5.2.0 RESULTS OF CYCLIC VOLTAMMETRY EXPERIMENTS.

5.2.1 CARROLLITE.

A literature survey on this mineral showed that little or no electrochemical and leaching studies have been done on carrollite ($CuCo_2S_4$). Ahmed[72] studied the electrochemical behaviour of linneaite (Co_3S_4) and Behret et al[68] studied the electrocatalytic oxygen reduction of thiospinels. The results of these studies showed that these minerals have similar behaviour. Carrollite would be expected to behave in a similar manner as that of linneaite as it is a derivative of this mineral due to the solid substitution of cobalt by copper from the main matrix. In fact it is a common feature to find carrollite occurring with linneaite and CuS in the matrix and it's behaviour will be influenced by the proportion of these two minerals.

Since this system was being studied for the first time with regards to its electrochemical characteristics, a series of qualitative experiments were done in order to have a feel of the system. A number of difficulties were anticipated in making reasonable interpretations of the voltammetric behaviour due to the non availability of thermodynamic data on the mineral with which to make comparisons of the observed electrodes and the potentials at which electrode reactions begun.

Voltammograms were recorded over a wide range of potential limits and scan rates before adopting the ranges used in the experiments. The main criteria used were to observe the appearance and disappearence of the peaks on the voltammograms as potential limits were either extended or reduced from the rest potential of the mineral at a particular solution pH. Particular attention was paid to any changes to the peak potentials and currents as a result of solution agitation. The solution was agitated by a stream of nitrogen bubbles.

Preliminary studies were also conducted to assess the solubility characteristics of the mineral in acidic and alkaline solutions at room temperature. In order to accelerate the dissolution processes, a few drops of $10^{-3}M$ hydrogen peroxide (H_2O_2) were used in each medium with 1.0 gram of +75 m mineral particles.

In a solution of pH 4.6, analysis for Fe^{2+}, Cu^{2+} and Co^{2+} by Atomic Absorption Spectroscopy (AAS) after six hours of dissolution showed only the presence of 5 parts per million (ppm) Cu^{2+}. However, after twenty – four hours, an analysis showed the presence of the three cations in solution as follows:

Cation	Concentration (ppm)
Fe^{2+}	10
Co^{2+}	247
Cu^{2+}	450

This showed that at any given time, more Cu ions passed into solution. The presence of Fe ions could be attributed to the leaching of the traces of chalcopyrite or pyrite in the mineral. Although this was a crude scientific method of assessing dissolution characteristics it atleast showed what kind of ions would be produced from a carrollite mineral immersed in an acidic medium. Hydrogen peroxide provided the oxidising atmosphere which was identical to the situation when the mineral surface is subjected to an anodic potential.

In alkaline media, there were no ions detected in solutions. This was expected as the stable species in alkaline solutions are oxides and hydroxides due to an increasing amounts of hydroxyl ions in solutions. However, a pinkish / blue precipitate was readily seen on the surface of the mineral particles. This was identified as cobalt (II) hydroxide ($Co(OH)_2$) due to its characteristic colour. Spots of a greyish precipitate was also observed but when compared to the pinkish precipitate, They were negligible. Those could have been oxides of copper or iron. With these preliminary observations, it was hoped that a correlation would be made with cyclic voltammetry in order to identify the processes which are responsible for causing a change in the mineral surface from a hydrophilic to a hydrophobic condition. All voltammograms in this report were recorded at a scan rate of 5 mVs^{-1} and the solutions were purged with " oxygen free" nitrogen (spot nitrogen), for which when the gas bubbler was above the experimental solution provided the quiescent conditions and when the gas bubbler was into the solution gave stirred conditions. The potential was stepped from the rest potential of the mineral in the solution of interest to the lower limit (more negative potentials) before a complete cycle was recorded.

Voltammograms for a freshly ground carrollite electrode surface in 'oxygen free' solutions at pH 4.6, 7.0, 9.2, 11.0 and 13.0 are shown in Figures 5.11, 5.12, 5.14, 5.15 and 5.16 respectively. Figure 5.13 shows the effect of changing the initial sweep direction to the upper limit (more positive potential) before a complete cycle is recorded at pH 7.0.

Figure 5.11 shows the voltammetric behaviour of a carrollite mineral electrode in an 'oxygen free' solution at pH 4.6. There is an anodic current rise at about 0.3 volts which tend to increase in magnitude with the potential. On the reverse scan, there is a cathodic peak at about 0.35 volts which could be assumed to be due to the reduction of the products of the initial anodic oxidation process. Extending the potential range to higher negative potentials introduced a cathodic rise in the current at about - 0.2 volts. This could be attributed to the reduction of water to give hydrogen or the reduction of excess sulphur which had not reacted during the reduction of the initial oxidation products to give hydrogen sulphide (H_2S). With an increase in the anodic potential, an additional anodic peak was introduced at about 0.8 volts. This peak was more pronounced at pH 7.0 in Figure 5.12. This peak is consistent with the expected potential
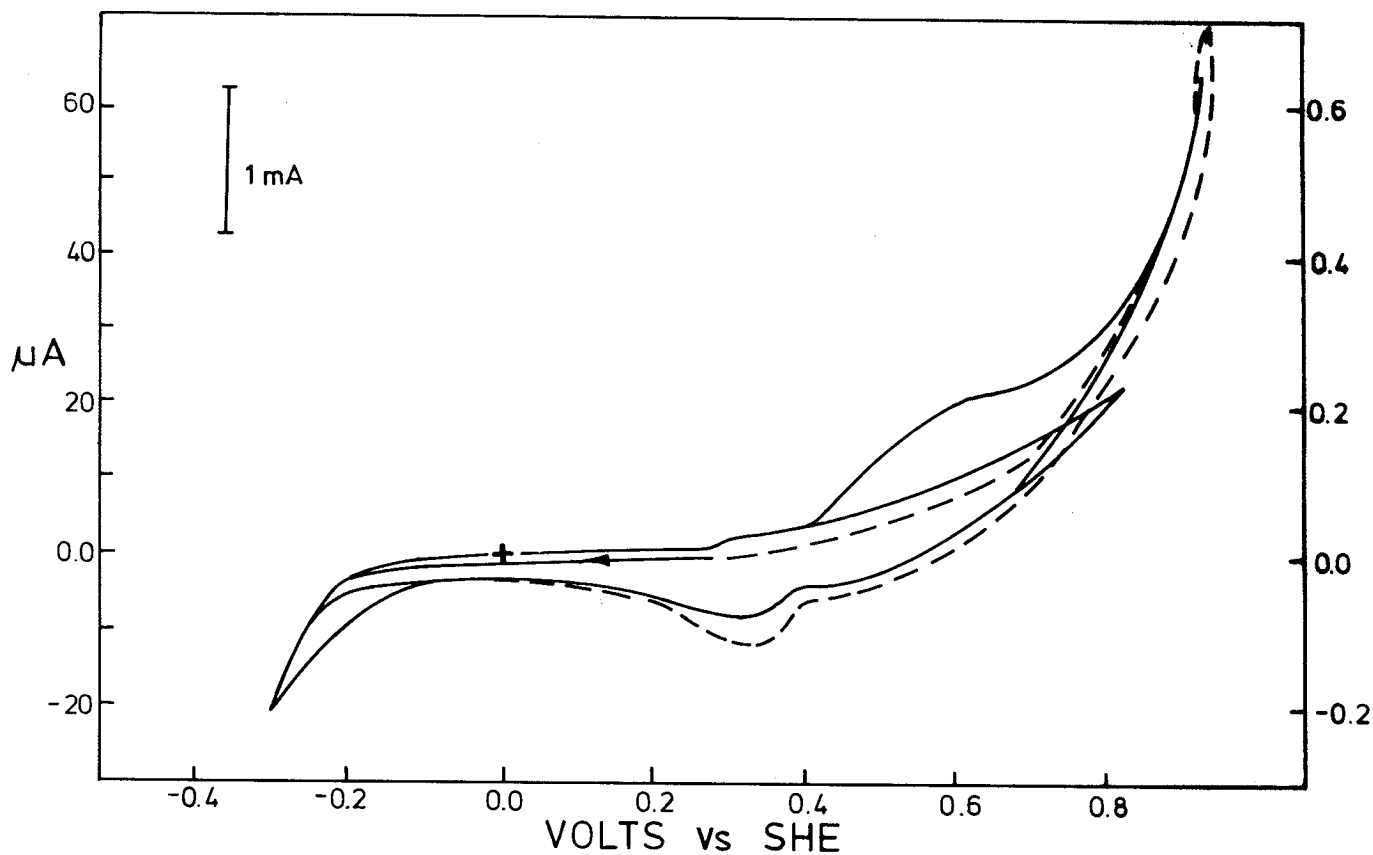
Figure 5.11: Cyclic voltammogram for carrollite in a buffer
solution of pH 4.6.

(_____) Quiesent Solution

(---------) Stirred Solution.
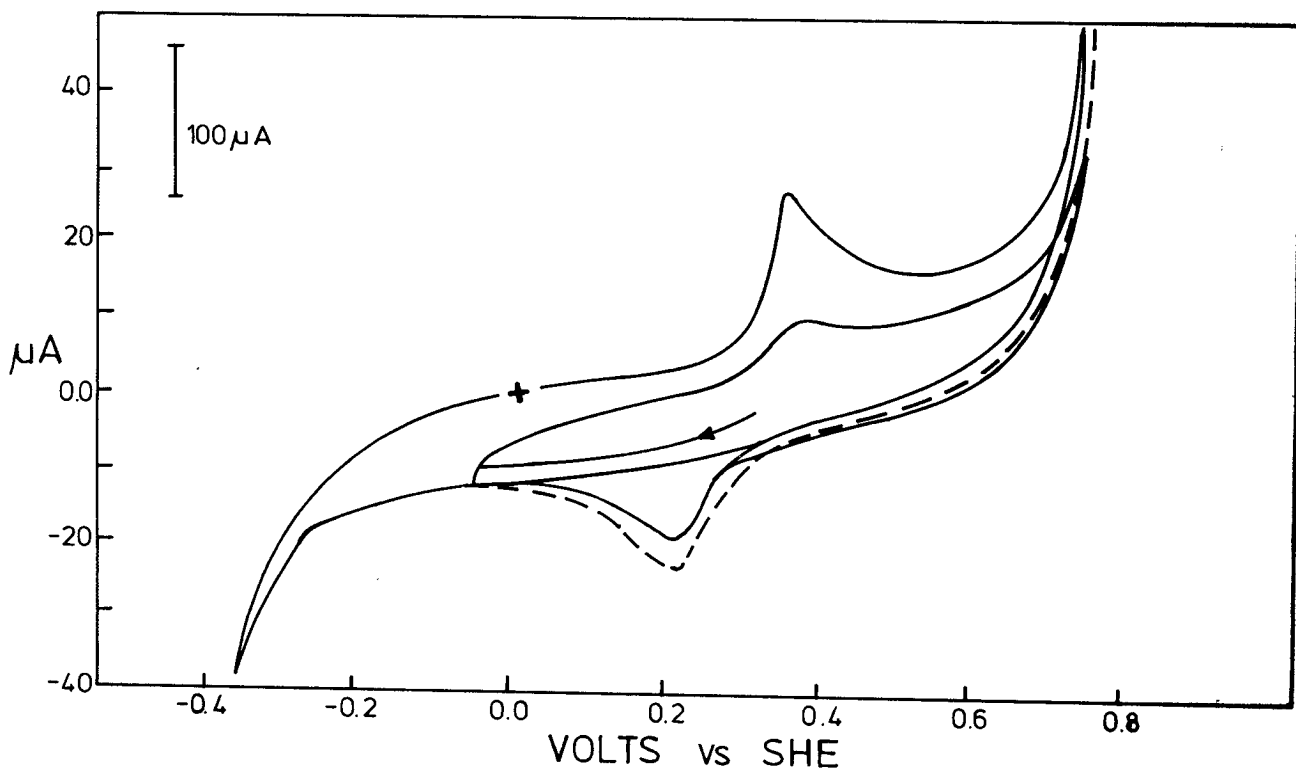

Figure 5.12: Cyclic voltammogram for Carrollite in a buffer solution
at ph 7.0.

for CoS_2 dissolution to give Co^{2+}. There was however, no corresponding reduction or cathodic peak. This probably implied that, if dissolution of CoS_2 occurred, it's products reduced at more or less the same potential as those of the initial products or that such a dissolution process produce species that may not undergo a reverse reaction.

The proposed mechanisms of the dissolution reactions for a carrollite mineral electrode in acidic solutions on the basis of the above results are:

Initially

$$CuCo_2 S_4 = 2 CoS_2 + Cu^{2+} + 2e^-$$

and then the following reaction occurs

$$2CoS_2 = CoS + Co^{2+} 3S 2e^- \qquad E^0 = 0.81 \text{ V}$$
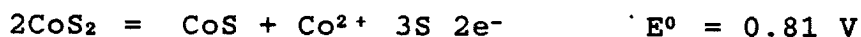
giving an overall anodic reaction of

$$CuCo_2 S_4 = CoS + Cu^{2+} + Co^{2+} + 3S + 4e^- \quad \dots\dots\dots\dots(5.7)$$

This equation suggests that stirring will result in the ionic species migrating into the bulb solution and will not be readily available for reduction when the potential is reversed. This does not appear to be the case at this pH (4.6) as stirring would be expected to reduce the anodic peak. This could only mean that in practice very little of the initial oxidation products were reduced to be available for re- oxidation on the positive scan. The reduction on the negative scan was a reverse of the reaction 5.7. Excess sulphur reacted as follows:

$$S + 2H^+ + 2e^- \rightleftharpoons H_2S \qquad E^0 = 0.14 \text{ V} \quad \ldots \ldots \ldots \ldots (5.8)$$
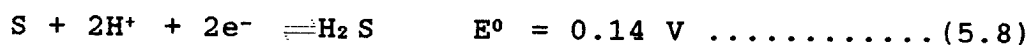
Thermodynamically, formation of an insoluble layer of sulphate rather than sulphur is a more favoured reaction. However, oxidation of sulphide minerals to sulphates generally exhibit a considerable degree of irreversibility.[32] Furthermore, sulphur can exist as a metastable phase. For these reasons, it was assumed that a sulphur phase rather than sulphate formed on the surface of the mineral.

Figure 5.12 shows the voltammetric behaviour of the carrollite mineral electrode in a solution saturated with nitrogen at pH 7.0. The electrode potential was swept from the rest potential to the lower limit before recording a complete cycle. If reaction 5.7 occurred reversibly and was independent of pH, the anodic wave would commence at the same or about the same potential as the reactions in acid media. In fact, the anodic currents that commenced at about 0.3 volts gave an anodic peak at about 0.4 volts. This anodic peak increased as the lower limit was extended as did the cathodic peak height, i.e it increased as the anodic peak increased. This observation appeared to justify the earlier suggestion that the initial oxidation of the mineral contributed to the anodic peak and that the resulting cathodic peak is due to the reduction of the oxidation products.

Figure 5.13 shows the behaviour of the carrollite mineral electrode in the same solution of pH 7.0 but the initial scan was taken to more positive potentials before reversing at different values of lower limits. There was anodic current flow almost instantaneously at potentials greater than 0.3 volts which gave a corresponding cathodic peak at 0.2 volts on the reverse scan. As the lower limit was increased to more cathodic potentials, the anodic peak increased too. The increase in the anodic currents at about 0.6 volts could be due to further oxidation of the mineral or the evolution of molecular oxygen.

One important conclusion which can be drawn from Figure 5.12 and 5.13 is that the carrollite mineral surface is reasonably stable in air. This is because there was no initial reduction peak observed at the start of the cathodic sweep from the rest potential. One would have expected that the mineral would undergo oxidation during grinding of the electrode and transfer to the electrochemical cell.

