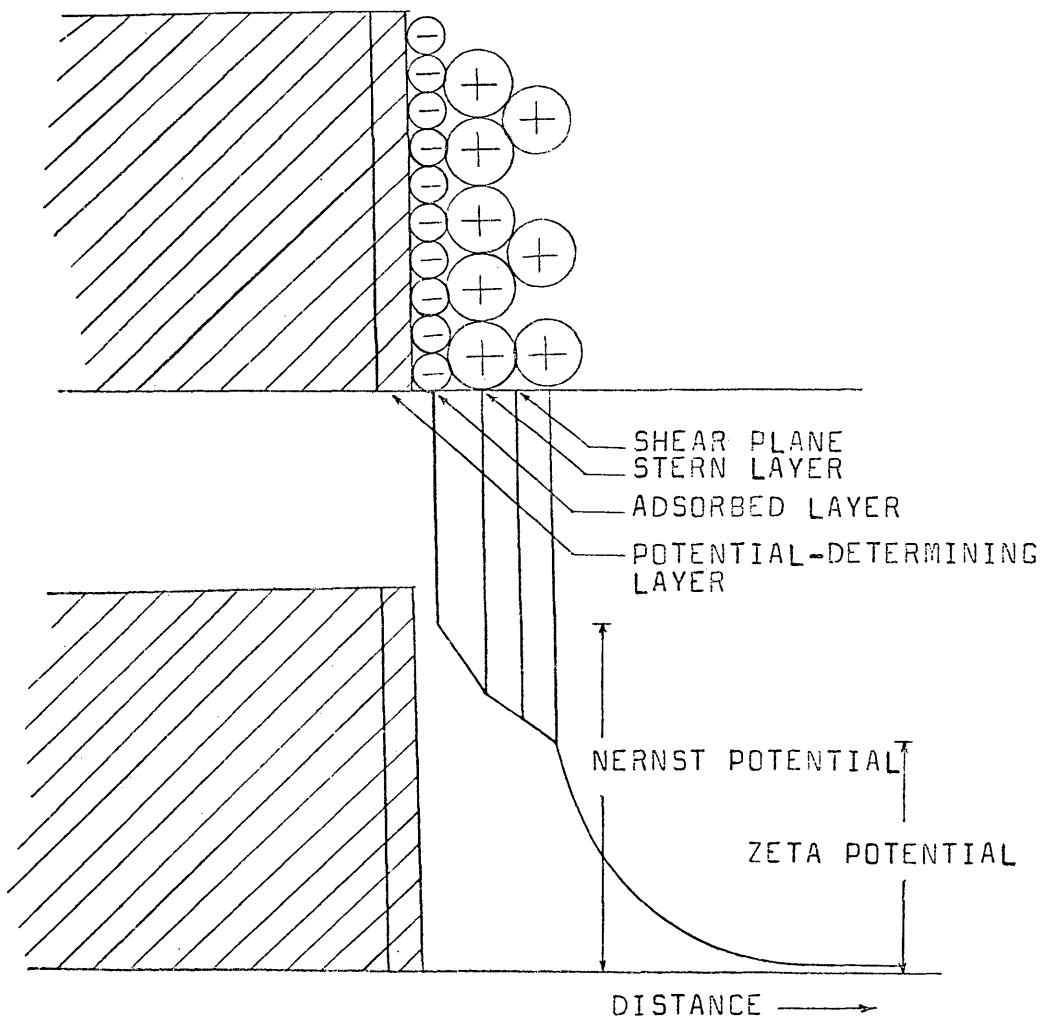
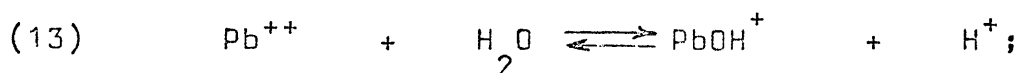


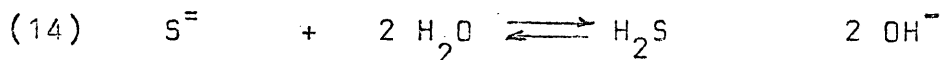
Figure 25. A model of the electric double layer.

can be seen that the zeta potential is represented as the potential difference between a point some distance from the surface and a point on the plane of shear. Negative values of zeta potential indicate predominance of negative ions at the Stern plane; positive values correspond to domination of cations, and very low values are indicative of a surface influenced by both positive and negative ions.