Figure 5.14 and 5.15 show the voltammetric behaviour of a carrollite mineral electrode in solutions saturated with spot nitrogen at pH 9.2 and 11.0 respectively. An anodic current commences at potentials greater than 0.3 volts. Above this potential, the current remained constant probably due to the 'passive' oxide layer produced. However, at sufficiently high overpotentials, a second oxidation process was observed. This could be assumed to be due to the further oxidation of the initial oxidation products. The most likely oxidation products at pH 9.2 are $Co(OH)_2$ or Cu_2O / $Cu(OH)_2$. However, at pH values well above 7.0, the most stable phase is $Co(OH)_2$.[88] Initial leaching experiments had revealed no presence of copper oxides / hydroxides in appreciable amounts. Hence in proposing a chemical equation for the reaction of carrollite in alkaline solutions, it is prudent to assume that the major copper species remain as CuS.
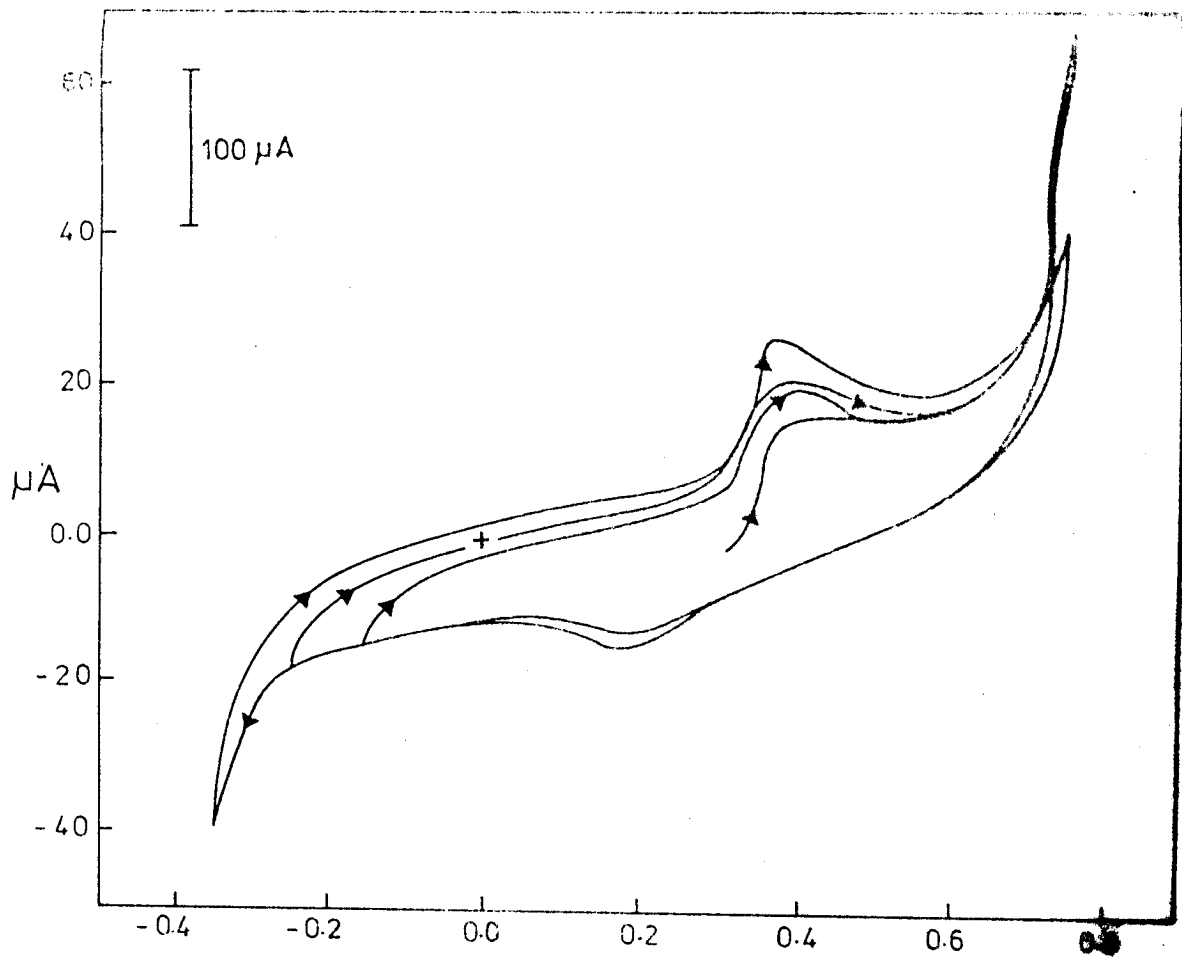
Figure 5.13: Cyclic Voltammogram of Carrollite in a buffer solution at pH 7.0 Effect of going to upper limit and reversing to different lower limits.
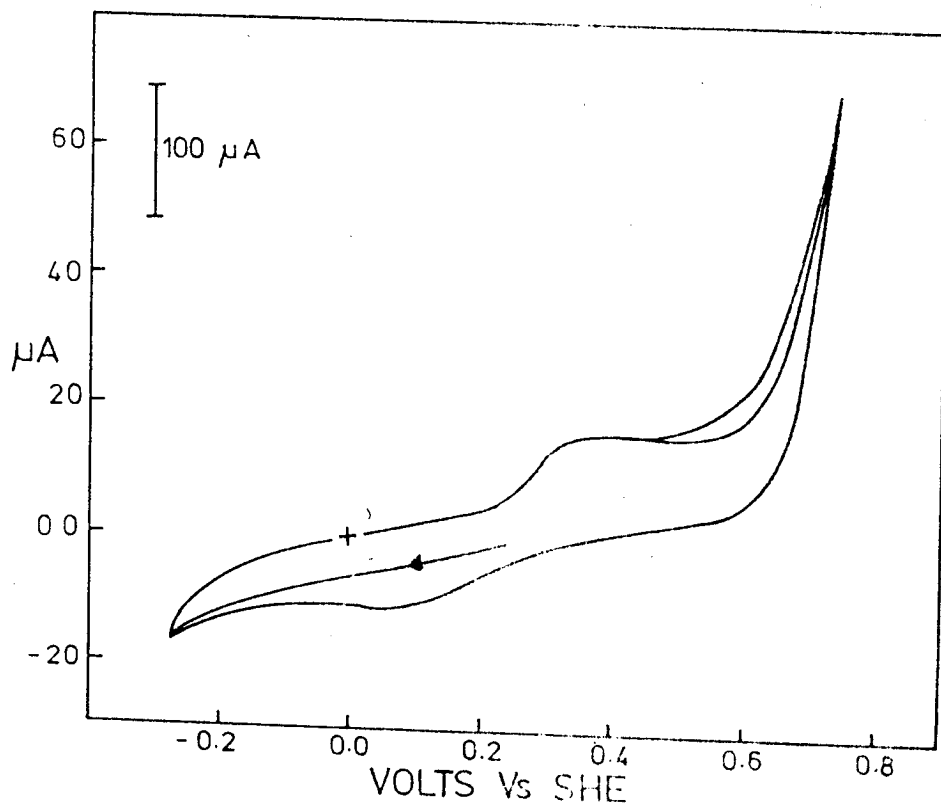

Figure 5.14. Cyclic Voltammogram for carrollite in a buffer solution at pH 9.2.

At above pH 10.5, $HCoO_2^-$ is the major stable cobalt species while $HCuO_2^-$ is the stable species for copper. But again whether these are formed in appreciable amounts could not be verified. What was certainly observed on the mineral surface was a pinkish precipitate of $Co(OH)_2$ and in the voltammetric behaviour it was therefore assumed that this was the major oxidation product.

Both the anodic and cathodic peaks at both pH values did not appear to affected by stirring the solution. This suggested that oxidation proceeded by reactions which produced insoluble products which remained on the surface of the mineral As the thickness of the insoluble layer increased the mineral would be expected to be less conducting. However, the time lapse of the experiment did not permit this to happen. On the basis of these observations, the proposed reaction equation in alkaline solutions was the following :

$$CuCo_2S_4 + 4H_2O \rightleftharpoons CuS + 2Co(OH)_2 + 3S + 4H^+ + 4e^- \quad ...(5.9)$$

In proposing the anodic oxidation mechanism to be that represented by equation 5.9, it has to be assumed that the cobalt in the surface zone was completely oxidised before any copper –

oxygen species were formed. i.e the initial oxidation product in alkaline media was represented by CuS rather than a cobalt - copper sulphide.

As the pH was increased from 7.0 to 11.0, both anodic and cathodic peaks shifted to more cathodic potentials by about 60 mV/pH unit.

At pH 13.0, there was an additional cathodic peak which was presumed to be as a result of either the reduction of $HCoO_2^-$ or $HCuO_2^-$ or other higher oxidation products. At very high oxidation potentials, $Co(OH)_3$ would form but because of it's instability it would readily decompose to $Co(OH)_2$ by the following reaction:

$$Co(OH)_3 + H^+ + e^- \rightleftharpoons Co(OH)_2 + H_2O \dots\dots\dots\dots (5.10)$$
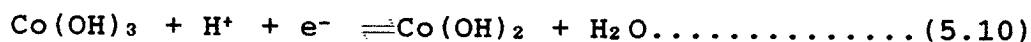
The other reaction which might have occurred was the possible reduction of excess sulphur to HS^- in the following reaction:

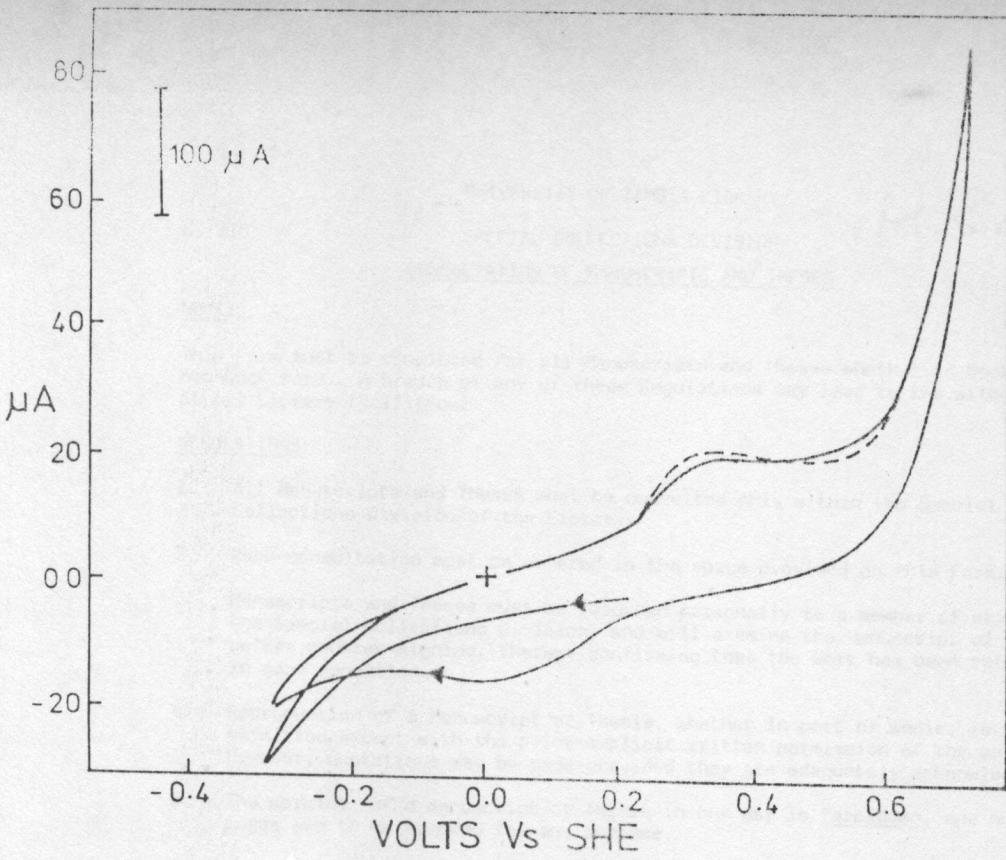$$S + H^+ + 2e^- \rightleftharpoons HS^- \dots\dots\dots\dots\dots\dots (5.11)$$

Figure 5.15 Cyclic Voltammogram for carrollite in a buffer
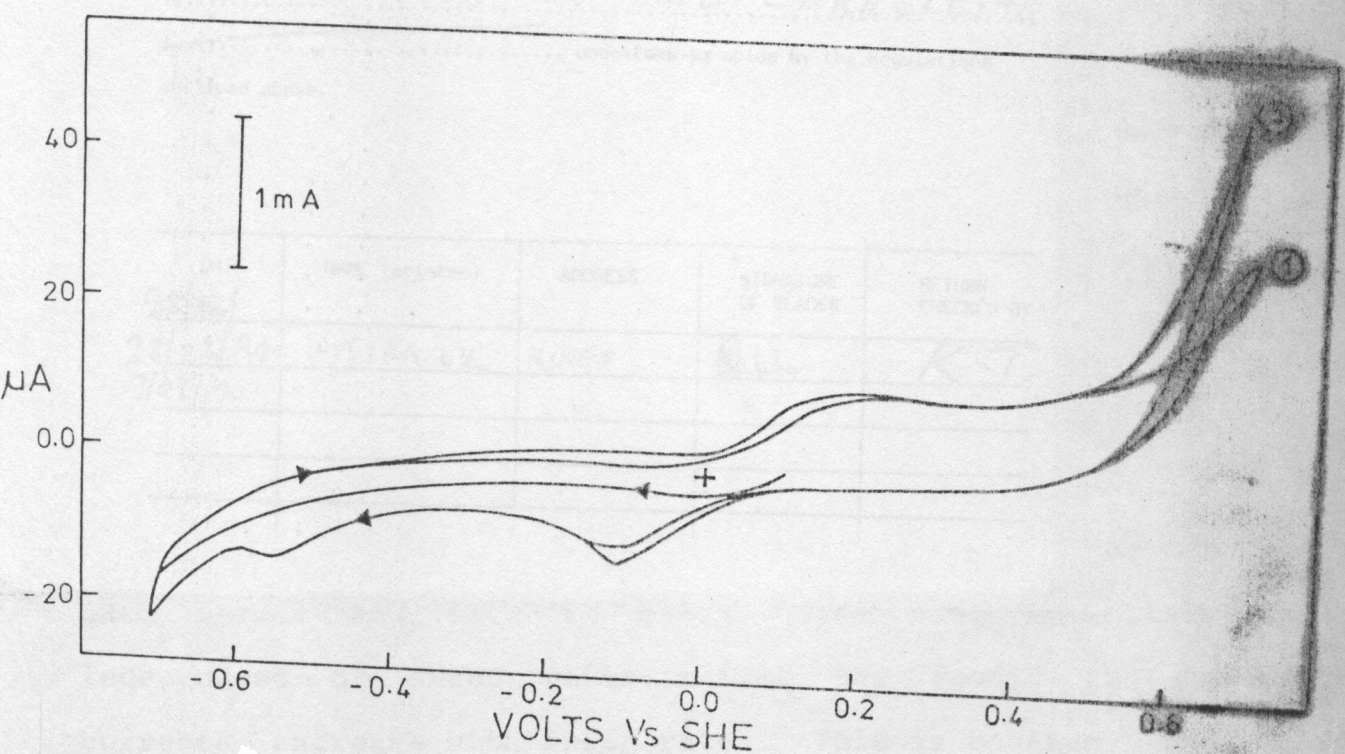solution at pH 11.0.

Figure 5.16 Cyclic Voltammogram of Carrollite in a buffer solution
at pH 13.0.

The reactions occurring on the carrollite mineral electrode in the solutions studied more especially in alkaline solutions show a great deal of reversibility. This shows that only surface species are formed under these conditions.

Sulphur was seen as one of the major oxidation products. No attempt was made to either quantify or identify the kind of sulphur species that was presumed to have formed on the surface of the mineral. This was due to the anticipated difficulties such as those reported by Luttrel et al[89]. However, it would be expected that the flotation of carrollite mineral without a collector might coincide with the potential at which the reaction generates sulphur, resulting in a hydrophobic surface. What is not clear is whether this sulphur is formed on the mineral surface or not and in what form it exists. It is important to recognise that the presence of sulphur species in whatever form is a critical factor in rendering any mineral naturally floatable.

Figure 5.17 (a) shows the effect of sweep rate on the nature of the anodic and cathodic peaks. The peak potentials are independent of sweep rates whilst the anodic and cathodic currents increase with sweep rates. This is because, the same reaction is proceeding for which the potential is a constant but,

however, the rate of application of the potential results in different magnitudes of current response. Figure 5.17 (b) shows a plot of anodic peak currents against the square roots of scan rates. A straight line relationship passing through zero or the origin was established. At higher sweep rates this linear relationship was no longer obeyed. In general, the anodic and cathodic processes at solutions of pH 7.0 to 13.0 are nearly equal. Hence the ratio I_A / I_C ~ 1.0. This observation further support the earlier suggestion that the system was fairly reversible.

The values of I_A and I_C can either be measured from the voltammograms or may be determined from the **Randles - Sevcik** equation which at 25^0C is of the form

$$I_P = - (2.69x10^5) n^{3/2} C_0 D^{1/2} v^{1/2} \quad \ldots\ldots\ldots\ldots(5.12)$$

where

I_P = the peak current density (Acm^{-2})

D   = the diffusion coefficient ($cm^2 s^{-1}$)

v   = scan (sweep) rate   (mVs^{-1})

C_0 = concentration of species i in the solution (mole. dm^{-3})
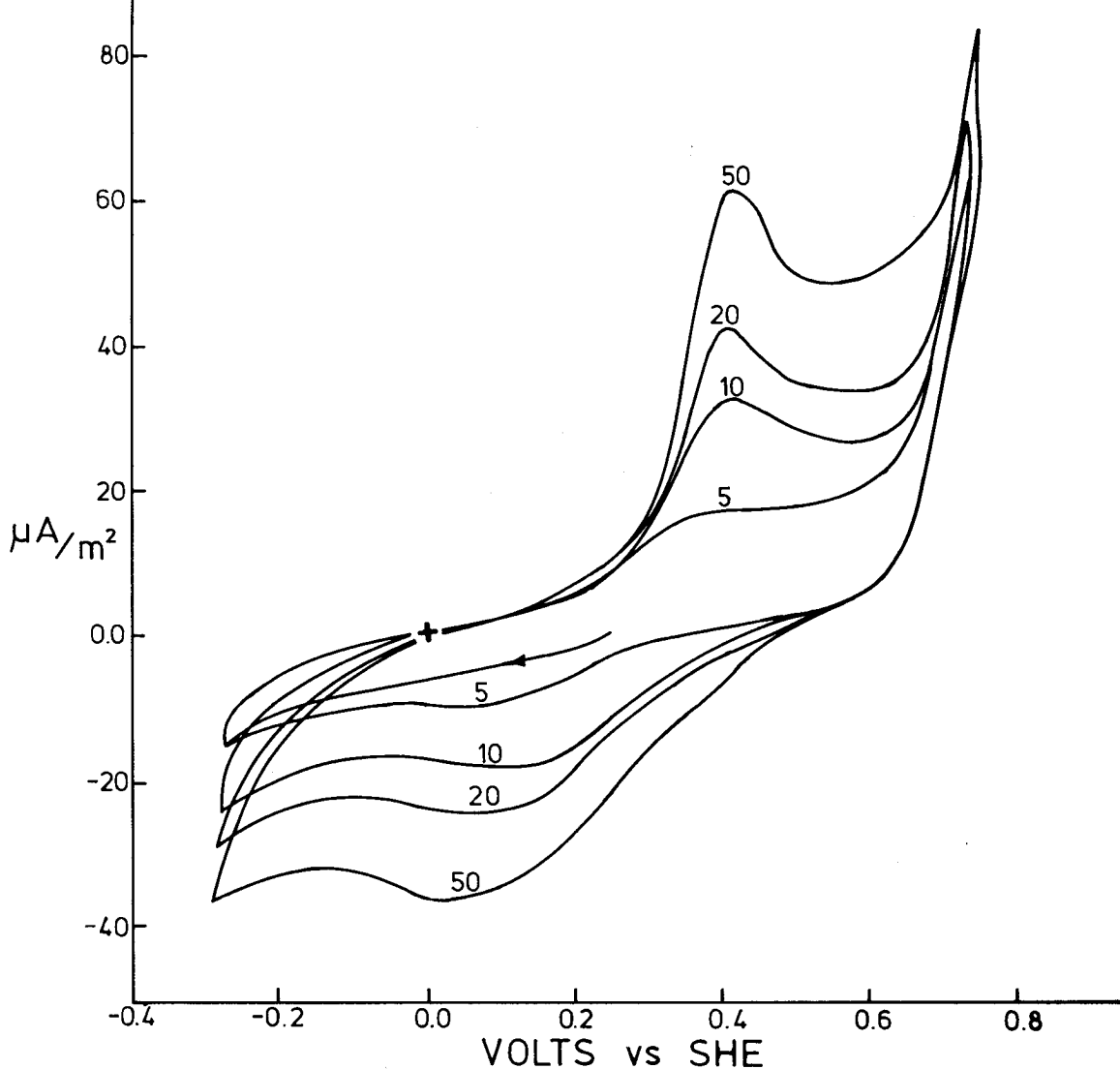
Figure 5.17(a) Cyclic voltammograms of carrollite in a buffer solution at pH 9.2. Effect of variation of scan rates
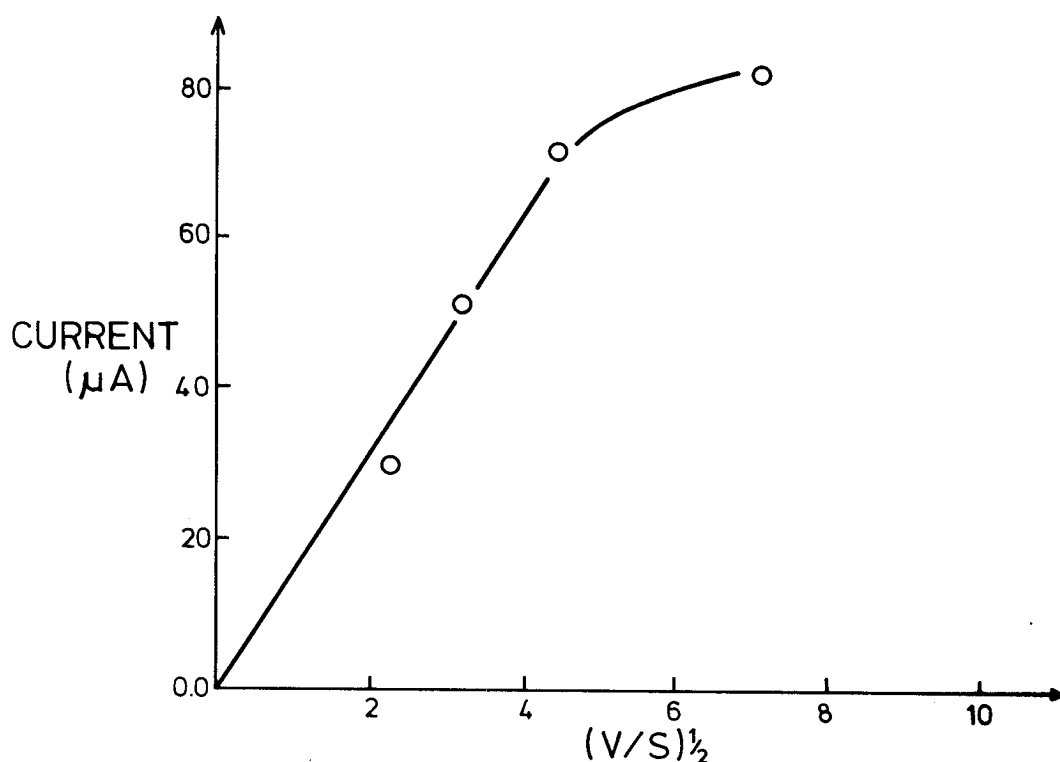

Figure 5.17(b) Plot of anodic peak current against square roots of scan rates,

5.2.1.1 THE INTERACTION OF CARROLLITE WITH XANTHATE.

The voltammetric behaviour of carrollite mineral electrode in solutions containing potassium ethyl xanthate is shown in Figure 5.18, 5.19, and 5.20 for solutions at pH 7.0, 9.2 and 11.0 respectively. The concentration of ethyl xanthate was varied from 5.5×10^{-5} to 2.75×10^{-3} M.

The main feature resulting from the presence of ethyl xanthate was the drastic reduction in the background currents as can be seen in Figure 5.18 for solutions at pH 7.0. The rise in currents due to the initial oxidation of the mineral was suppressed as was the cathodic peak of the reduction of the oxidation products. As the amount of ethyl xanthate increased, the rise in anodic peak was clearly observed at a potential of about 0.3 volts which gave rise to a peak at about 0.5 volts. The limiting anodic currents were mass transport controlled as depicted by their dependence on stirring. In the potential range covered, no significant cathodic peak was observed which could be associated with the reduction of the ethyl xanthate oxidation products. At higher ethyl xanthate concentrations, a cathodic peak was observed which could be assigned to the reduction of the ethyl xanthate oxidation product, di- ethyl dixanthogen. The reduction process was not
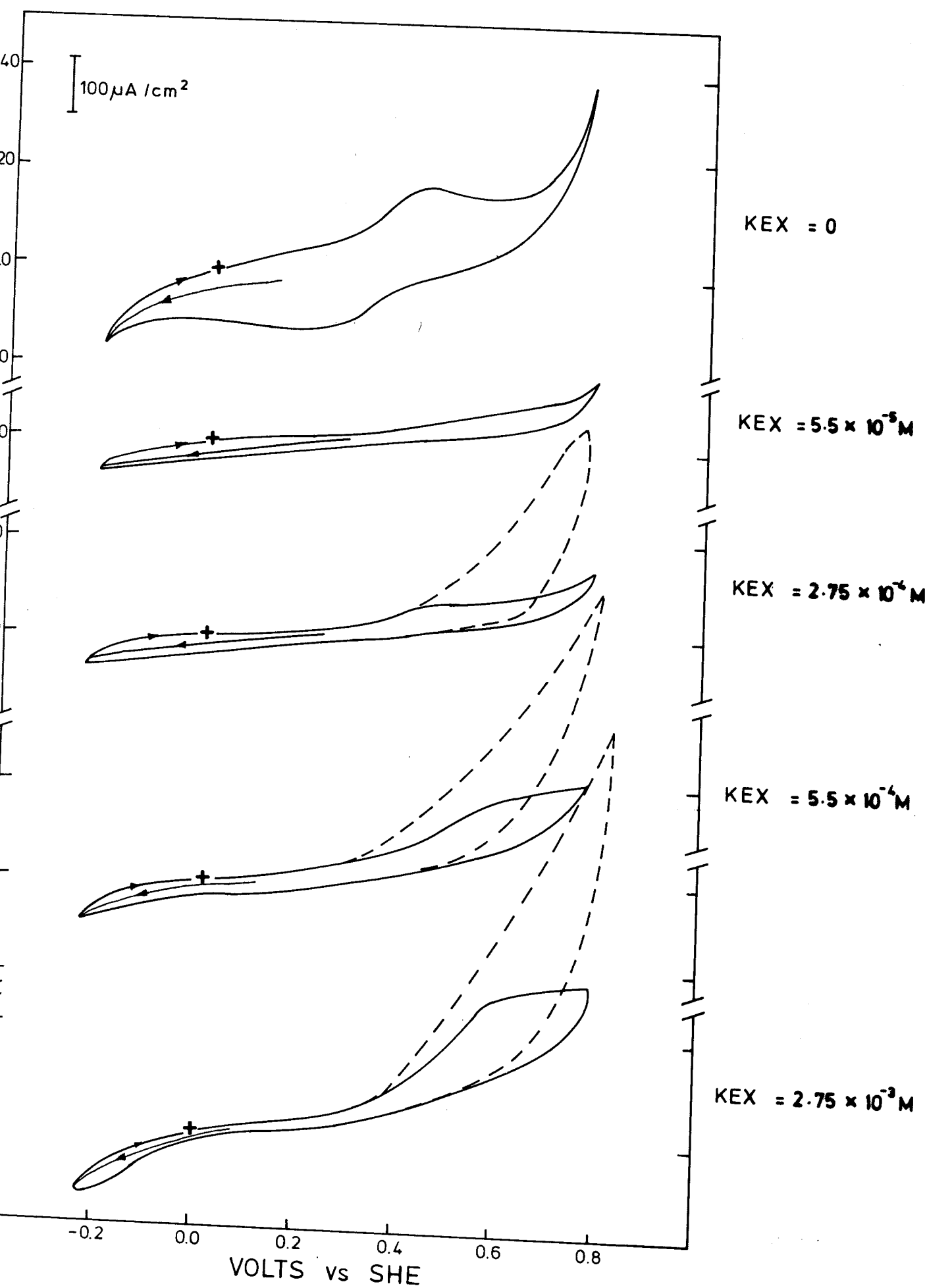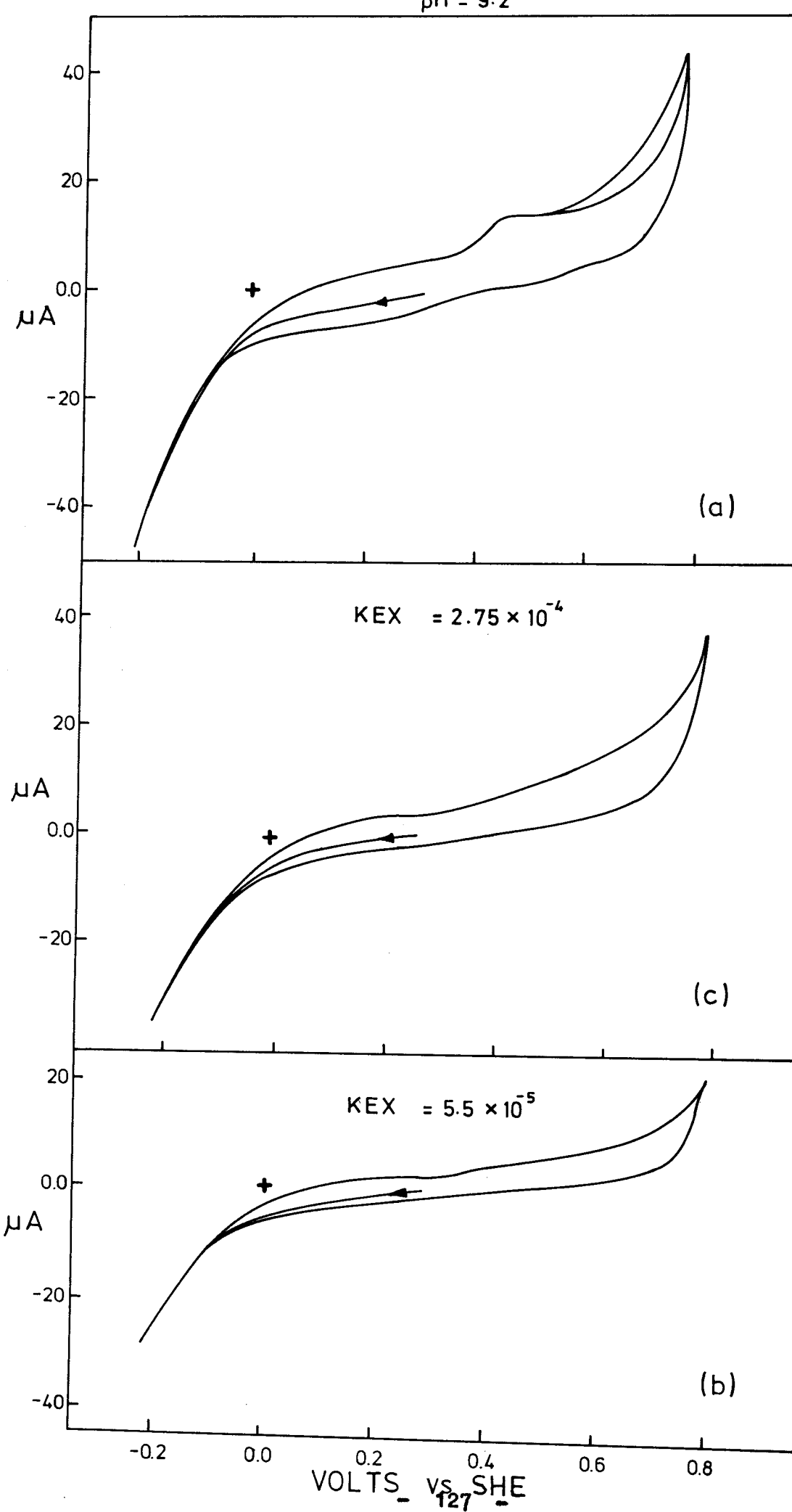
Figure 5.18: Cyclic voltammograms for carrollite in buffer solutions at pH·7.0, containing varying concentrations of Potassium ethyl Xanthate.

dependent on stirring, which lead to the suggestion that the ethyl xanthate oxidation to di- ethyl dixanthogen occurred at the carrollite mineral surface and remained on the mineral electrode surface and this would render the carrollite mineral surface hydrophobic. However, the product of ethyl xanthate oxidation at this solution pH did not render the carrollite mineral surface sufficiently hydrophobic as gas bubbles only weakly adhered to the mineral electrode surface.

The anodic currents shifted by about 60 mV when the ethyl xanthate concentration was increased by an order of magnitude.i.e 2.75×10^{-4} to 2.75×10^{-3} M. This is expected of a reaction involving one electron transfer.[107]

Figure 5.19, shows the oxidation currents arising from ethyl xanthate on the carrollite mineral electrode at pH 9.2. It is clear from the voltammograms that at any given ethyl xanthate concentration, the amount of the oxidation products, di-ethyl dixanthogen is higher than that obtained at the previous solution pH. In fact, the mineral surface was rendered sufficiently hydrophobic so that nitrogen bubbles readily adhered to the carrollite mineral electrode. Bubble attachment to the mineral was observed at potentials well above 0.3 volts. This would be

Figure 5.19

- 127 -

pH = 9.2

KEX = 5.5×10^{-4}

(graph d, μA vs volts)

(d)

KEX = 2.75×10^{-3}

(graph e, μA vs volts)

(e)

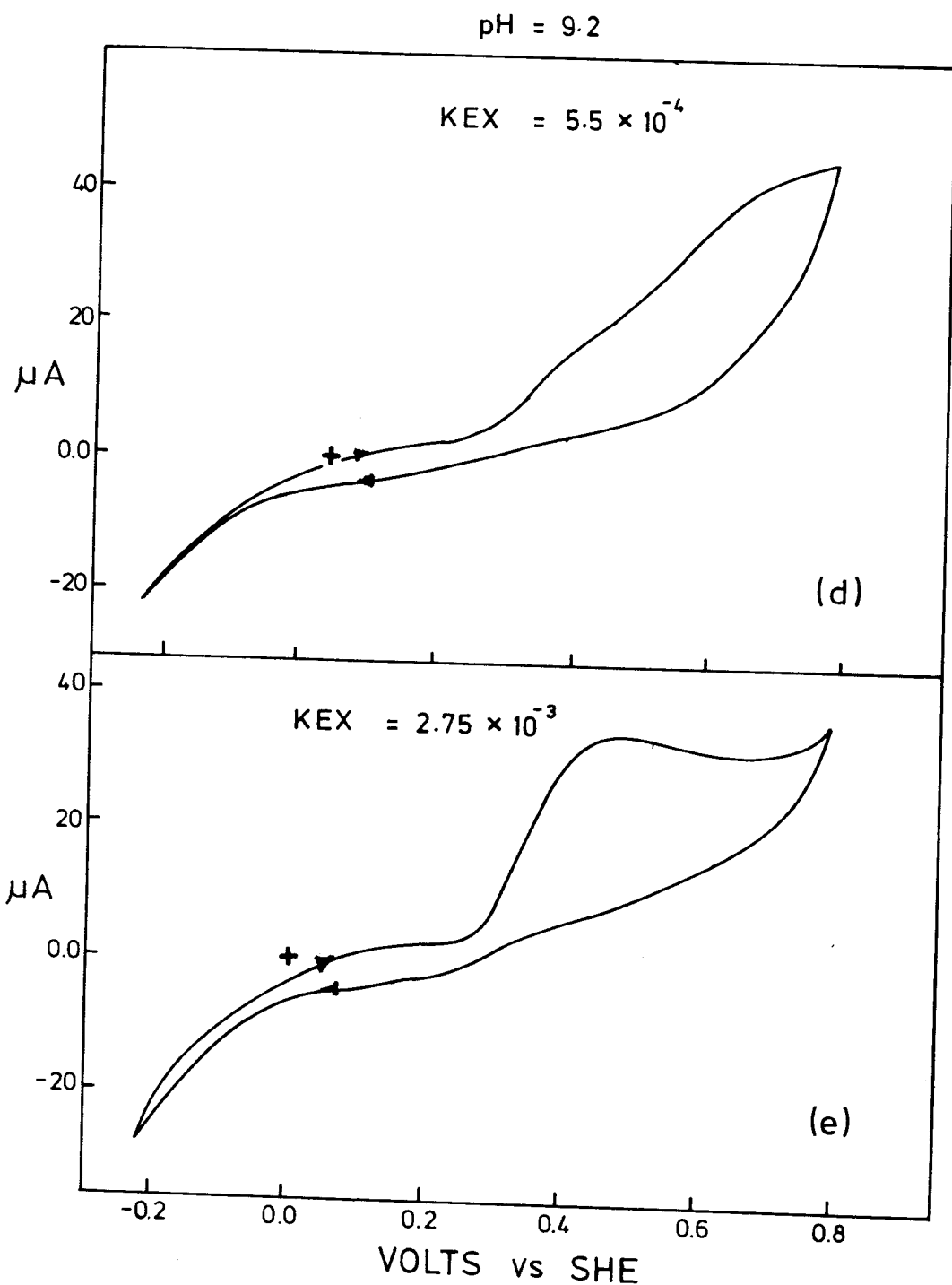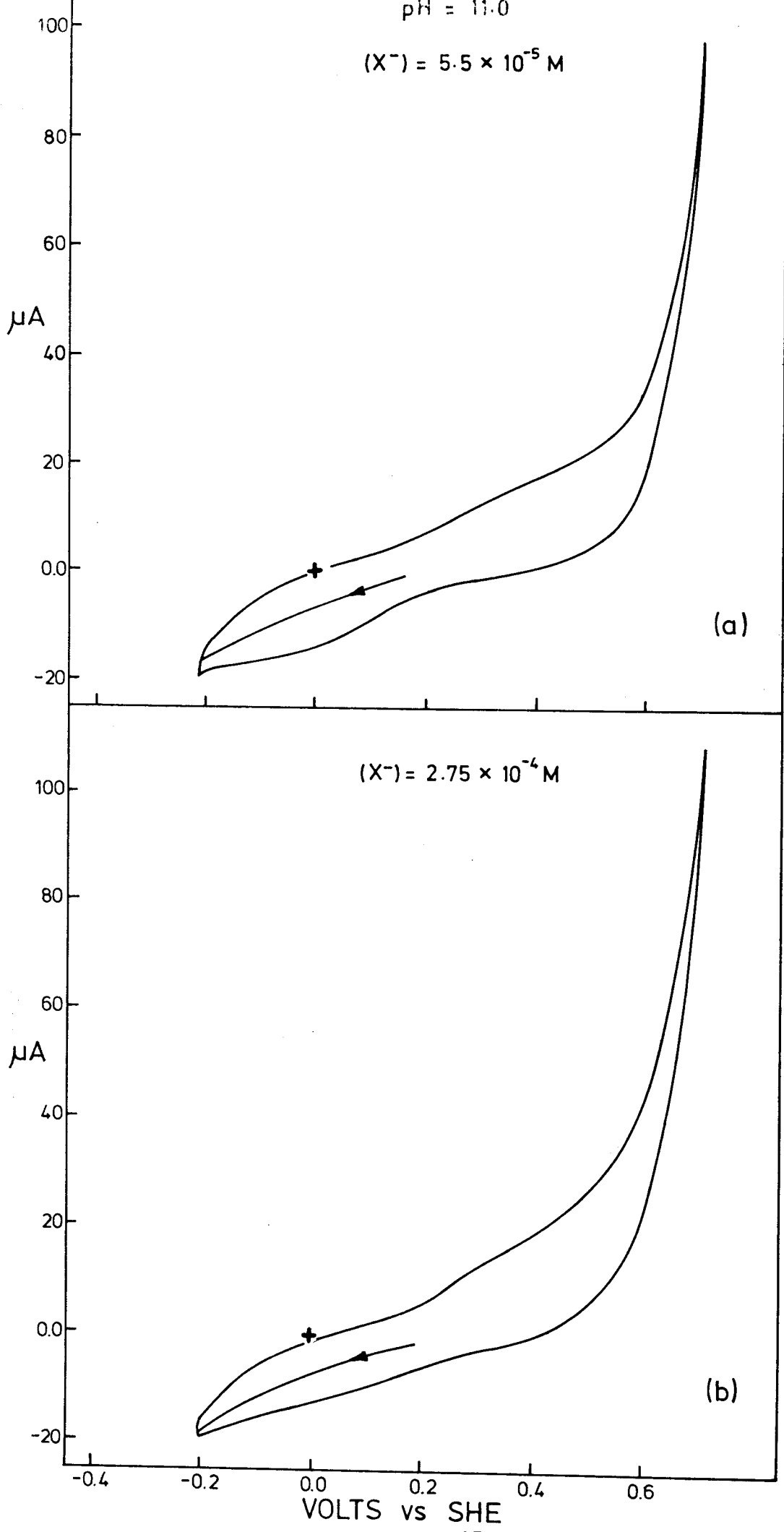-0.2   0.0   0.2   0.4   0.6   0.8

VOLTS vs SHE

FIGURE 5.13 : Cyclic voltammograms for carrollite in buffer solutions
at pH 9.2 containing varying concentrations of Potassium
ethyl xanthate.

the expected condition for flotation to take place. The most interesting feature was that the anodic currents were observed to begin at almost the same potentials as those obtained during rest potential measurements.