The results of zeta potential measurements of galena in conductivity water are shown in Figure 19. The zero-point-of-charge (ZPC) is pH 6.7. The negative charge above the ZPC may be due to hydrolysis of surface lead ions:



and the positive charge below the ZPC may be caused by hydrolysis of surface sulfide ions:



The corresponding zeta potential measurements for zinc hydroxide appear in Figure 22, with the ZPC at pH 8.8. This value is in good agreement with the value reported by Parks⁽¹⁴⁾.

Since both the galena and zinc hydroxide are negatively charged above about pH 9.0, it is apparent that depression of galena above this pH is not due to electrostatic attraction of the colloids onto the galena. At higher sulfate additions, however, flotation occurs at high pH values which indicates that electrical phenomena are involved to a minor extent, since the zeta potential of the colloids became more negative under these conditions (Figure

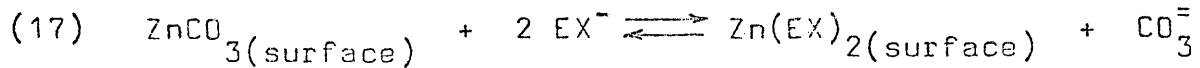
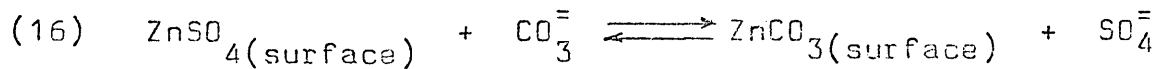
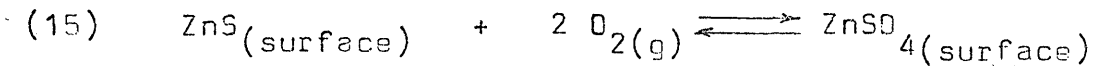
7). The colloids changed from a white to a blue color which suggests some kind of interaction between the colloids and the mineral. This effect is even more pronounced when the collector addition is relatively small compared to the zinc sulfate addition. See Figures 8, 9, and 10. The explanations of these phenomena are not readily apparent, and additional work will have to be conducted before they are learned.

The ability of xanthates to collect sphalerite has been a matter of considerable discussion; some experiments have indicated a high degree of collecting power, others a low degree. As stated by Gaudin ⁽¹⁵⁾, "This was eventually traced to the unintentional and uncontrolled activation of the mineral by metallic salts in solution, particularly copper salts. When this activation is rigidly excluded, short-chained xanthates are not collectors for sphalerite but longer-chained homologs show appreciable collecting power."

The flotation behavior of sphalerite as a function of pH for a collector addition of 1×10^{-4} mole per liter KEX (Figure 11) confirmed that poor recoveries of the mineral are obtained with a short-chained xanthate (ethyl xanthate). Better flotation recoveries were obtained with 1×10^{-4} mole per liter potassium amyl xanthate (Figure 12), which corroborated the fact that longer-chained xanthates are stronger collectors for sphalerite.

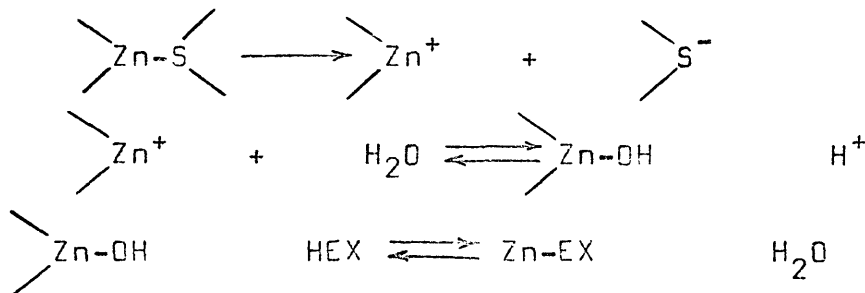
Flotation of sphalerite has been considered to occur through chemical adsorption of the collector on the oxidized mineral surface,

according to the following reactions:



Although reaction 15 tends to proceed as written from thermodynamic considerations, it has been shown⁽¹⁶⁾ that it is a very slow reaction from the point of view of kinetics, requiring high temperature and pressure if it is to occur.