In Figure 5.20, the oxidation of ethyl xanthate on the carrollite mineral electrode at pH 11.0 is only slight so that the di-ethyl dixanthogen produced does not lead to surface of the mineral being sufficiently hydrophobic. This was supported by weak adherence of bubbles on the carrollite mineral surface even when the mineral electrode was held at a potential well above 0.4 volts for a long time. At this overpotential the oxidation of ethyl xanthate is expected to proceed very rapidly.

The anodic oxidation currents due to ethyl xanthate oxidation appeared not to dependent on the concentration of ethyl xanthate. This in principle, means that at pH 11.0, the oxidation of ethyl xanthate was so slow that it does not form a sufficient layer of di- ethyl dixanthogen on the carrollite mineral surface to render it hydrophobic. The potentials at which the anodic currents begun to flow at pH values 7.0, 9.2 and 11.0 were almost the same for any given ethyl xanthate concentration. This is expected of the ethyl xanthate / di- ethyl dixanthogen redox couple which is independent of solution pH. However, as could be seen from the limiting anodic currents, the oxidation rates may be dependent on the solution pH.

Figure 5.20
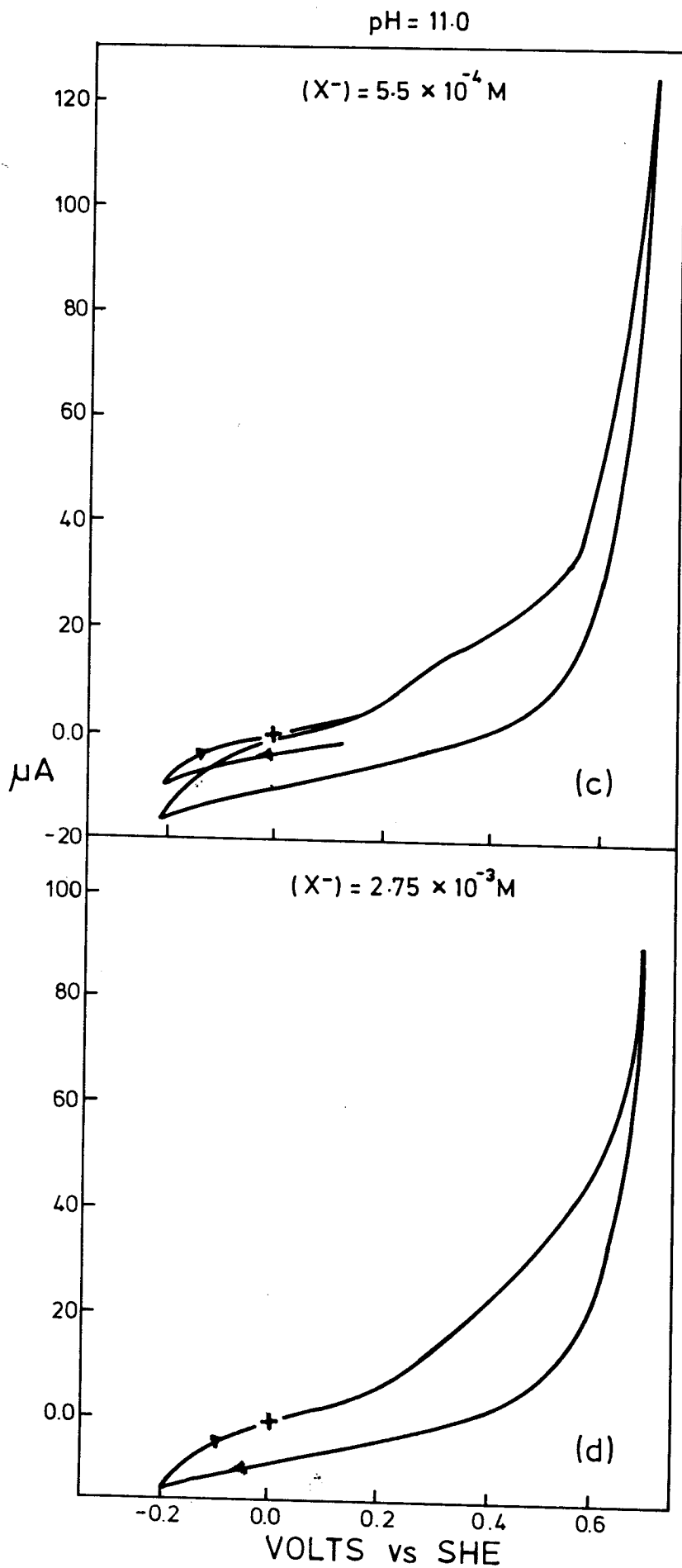
pH = 11.0

$(X^-) = 5.5 \times 10^{-5}$ M

(a)

$(X^-) = 2.75 \times 10^{-4}$ M

(b)

VOLTS vs SHE

Figure 5.20: Cyclic Voltammograms for Carrollite in buffer solutions at pH 11.0, containing varying concentrations of Potassium ethyl xanthate.

The control of the solution pH is one of the most widely applied method for the modulation of mineral flotation. The electrochemical evidence from the voltammograms reveals that an isolated carrollite particle in solution containing both ethyl xanthate and oxygen will exhibit a mixed potential at which oxygen is reduced and ethyl xanthate oxidised. This process results in a hydrophobic layer of di-ethyl dixanthogen being formed on the carrollite surface and renders the mineral floatable. This process is only significant in solutions at pH 9.2.

Figures 5.21 (a), 5.21 (b) and 5.21 (c) show current-time curves foe the carrollite mineral electrode when the potential is stepped from the rest potential to anodic potentials of 0.3 and 0.4 volts. The Figures show typical current-time curves depicting processes involving adsorption of an electroactive species from the solution on to a mineral electrode. This adsorption involves the chemical bonding of ethyl xanthate with the mineral surface and is generally called chemisorption. This chemisorption occur

more or less in the first two or so minutes after which it is strongly suppressed. This is typical of chemisorption processes as there is a reduction of active electrode area for electron transfer to occur. Furthermore, if electron transfer has to occur then it will have to occur over a greater distance.
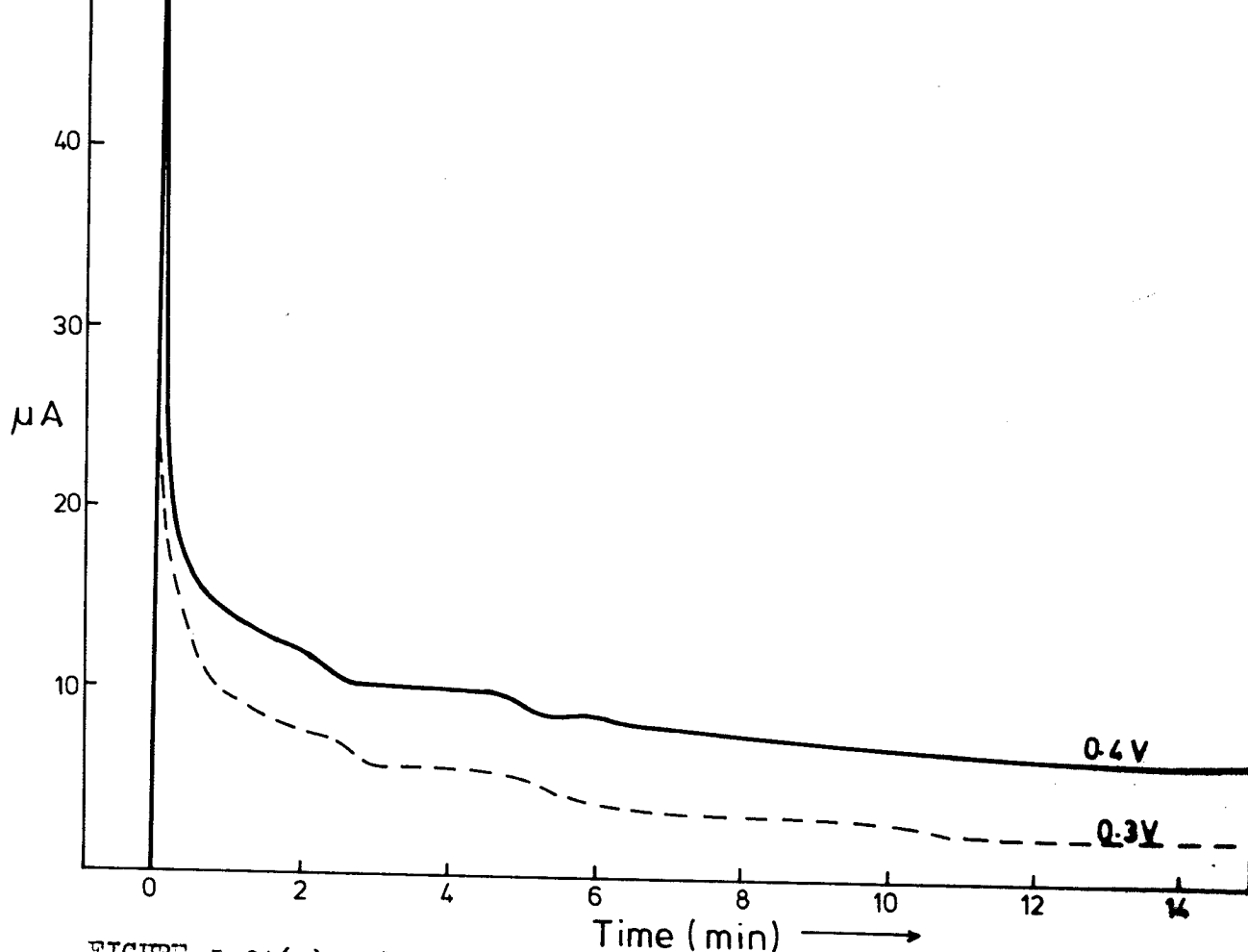
FIGURE 5.21(a) Current-time curves for a carrollite electrode in a
buffer solution at pH 7.0 containing 5.5 x 10⁻⁴M
ethyl xanthate with the electrode held at constant
potential of 0.3V and 0.4V Vs SHE.

FIGURE 5.21(b): Current-time curve for a carrollite electrode in a
buffer solution at pH 9.2 containing 5.5 x 10⁻⁴M ethyl
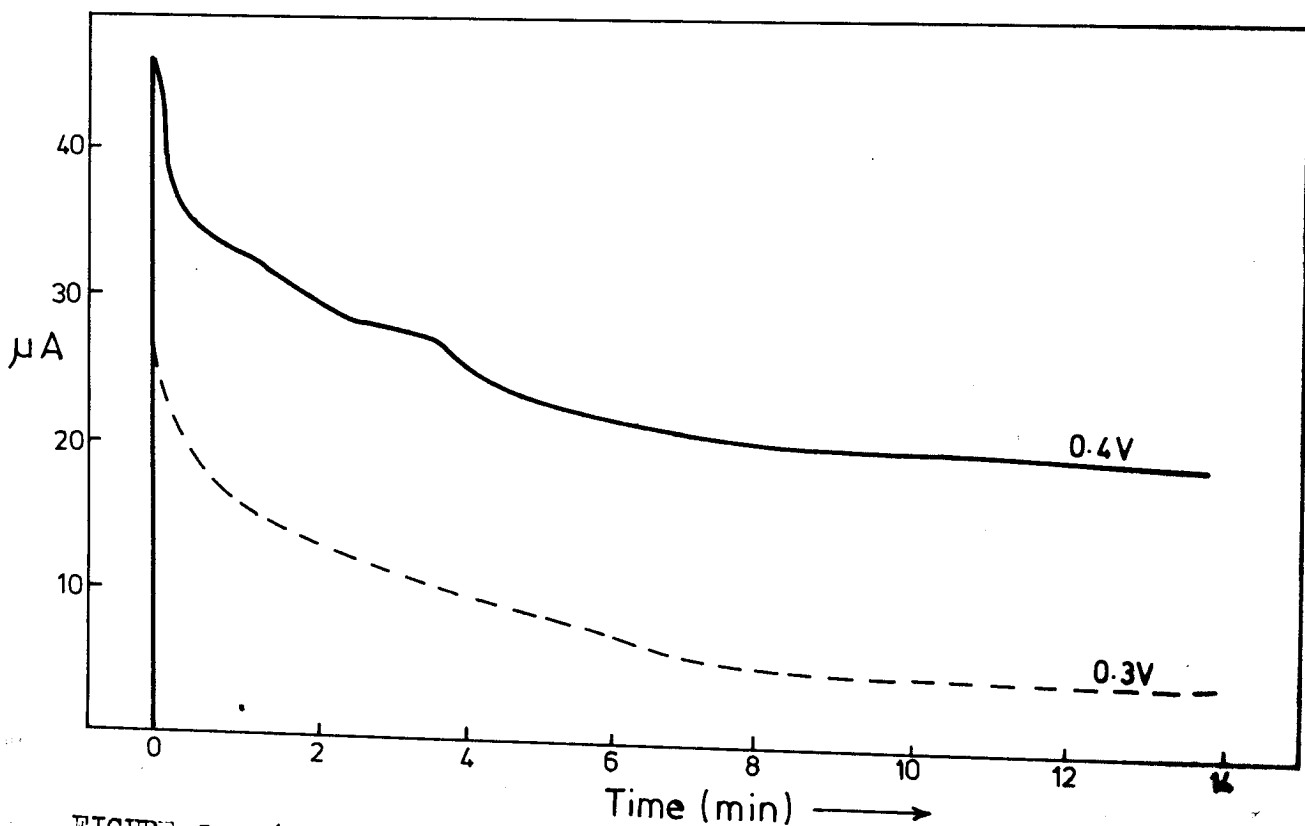xanthate with the electrode held at constant potential.
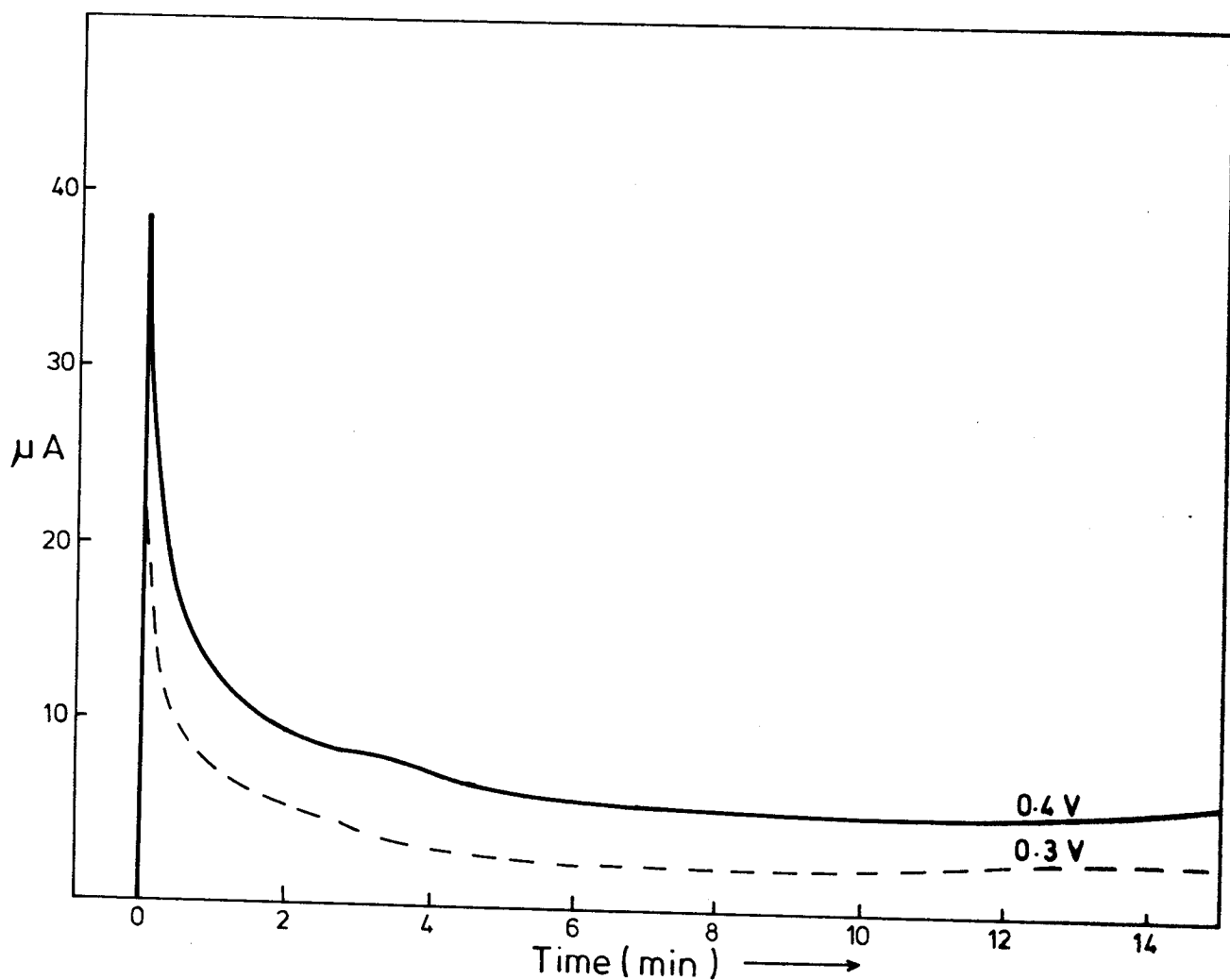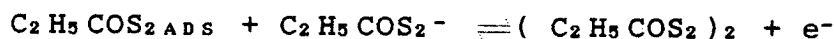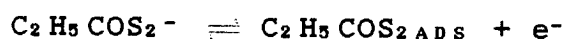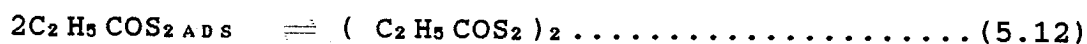
- 133 -

FIGURE 5.21(c): Current-time curve for a carrollite electrode
in a buffer solution at pH 11 containing 5.5×10^{-4}M
ethyl xanthate with the electrode held at constant
potential of 0.4V and 0.3V vs SHE.

From the foregoing discussion, it is apparent that the characteristics of the anodic oxidation of potassium ethyl xanthate and the cathodic reduction of it's oxidation product di-ethyl dixanthogen, can be explained by a two step mechanism for a carrollite mineral electrode as follows:

$$C_2H_5COS_2^- \rightleftharpoons C_2H_5COS_{2\,ADS} + e^-$$

$$C_2H_5COS_{2\,ADS} + C_2H_5COS_2^- \rightleftharpoons (C_2H_5COS_2)_2 + e^-$$

with the overall reaction:

$$2C_2H_5COS_{2\,ADS} \rightleftharpoons (C_2H_5COS_2)_2 \dots\dots\dots\dots\dots\dots(5.12)$$

This mechanism is analogous to that which has been proposed for Halide-Halogen systems.[90] The rate determining reaction is the slowest reaction of the above suggested equations.

The ethyl dixanthogen is formed on the surface of the mineral and only when its coverage is sufficiently high, does it render the mineral surface hydrophobic and hence floatable.

However, it should be pointed out that the interaction of ethyl xanthate with oxygen in the solution can be catalysed by the mineral surface. The catalysis will take place by a mixed potential mechanism involving the anodic oxidation of ethyl xanthate and cathodic reduction of oxygen as follows:

$$2ROCS_2^- \rightleftharpoons (ROCS_2)_2 \dots\dots\dots\dots\dots\dots\dots\dots(5.13)$$

where $R = C_2H_5$

$$1/2O_2 + H_2O + 2e^- \rightleftharpoons 2OH^- \dots\dots\dots\dots\dots\dots\dots(5.14)$$

5.2.1.2 THE INTERACTION BETWEEN CARROLLITE, POTASSIUM ETHYL XANTHATE AND SODIUM CYANIDE.

Investigation were also carried out to determine the influence of sodium cyanide on the electrochemical reactions occurring on the carrollite mineral electrode in the absence and presence of potassium ethyl xanthate.

Figure 5.22, 5.23 and 5.24 show the voltammetric behaviour of carrollite electrode in solutions containing different concentrations of sodium cyanide at pH 7.0, 9.2 and 11.0 respectively.

In Figure 5.22, a noticeable effect on the voltammograms is the shift in the anodic wave to more anodic potentials. This in principle, means that the mineral was partially rendered 'inactive' to take part in any electrochemical reactions. It appears that the peak which was initially assigned to the oxidation of the mineral was progressively diminished as the cyanide concentration increased. The peak was eliminated completely at a cyanide concentration of 2.5×10^{-4}M. At

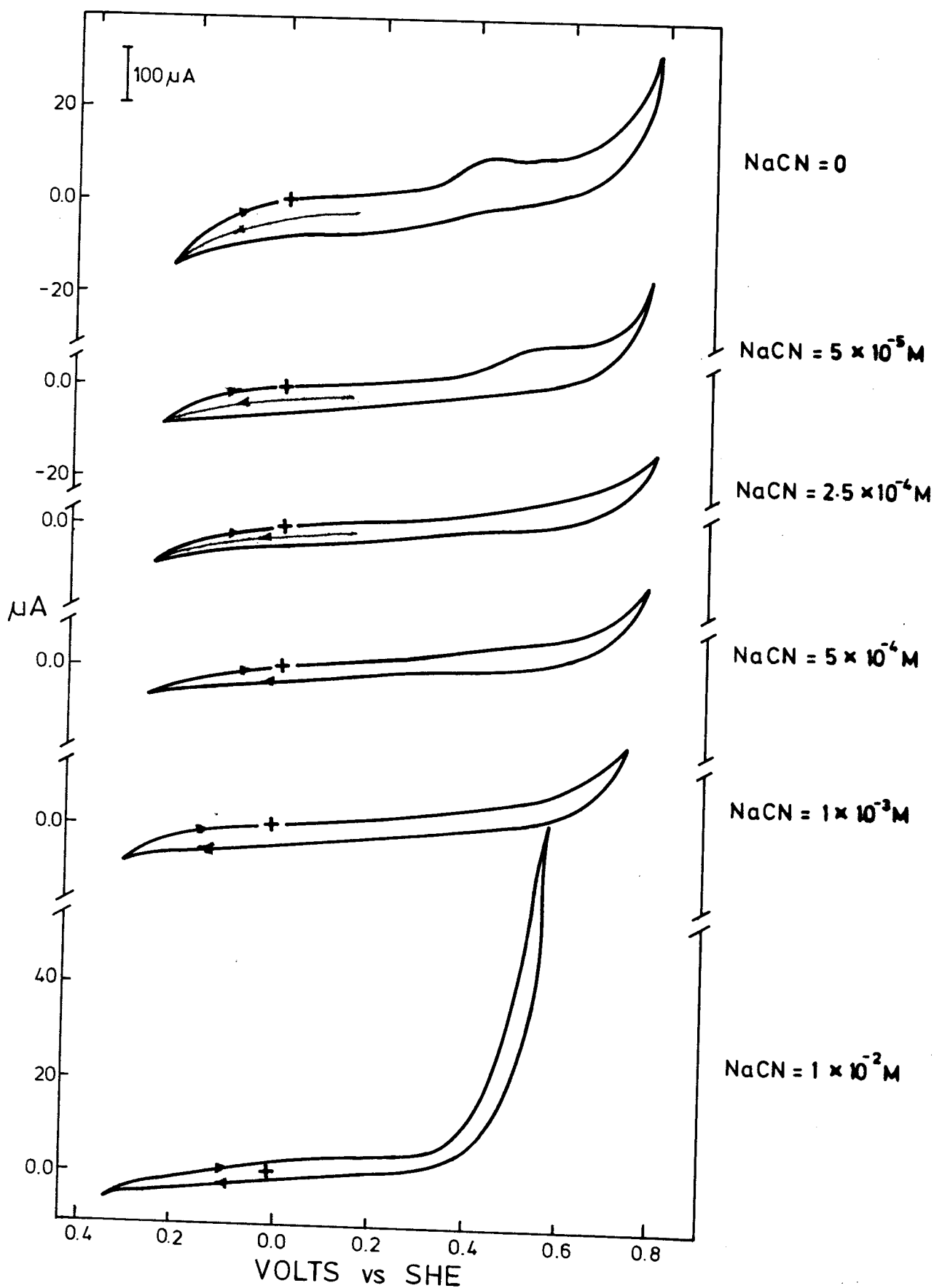Figure 5.22: Cyclic voltammograms of Carrollite in a buffer solution at pH 7.0 containing varying concentrations of sodium cyanide.

- 137 -

relatively high cyanide concentration, there was the introduction of another anodic reaction at 0.4 volts which might be due to some interaction between the mineral surface and cyanide ions. Whether, this lead to formation of a cyanide complex of some form or was due to enhancement of the anodic oxidation of the mineral is not possible to say.

Figure 5.23 shows the effect of cyanide addition on the voltammetric behaviour of a carrollite mineral electrode at pH 9.2. The anodic curve was again shifted to more anodic potentials and there occurred lead to a rapid rise in the anodic currents at higher overpotentials. The first anodic currents rise probably corresponds to the initial oxidation of the mineral to form an oxide or hydroxide. The subsequent rapid anodic current could be due to the cyanide effect of enhancing further oxidation of the mineral. There is a cathodic elbow on the reverse of the potential which could be associated with the decomposition of some cyanide complex which might have formed during the anodic process.

pH = 9.2

NaCN = 5×10^{-5} M

(a)

NaCN = 5×10^{-4} M

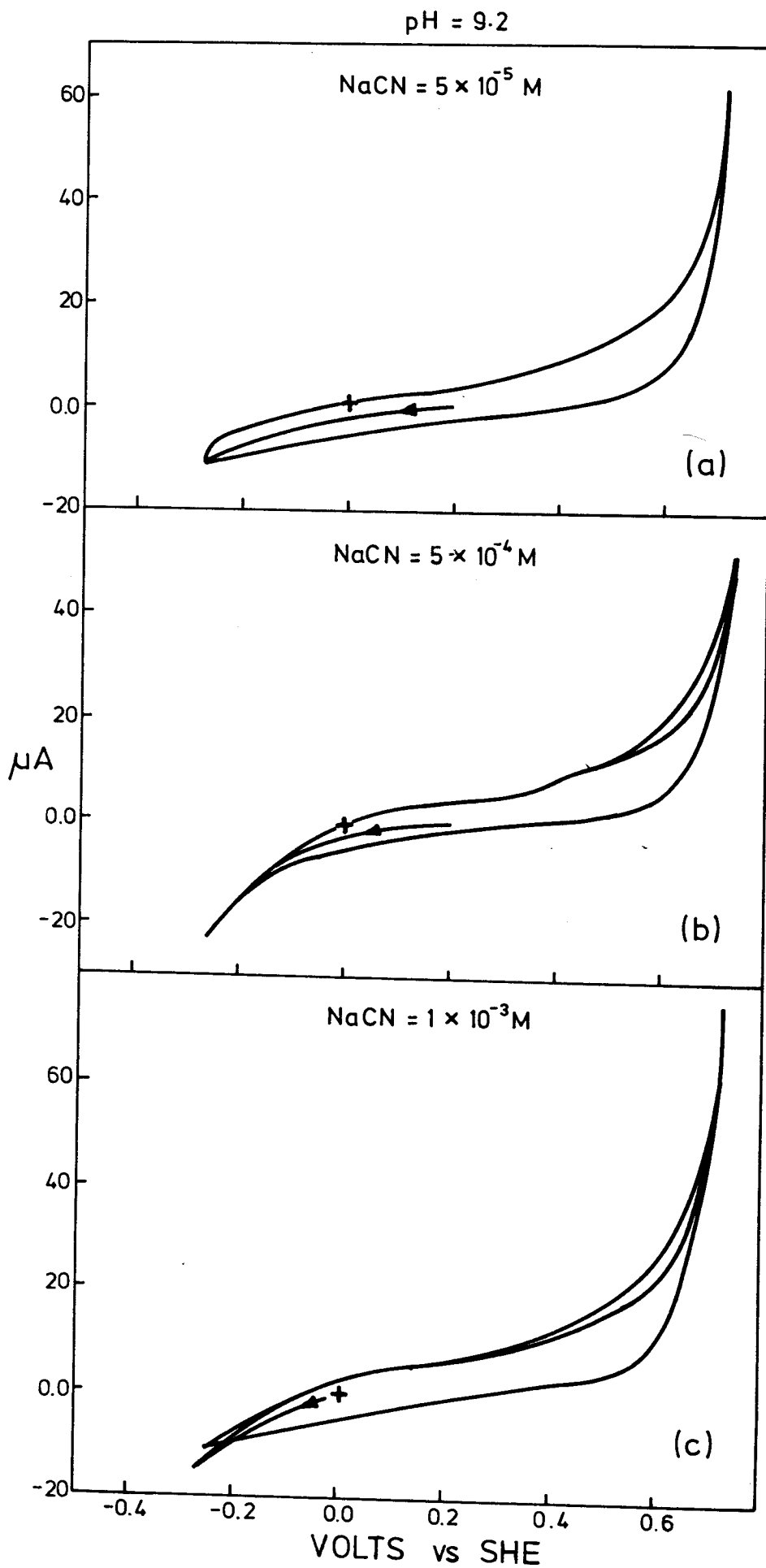(b)

NaCN = 1×10^{-3} M

(c)

μA

VOLTS vs SHE

Figure 5.23: Cyclic Voltammograms of Carrollite in a buffer solution at pH 9.2 containing varying concentrations of sodium cyanide.

The effect of cyanide on the voltammetric behaviour of carrollite mineral electrode in solutions of pH 11.0 is shown in Figure 5.24. Clearly the anodic oxidation of the mineral was enhanced and the rise in the anodic currents due to further oxidation of the mineral tended to increase as the cyanide concentration increased. This shows, that where as cyanide ions merely adsorb on the mineral at near neutral pH, they would probably react with the mineral at higher solution pH. This was attributed to the increased number of free cyanide ions as compared to the free acid molecules as the pH of the solution was increased.

Cyclic voltammograms for carrollite in solutions containing different concentrations of potassium cyanide with a constant amount of potassium ethyl xanthate are shown in Figure 5.25, 5.26 and 5.27 solutions of pH 7.0, 9.2 and 11.0.