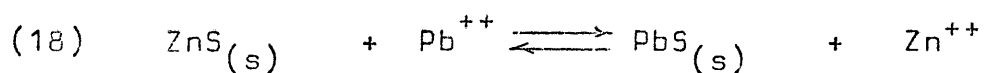
Consideration has also been given to flotation of the mineral by neutral collector molecules⁽¹⁷⁾, with the following proposed scheme:



Adsorption of hydroxyl groups on the surface of zinc sulfide minerals in water takes place, followed by adsorption of neutral collector molecules, HEX, on hydroxylated zinc surface sites. The experimental results shown in Figures 11 and 12 conform to this mechanism. Flotation in the pH region from 3.5 to 5.5 appears to be due to physical adsorption of xanthate anions on the positively charged sphalerite surface (ZPC is pH 5.8). The flotation region from pH 7.0 to pH 8.5 may be due to adsorption

of neutral collector molecules (xanthic acid) on the hydroxylated zinc surface. Depression at pH 9.0 and above is probably due to further hydrolysis which leads to the formation of surface zinc hydroxide. At pH values lower than 3.0 the mineral is depressed because of decomposition of the collector.

The flotation response of sphalerite is changed appreciably when activating agents are added to the system. An addition of 1×10^{-5} mole per liter lead chloride is sufficient to obtain complete flotation of the mineral with a collector addition of 1×10^{-4} mole per liter KEX (Figure 13). Activation of sphalerite by lead ions take place with the formation of an insoluble coating of lead sulfide on its surface, according to the following reaction:



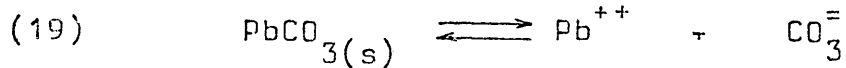
$$K = 1000$$

The occurrence of chemical adsorption of the collector on the new surface explains the complete flotation of lead-activated sphalerite in the pH range from 3.0 to 10.0. Depression below pH 3.0 is due to collector decomposition into carbon disulfide and ethyl alcohol; at pH values higher than 10.0 depression results from the formation of surface lead hydroxide.

As suggested by Fuerstenau⁽²⁾, activation of sphalerite by lead ions can be controlled by the addition of zinc salts because of the relatively small difference between the solubility of ZnS and PbS. The flotation behavior of lead-activated sphalerite in the presence of zinc sulfate showed a significant difference

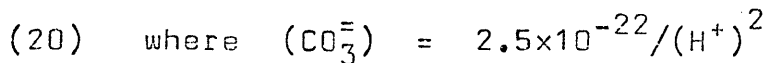
depending on the sequence of addition of mineral and reagents. Flotation recoveries were much lower when the mineral was added after the reagent solutions were conditioned than when the mineral was added at the beginning with the activating agent.

When the sphalerite was conditioned with 1×10^{-5} mole per liter lead chloride prior to the introduction of 1×10^{-4} mole per liter zinc sulfate, complete flotation was obtained from pH 3.0 to pH 6.5. Complete depression was noted to occur at pH 8.0 and above. These facts may be explained with the following equilibria:

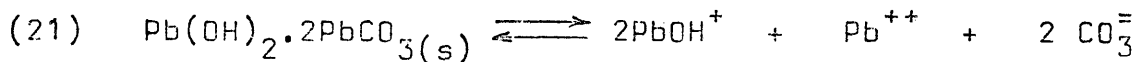


$$K = 1.5 \times 10^{-13}$$

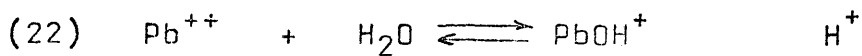
$$(\text{Pb}^{++}) = 1.5 \times 10^{-13} / (\text{CO}_3^{=})$$



Lead ion from basic lead carbonate as a function of pH:



$$K = 3.16 \times 10^{-32}$$

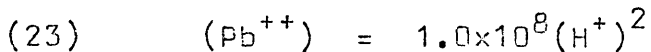


$$K = 6.67 \times 10^{-7}$$

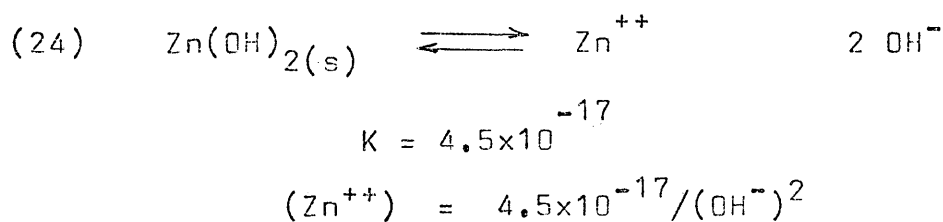
From Eq. (22):

$$(\text{PbOH}^+) = 6.67 \times 10^{-7} (\text{Pb}^{++}) / (\text{H}^+),$$

and from Eq. (21), making substitutions,



Zinc ion concentration as a function of pH can be obtained from the solubility product:

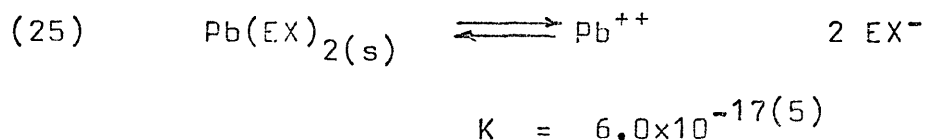


All of the thermodynamic data used for calculating these equilibrium expressions were taken from Latimer⁽¹⁸⁾.

With reference to Figure 14, an activity of 1.0×10^{-8} mole per liter Pb^{++} will be present in solution at pH 8.0 (determined by basic lead carbonate), while an activity of 4.5×10^{-5} mole per liter Zn^{++} will be present at the same pH (determined from zinc hydroxide). This is a ratio of $(\text{Zn}^{++})/(\text{Pb}^{++})$ of about 4500, and as a result activation cannot take place.

At pH 5.0, for example, the ratio of $(\text{Zn}^{++})/(\text{Pb}^{++})$ is 10; activation results and flotation is effected.

When all of the reagents are combined before the sphalerite is added to the flotation system, lead xanthate controls the Pb^{++} activity in solution:



With an addition of 1×10^{-4} mole per liter KEX, an activity of 6.0×10^{-9} mole per liter Pb^{++} will be present in solution, and again no activation will result.

As the additions of zinc sulfate were increased (Figures 15, 16, and 17), the regions of maximum flotation were decreased. This phenomenon may be due to the dissolution of the sphalerite

in acid media. That is, the additional zinc gained from the mineral plus that which was added may have been sufficient to prevent activation under these conditions.

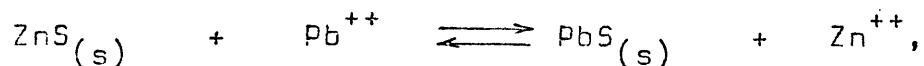
CONCLUSIONS

Several conclusions regarding the flotation behaviors of galena and lead-activated sphalerite in the presence of zinc sulfate were developed from this investigation, as follows:

1. Flotation of galena with potassium ethyl xanthate occurs through chemical adsorption of the collector on the mineral surface in the pH range from 2.5 to 10.5.
2. The zero-point-of-charge (ZPC) of galena is pH 6.7.
3. The zero-point-of-charge of zinc hydroxide colloids is pH 8.8.
4. Depression of galena at zinc sulfate additions higher than 3×10^{-3} mole per liter and a collector addition of 1×10^{-4} mole per liter KEX is practically nil. The zeta potential of the colloids becomes more negative under these conditions, which indicates that electrical phenomena are involved to a minor extent in the galena-xanthate-zinc sulfate system.
5. When the collector addition to the flotation system is relatively small compared to the zinc sulfate addition the electrical interaction between the phases present in the system

is more pronounced. Additional work will have to be conducted in order to explain the nature of the phenomena involved in this particular system.

6. The zero-point-of-charge of sphalerite is pH 5.9; the corresponding value for lead-activated sphalerite is pH 6.1.
7. Flotation of sphalerite with potassium ethyl xanthate in the pH range from 3.5 to 5.5 appears to occur through physical adsorption of xanthate anions on the positively charged mineral surface. The experimental results indicate that flotation of sphalerite in the pH region from 7.0 to 8.5 is effected by adsorption of neutral collector molecules, HEX, on the hydroxylated zinc surface.
8. Flotation of lead-activated sphalerite occurs through chemical adsorption of the collector on the lead sulfide coating covering the sphalerite surface.
9. Depression of lead-activated sphalerite by zinc sulfate is controlled by the extent of the reaction



and by the sequence of addition of mineral and reagent solutions.

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