In figure 5.25 the increase in cyanide concentration progressively shifted the ethyl xanthate oxidation wave to more anodic potentials. At sufficiently high concentrations of
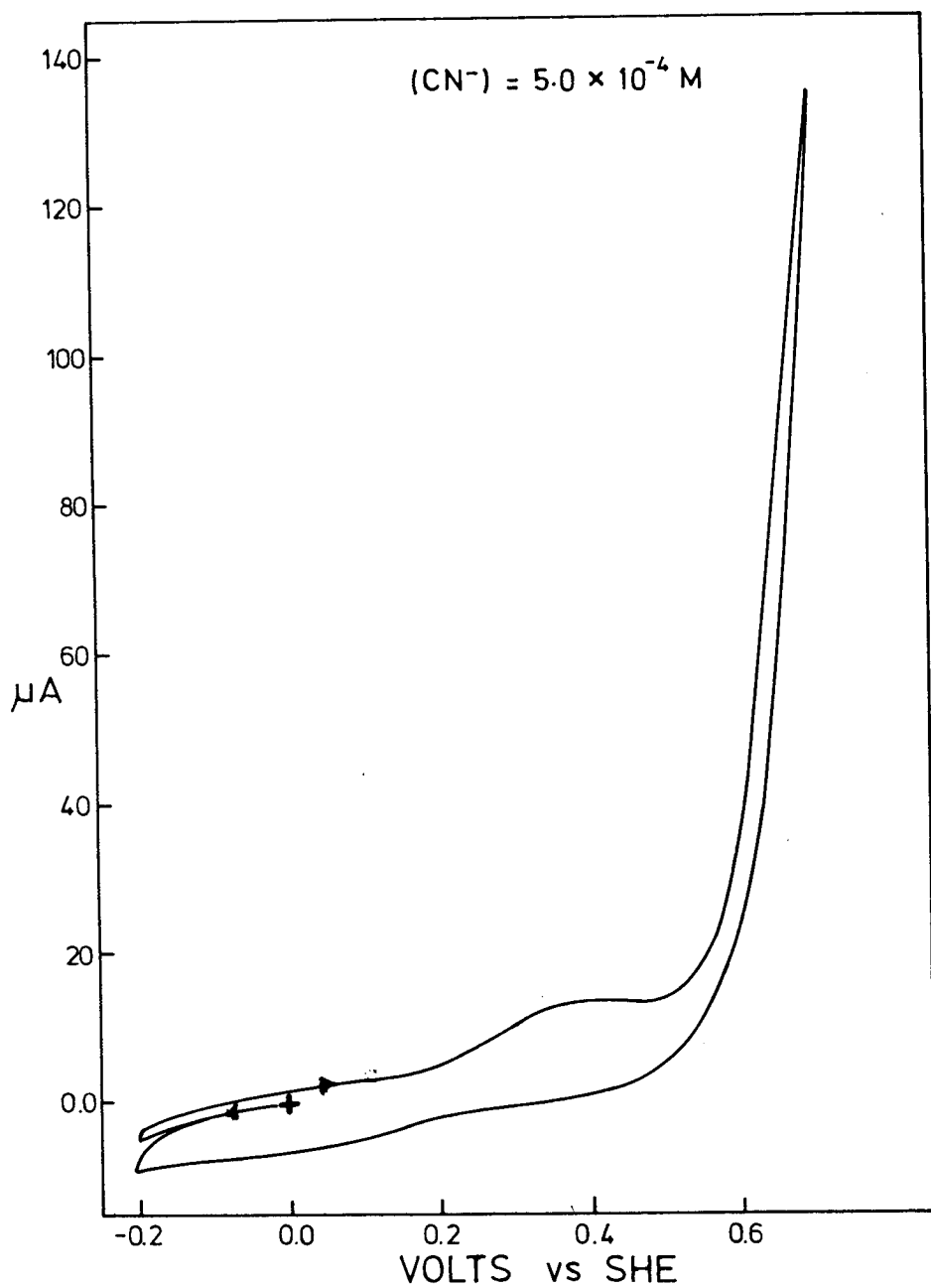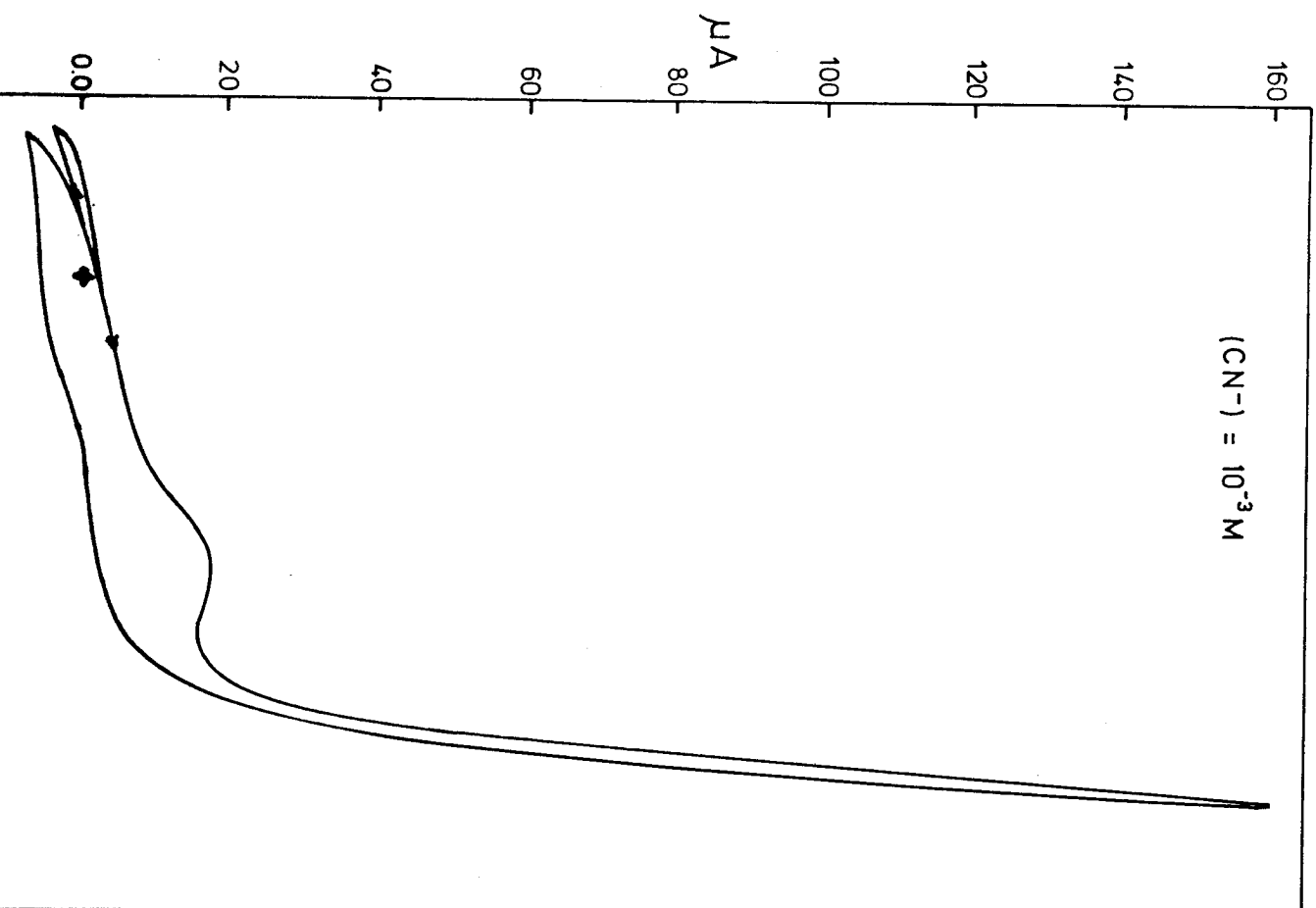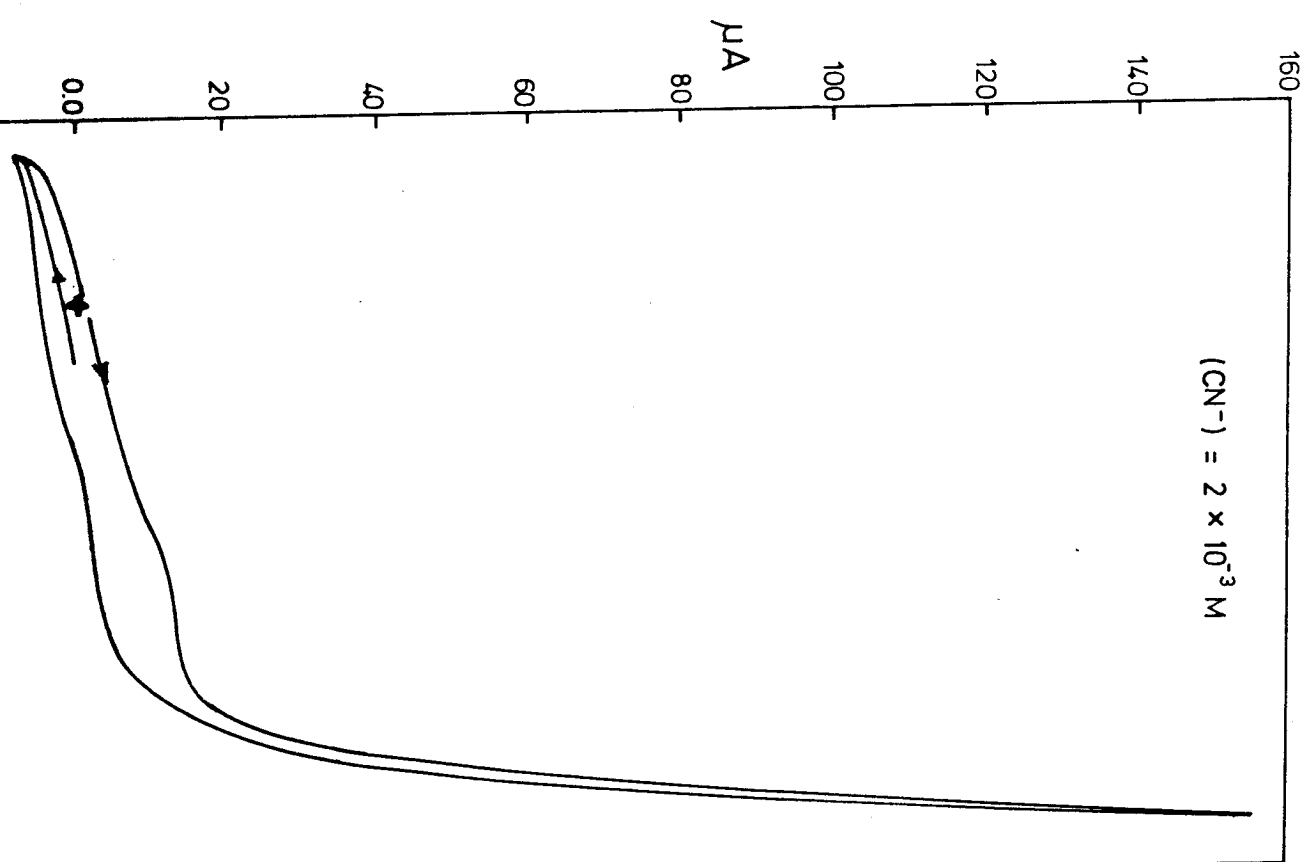
FIGURE 5.24: Cyclic voltammograms of carrollite in a buffer solution at pH 11.0 containing varying concentrations of sodium cyanide.

μA

0.0

20

40

60

80

100

120

140

160

(CN⁻) = 10⁻³ M

μA

0.0

20

40

60

80

100

120

140

160

(CN⁻) = 2 × 10⁻³ M

pH = 11.0

cyanide, the ethyl xanthate oxidation curve merges with the oxidation of the mineral. Thus, the presence of cyanide ions results in an inhibition of the electrochemical oxidation of ethyl xanthate to form dixanthogen. Corresponding weak bubble attachment to the mineral electrode at relatively low cyanide concentrations was observed. This could be due to some dixanthogen formation on the mineral surface but not in sufficient quantities to render the mineral surface hydrophobic.

Figure 5.26 shows the voltammetric behaviour of carrollite at pH 9.2. The depression effect of cyanide seemed to be less severe compared to its effect at pH 7.0. There was anodic oxidation of ethyl xanthate with pronounced production of sufficient hydrophobic surface species resulting in relatively stable bubble attachment on the mineral surface. The hydrophobicity, however, progressively diminished as the cyanide concentration increased. At sufficiently high cyanide concentration, there was only weak bubble attachment on the mineral surface indicating that there still was some hydrophobic species on the mineral surface.
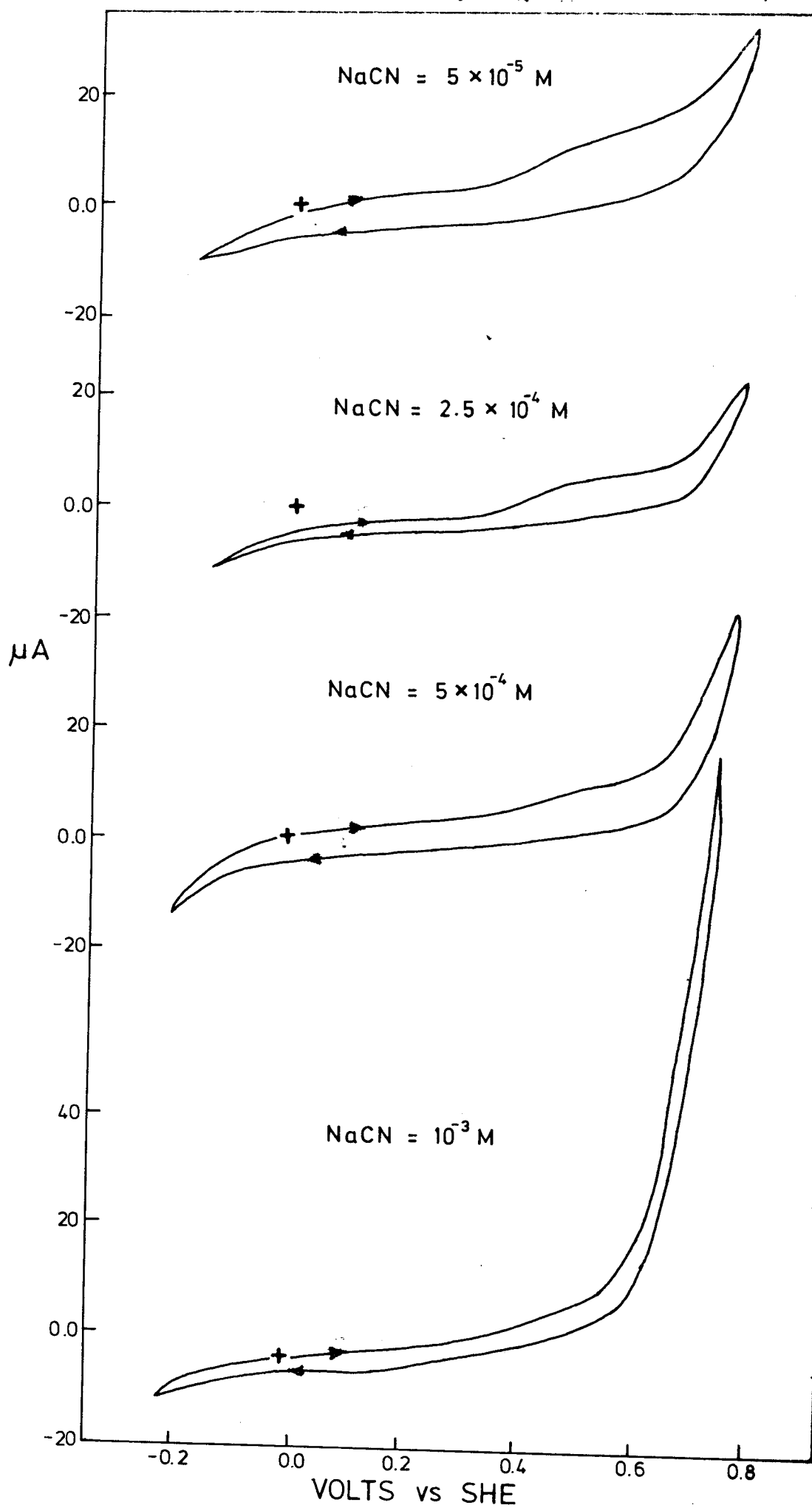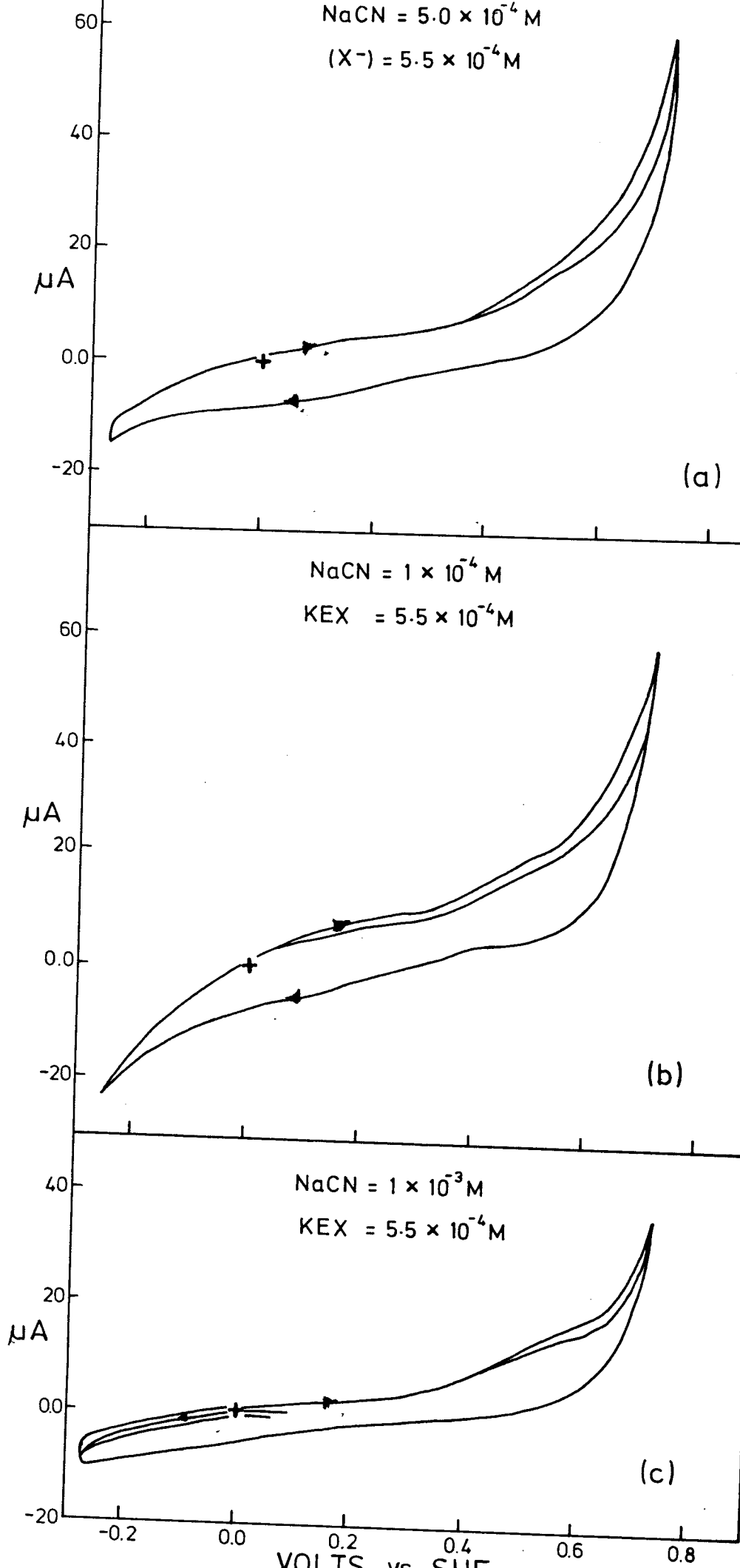
FIGURE 5.25: Cyclic voltammogram of carrollite in a buffer solution at pH 1.0 containing constant amounts of ethyl xanthate with different concentration of sodium cyanide.

FIGURE 5.26: Cyclic voltammograms of Chalcocite in a buffer solution at pH 9.2 containing certain amounts of mixtures of potassium ethyl xanthate with different concentrations of sodium cyanide.

- 145 -

However, the small amounts of the hydrophobic species would not enhance flotation of the mineral. There was certainly some cyanide products which may have formed on the mineral surface preventing the oxidation of ethyl xanthate. It is possible that there could still be some ethyl xanthate ions which could be physically adsorbed on the mineral surface through electrostatic forces to give a weak bond. This could be present in the double layer but would not contribute to hydrophobicity on the mineral surface. Infrared spectra in Figure 5.8, showed evidence of other ethyl xanthate products besides di-ethyl dixanthogen which could be assigned to metal xanthate most likely cobalt xanthate. However, the evidence was not completely conclusive. The voltammetric behaviour of a carrollite mineral electrode in solutions at pH 11.0 containing various concentrations of sodium cyanide at a constant amount of potassium ethyl xanthate is shown in Figure 5.27. The suppression of ethyl xanthate oxidation was quite pronounced at this pH value. The anodic oxidation of the mineral was practically faster than that of ethyl xanthate oxidation even at lower cyanide additions. The depressant effect of cyanide at this pH value was probably that of enhancing the anodic oxidation of the mineral yielding hydrophilic surface species which rendered the mineral non- floatable. It is not certain, however, whether it is these oxidation products or the

FIGURE 5.27: Cyclic voltammograms of Carrollite in a buffer solution at pH 11.0 containing a constant concentration of ethyl xanthate and varying concentration of sodium cyanide.
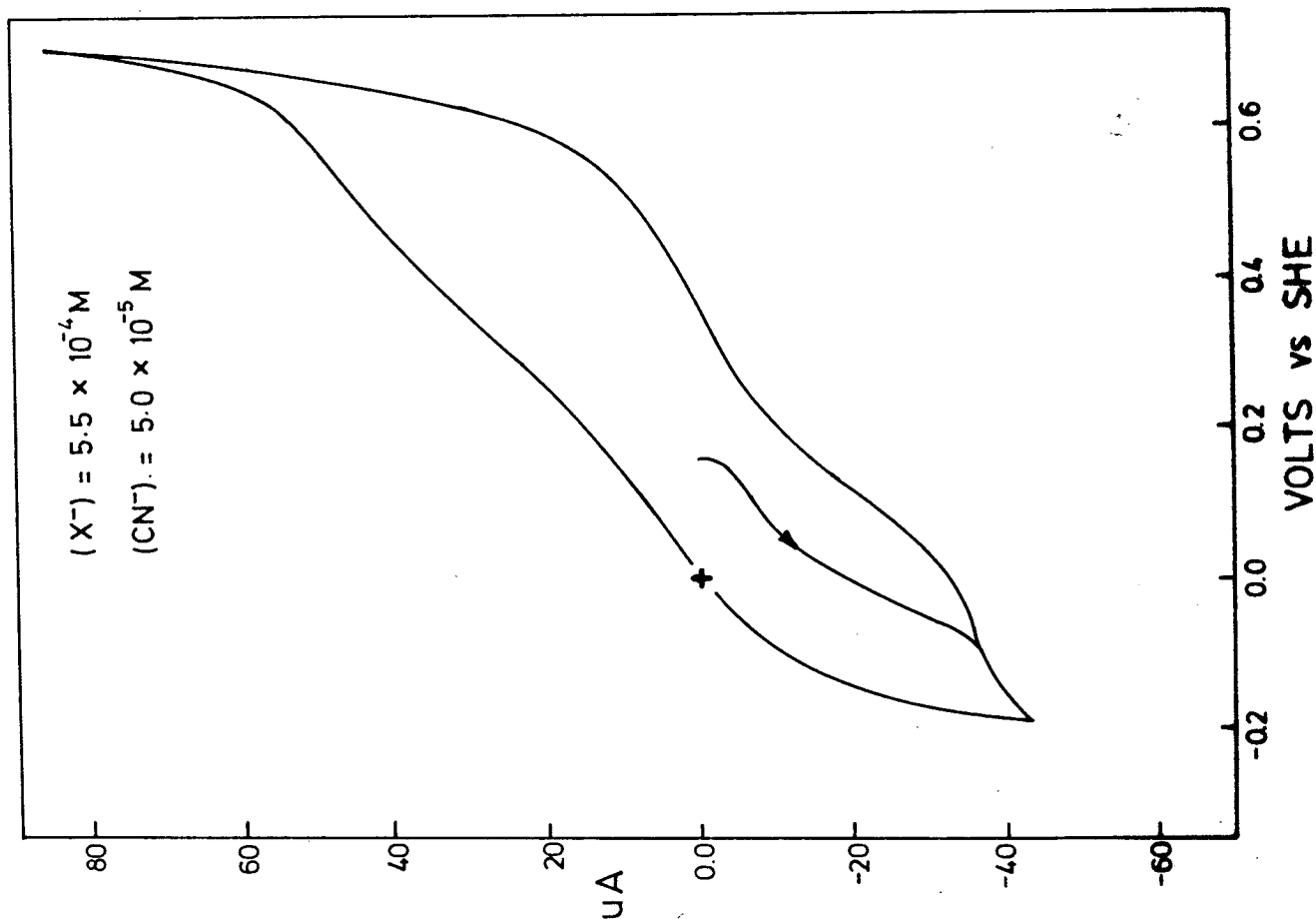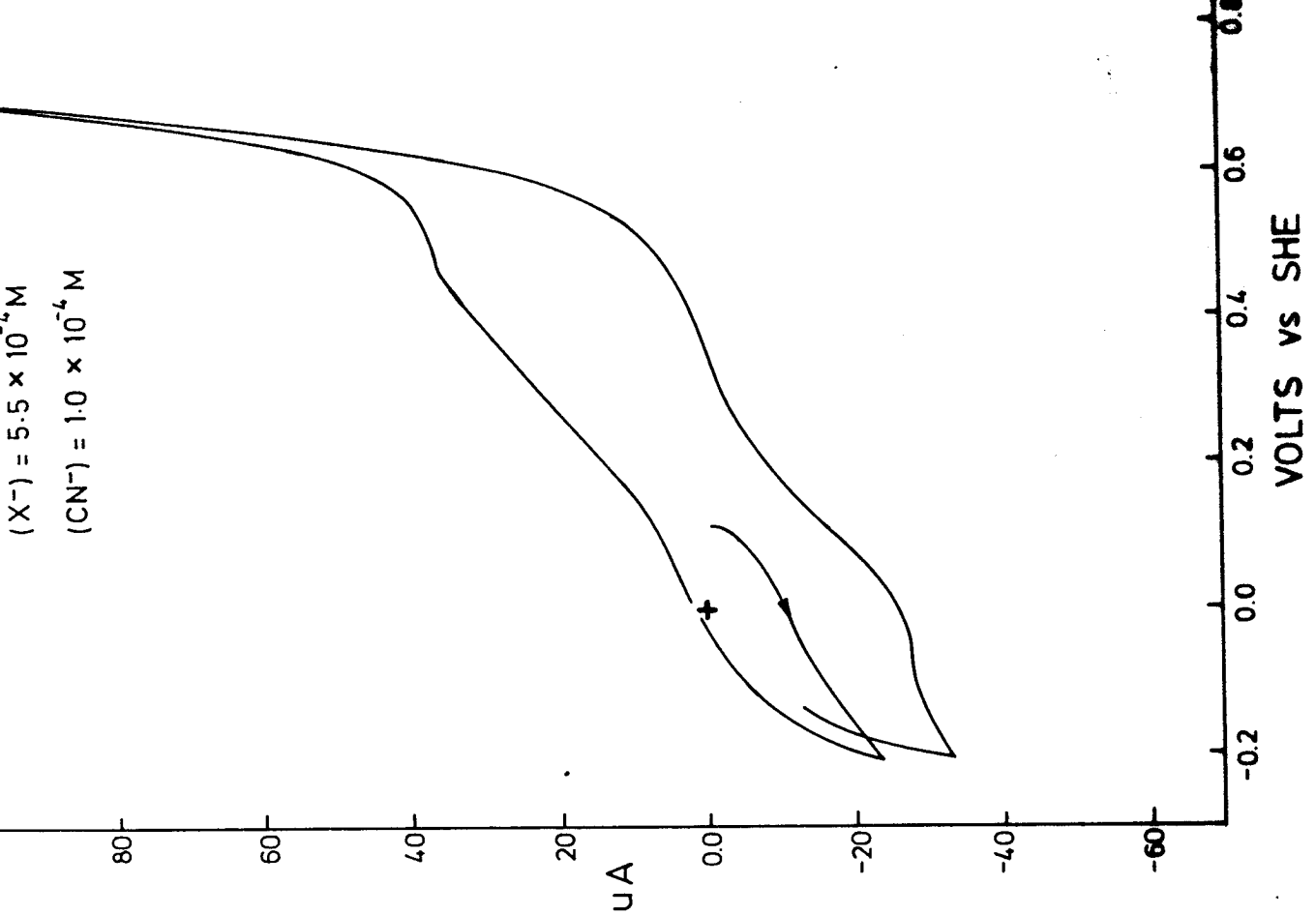
FIGURE 5.27: Cyclic voltammograms of carrollite in buffer solution at pH 11.0 containing a constant concentration of ethyl xanthate and varying concentration of sodium cyanide.

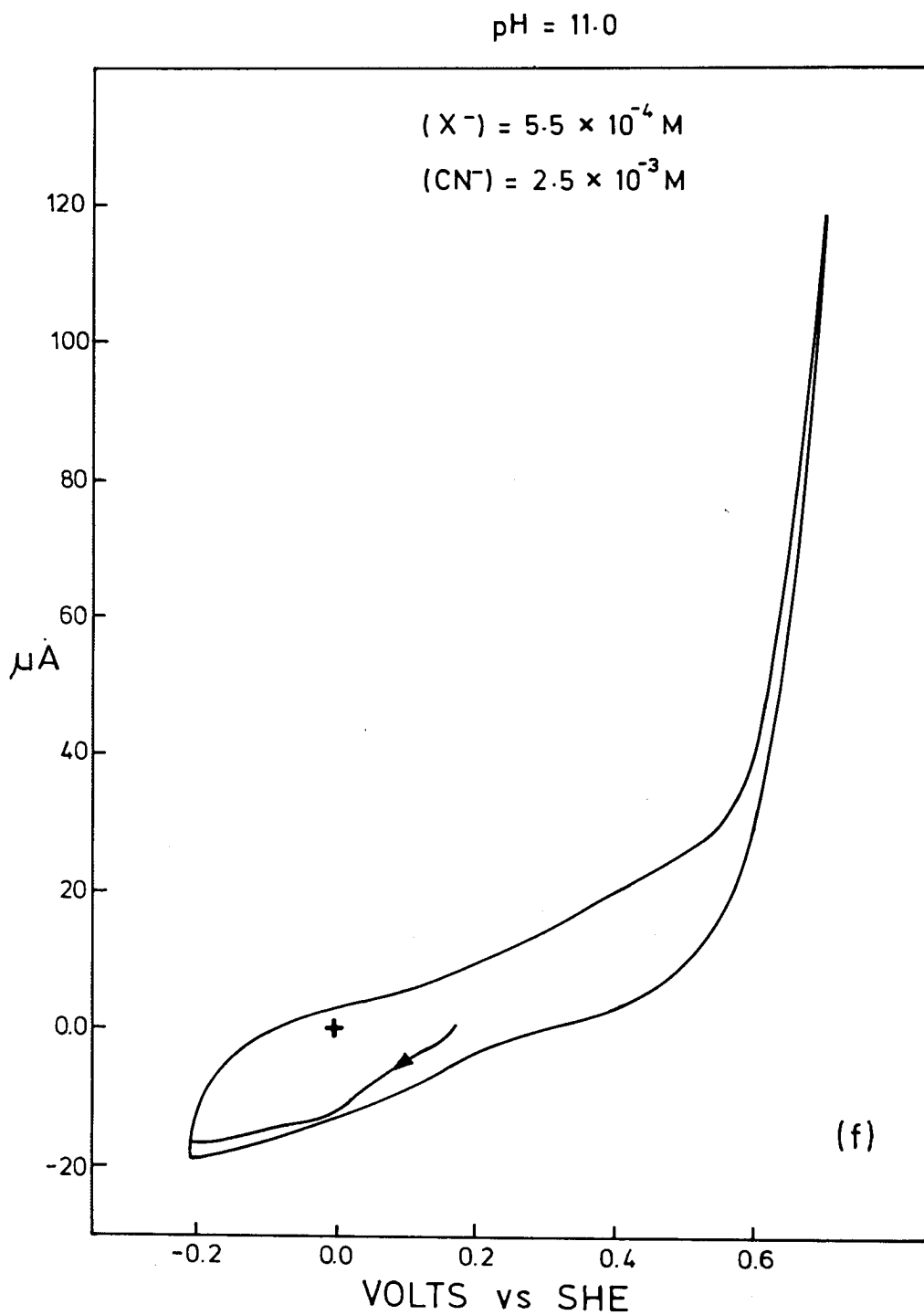blocking action by cyanide complexes that retards the xanthate oxidation on the mineral surface. It appears that the inhibition of xanthate oxidation could best be described by the presence of a surface cobalt cyanide species of some kind. This behaviour could be explained by either the dissolution of the surface oxides by complexing with cyanide or their conversion to an insoluble surface species which does not appreciably change within the potential limit of the experiments. The formation of surface cyanide species was also noted by **Elgillani and Fuerstenau** [91] who identified a ferric ferro cyanide complex on the surface of pyrite in the presence of cyanide ions which was believed to be responsible for the depression of this mineral. They postulated that these species were formed by some reaction between the iron oxide layer and cyanide ions in solution. This was further supported by the observation that cyanide is a much more efficient depressant when the mineral is extensively oxidised as has been suggested by **Ball and Richard** [92] for the same mineral.

Although, the anodic currents showed that the main effect of cyanide is to move the initial anodic oxidation potentials to higher potentials than that of ethyl xanthate / di-ethyl dixanthogen redox potential, the presence of surface cyanide

species inhibited ethyl xanthate oxidation. Furthermore, these species were themselves probably hydrophilic.

The relevance of this to practical flotation is that, it is possible to exploit the fact that the ethyl xanthate / di-ethyl dixanthogen process is progressively diminished on the carrollite mineral surface as the pH was increased. Hence the mineral will be rendered unfloatable in a mixed ore, while the components whose ethyl xanthate / di-ethyl dixanthogen reaction still proceeds at an appreciable rate will be rendered hydrophobic and hence float. However, it is always good practice to make correlations of electrochemical behaviour of the mineral with its floatability both as a single mineral and in a mixtures with other components. This correlation might require the establishment of the potential dependence of flotation of the mineral components say, an ore in relation to their separation. The approach developed by Trahar[93] for the determination of the potential dependence of flotation rate would particularly be valuable in this area.

CHALCOPYRITE

The chalcopyrite - aqueous solution interface was studied using lineral potential sweep voltammetry (cyclic voltammetry) in an attempt to understand the oxidation behaviour of this mineral and how this would influence its floatability. Voltammograms for freshly ground chalcopyrite electrodes in ' oxygen free' solutions are shown in Figures 5.28 (A), 5.28 (B), 5.28 (C) and 5.28 (F) for solutions of different pH values of 4.6, 7.0, 9.2 and 11.0. The potential sweep was commenced from the rest potential of the mineral in each solution to more negative potential values (lower limit) before a complete cycle was recorded. Figures 5.28 (D) and (E) show the voltammograms at the indicated solution pH values in which the potential was stepped from the rest potential to more positive potentials (upper limit) before a complete cycle was recorded. This allowed an evaluation of the effect of the initial scan direction on the electrochemical behaviour of the mineral.

In Figure 5.28 (A), there was a cathodic current rise in the initial scan which led to a cathodic peak at about - 0.2 volts. As the potential was taken to more anodic potentials, an anodic currents flowed at potentials above - 0.1 volts and that gave rise to a peak at about 0.2 volts. As the potential was taken

Figure 5.28

pH = 4.6

(A)

pH = 7.0

(B)

pH = 9.2

(C)

(D)

VOLTS vs SHE
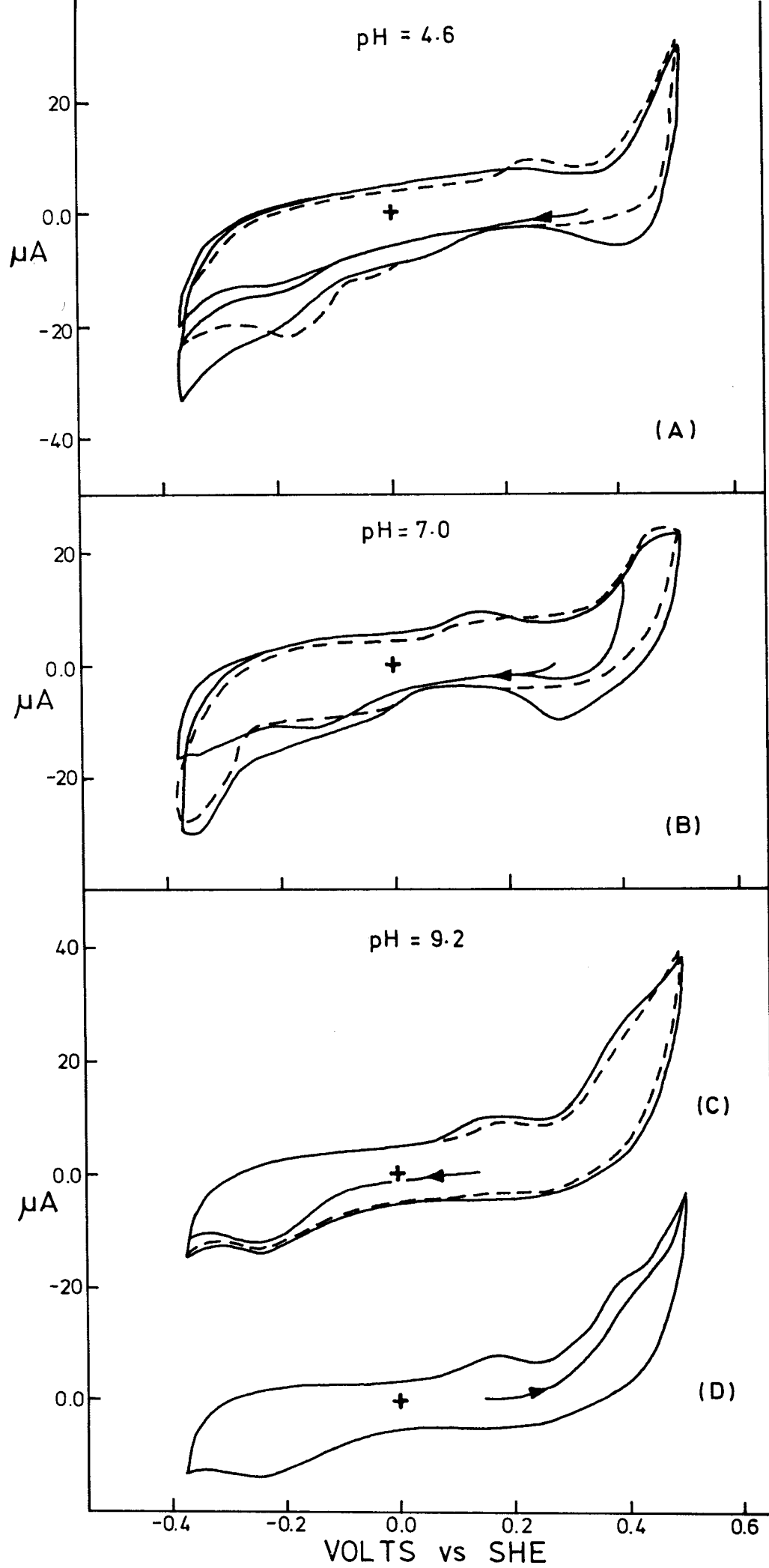
beyond 0.4 volts, there occurred a rapid increase in the anodic currents. This increase in anodic currents was certainly due to the further oxidation of the mineral. The additional cathodic peak which appeared at the start of the negative going scan was due to the reduction of the further oxidation products of the mineral. The voltammogram in stirred solutions showed that the cathodic process (as depicted by the peak) was stirring dependent and hence could be assumed to be related to the reduction of soluble products. However, this explanation is doubtful as such products would not be therefore available for reduction during the cathodic sweep. The peak must therefore be ascribed to the reduction of other oxidation products others than the soluble ones. In Figure 5.28 (C), there is a cathodic peak on the initial negative scan. This could be accounted for by reduction of some oxidation products on the mineral surface during grinding and transfer to electrochemical cell. On the positive scan as shown in Figure (D) there was no peak which could be assigned to the initial oxidation of the mineral. However, as the potential was extended to more positive potentials further oxidation of the mineral was readily observed. This conclusion was further supported by the positive scan which was smaller than the peak observed when the initial direction of the scan was cathodic. This is shown for the solution of pH 11.0
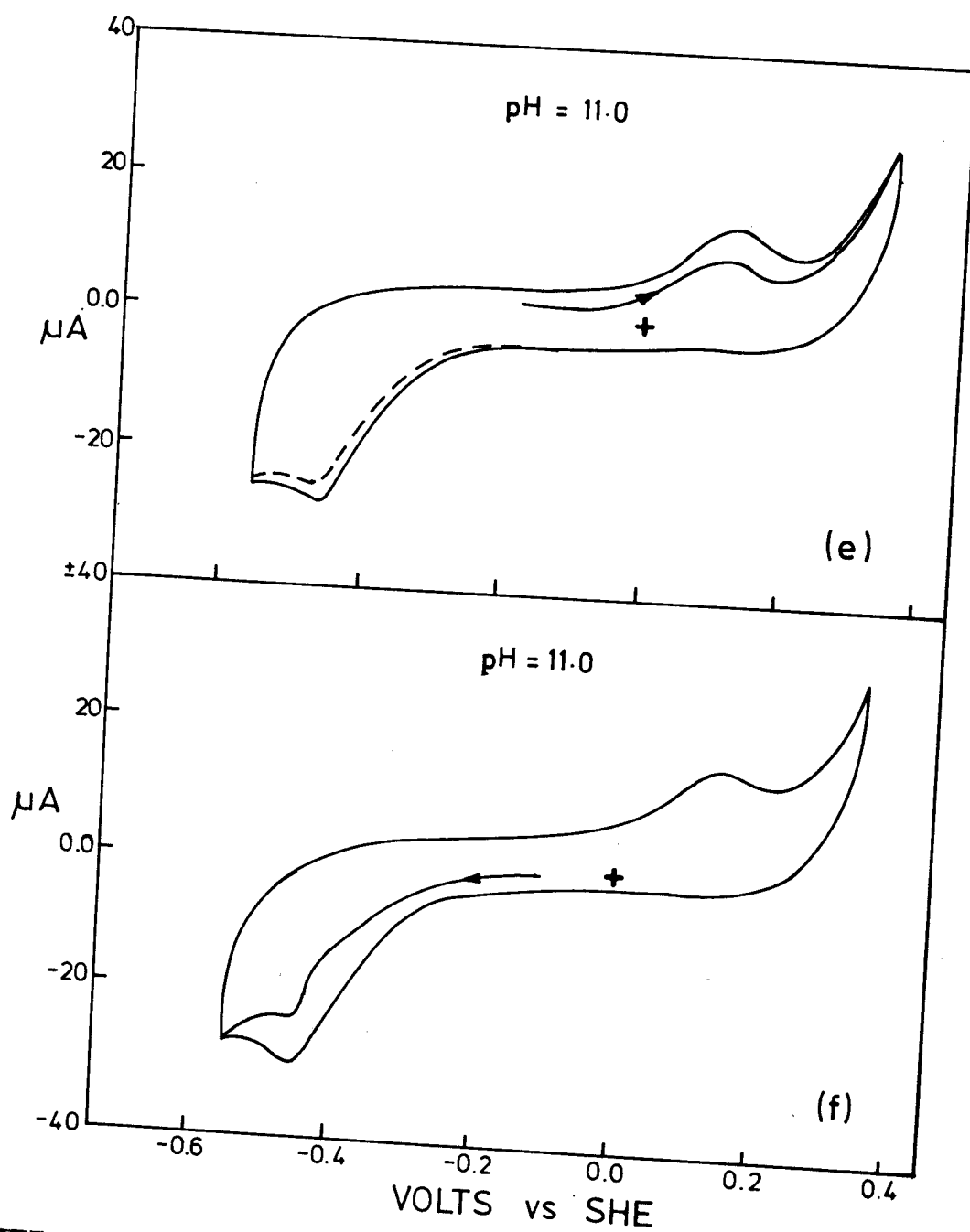
FIGURE 5.28: Cyclic voltammograms of chalcopyrite in aqueous solutions at the indicated pH values showing the effect of the initial scan direction.

in Figure 5.28 (E). This is only possible if the mineral underwent some form of initial oxidation. Also, both the anodic and cathodic peaks were independent of stirring and were thus associated with reaction products which remained on the surface of the mineral.

When the chalcopyrite electrode was held in an oxygen saturated solution prior to inserting into the electrochemical cell, the resulting cathodic peak showed that more charge was passed. This could be accounted for by an increase in the oxidation products on the mineral surface. The role of oxygen is to increase the layer of the oxidation products.

At pH 9.2 and 11.0, the system showed that only surface species were formed as stirring showed no marked effect on the anodic and cathodic peaks. The anodic and cathodic charges were nearly equal for a complete cycle between the potential limits and the shape of the voltammograms did not change significantly between the consecutive cyclic sweeps. This is typical of processes involving the production of oxidised surface species which readily reduce back to the original substance when the potential is reversed. Wadsworth [94] and Linge [95] showed that iron is dissolved preferentially from the surface of chalcopyrite during acid oxidative leaching and that a hydroxide or hydrated oxide results

in alkaline solutions. Using Auger electron spectroscopy Eadington[96] showed that oxygen is incorporated into the surface of chalcopyrite when the mineral is exposed to oxygen saturated solutions. In the light of these considerations, the suggested oxidation mechanisms of the chalcopyrite mineral electrode in acid media can be represented by the following equation:

$$CuFeS_2 \rightleftharpoons CuS + S^0 + Fe^{2+} + 2e^- \quad E^0 = 0.293 \text{ V} \quad ...(5.15)$$
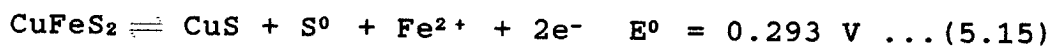
and in the alkaline solution to be:

$$CuFeS_2 + 3H_2O \rightleftharpoons CuS + Fe(OH)_3 + S^0 + 3H^+ + 3e^- ...(5.16)$$
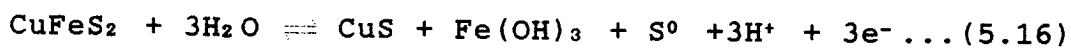
The potential at which the anodic reaction occurred or commenced was found to be in close agreement with the reversible potentials of these processes as calculated from free energy data obtained from Latimer.[97] The further oxidation peak of the chalcopyrite mineral electrode could be represented by :

$$CuS \rightleftharpoons Cu^{2+} + 2e^- + S \quad E^0 = 0.59 \text{ V} \quad ....(5.17)$$

in acid solutions and

$$CuS + 2H_2O \rightleftharpoons Cu(OH)_2 + S + 2H^+ + 2e^- \quad E^0 = 0.85 \text{ V} \quad .(5.18)$$
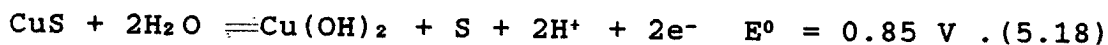
in alkaline solutions.

In proposing these reactions, it has to be assumed that the iron in the surface zone is completely oxidised before any copper-

oxygen species are formed.

Early x-ray photoelectron spectroscopic studies appeared to support reactions 5.15 and 5.16. However, more detailed investigations showed that sulphur is not a product of oxidation of chalcopyrite. Furthermore, a small amount of sulphate could be detected on chalcopyrite treated with hydrogen peroxide. In the light of this, the x-ray photoelectron spectroscopic data were interpreted as involving the initial oxidation of a stoichiometry close to CuS_2. Thus reaction 5.16 should be represented as follows:

$$CuFeS_2 + 3H_2O \rightleftharpoons CuS_2 + Fe(OH)_3 + 3H^+ + 3e^- \quad \ldots\ldots\ldots (5.19)$$
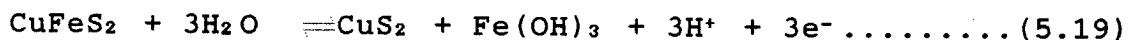
The reversible potential for this process must however be assumed to be close to that of reaction 5.16 since the calculated value for reaction 5.16 coincided closely with the on set of anodic currents in Figure 5.29. This implies that the free energy of formation of CuS_2 is not very different from that of CuS. Hence whilst the reactions can be represented by reaction 5.15 and 5.16, the most likely one is that which involves CuS_2 production. The natural floatability of chalcopyrite was found to occur at about the same potential as the commencement of the anodic process.[29] The floatability would continue as long as the potential was kept above this critical value. A similar conclusion was also drawn by Heyes et al.[33]

This would suggest that natural floatability of chalcopyrite is associated with anodic oxidation of the surface to produce sulphur leading to hydrophobicity. But, whether it is the actual sulphur or the other stoichiometrically deficient sulphur species responsible for this behaviour has not been yet established. What is certain, however, is that sulphur [48] and sulphide minerals with layer structures like molybenite[101] are known to be naturally floatable. Also Finkelstein et al [102] have shown that sulphide minerals can be rendered floatable by formation of sulphur layer on their surfaces. However, no correlation could be established between flotation efficiency and the quantity of sulphur present.

5.2.2.1 THE INTERACTION BETWEEN CHALCOPYRITE AND POTASSIUM ETHYL XANTHATE

The voltammetric behaviour of chalcopyrite in aqueous solutions containing various concentrations of potassium ethyl xanthate is shown in Figures 2.29, 5.30 and 5.31 for solutions at pH 7.0, 9.2 and 11.0 respectively. As in the case of carrollite ,the ethyl xanthate concentration was varied from 5.5×10^{-5} to 2.75×10^{-3} M.
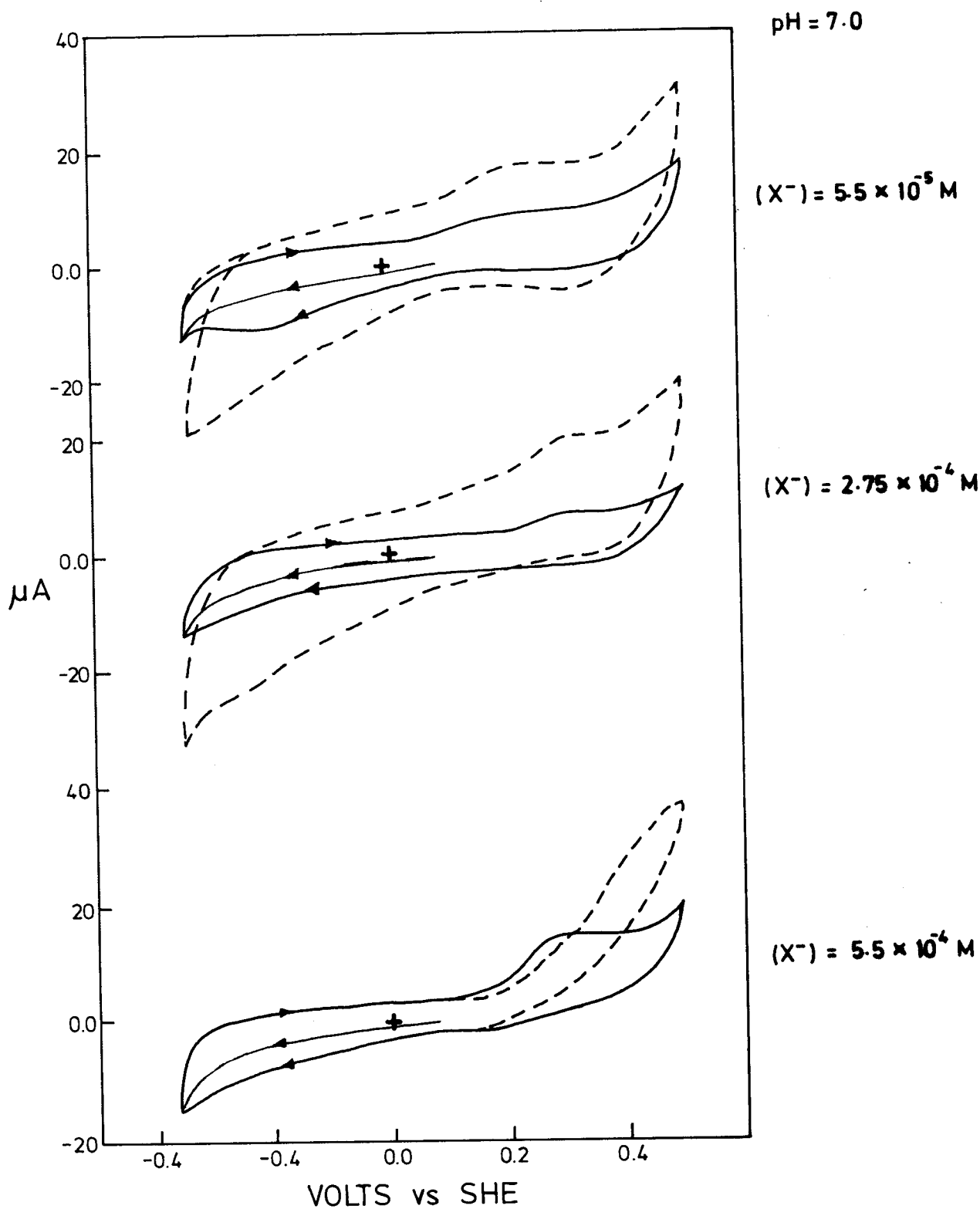
Figure 5.29: Cyclic voltammograms of chalcopyrite in buffer
solutions at pH 7.0 , containing different
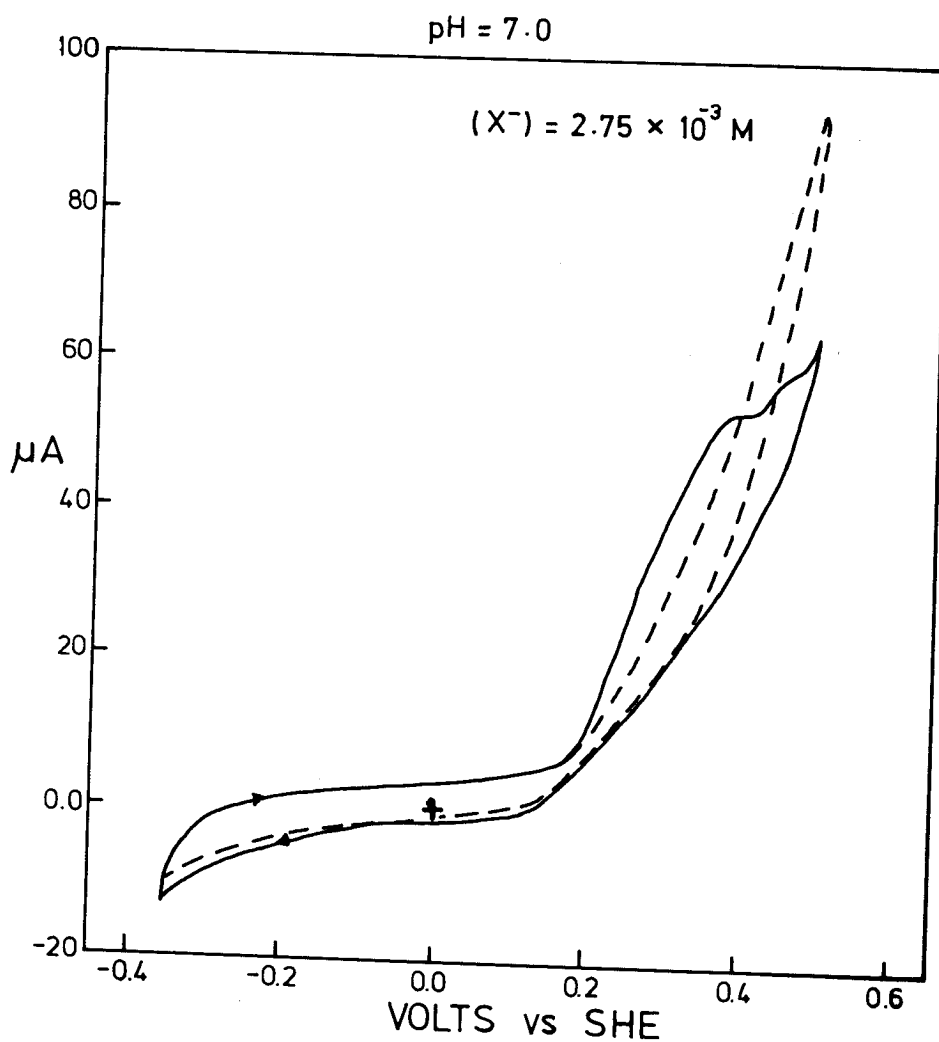concentrations of potassium ethyl xanthate.

Figure 5.29 Cyclic voltammograms of chalcopyrite in **buffer**
solutions at pH 7.0 , containing different **concent-**
rations of potassium ethyl xanthate

The voltammograms in Figure 5.29 show that as the ethyl xanthate concentration increased at pH 7.0, the anodic oxidation of the mineral was progressively inhibited and was subsequently replaced by the oxidation of ethyl xanthate to di-ethyl dixanthogen. The previously observed cathodic peak ascribed to the reduction of further oxidation products on chalcopyrite as the potential was extended beyond 0.4 volts was no longer apparent. This supports the fact that the anodic currents observed in Figure 5.29 are solely due to the anodic oxidation of ethyl xanthate. As the ethyl xanthate amount increased to 5.5×10^{-4} M, the anodic rise in the current gave a peak at about 0.2 volts which was the limiting current. The peak height increased as the amount of ethyl xanthate was increased. The anodic current is mass transfer controlled as could be seen by the effect of stirring the solution. The anodic currents began at more or less the same potential although the pH of the solution increased from pH 7.0 to pH 9.2. This is shown in Figure 5.30. This anodic current increase with increasing amounts of ethyl xanthate was associated with increasing quantities of ethyl xanthate oxidation products. At a high ethyl xanthate concentration of 2.75×10^{-3} M, the voltammograms appeared to give a second oxidation peak as the

Figure 5.30

Figure 5.30   Cyclic voltammograms of chalcopyrite in buffer **solutions**
at pH 9.2, containing different concentrations **of ethyl**
xanthate

potential was made more anodic. Whether this was due to further oxidation of ethyl xanthate or the formation of a metal ethyl xanthate is not possible to tell. It was difficult to extract any oxidation products on the mineral surface even when the electrode was held for prolonged times at potentials well above those required for the anodic currents to flow. This is why some researchers use electrochemical cell which have a facility for applying in-situ spectroscopic techniques to directly analyse for surface species formed.

At pH 11.0 as shown in Figure 5.31, the anodic oxidation of the mineral seemed to be responsible for the anodic currents observed at low ethyl xanthate concentration. As the ethyl xanthate concentration increased, it appeared that the oxidation of the mineral was progressively replaced by that of ethyl xanthate. At 2.75×10^{-3}M sufficiently high ethyl xanthate concentration, an anodic current was observed which occurred at more or less the same anodic potential as was the case at pH 7.0 and 9.2. The observed anodic currents appeared to be pH independent and hence could be identified with di-ethyl dixanthogen formation. From the observed anodic currents, it is reasonably certain, however, that

Figure 5.31

$(X^-) = 5.5 \times 10^{-5}$ M

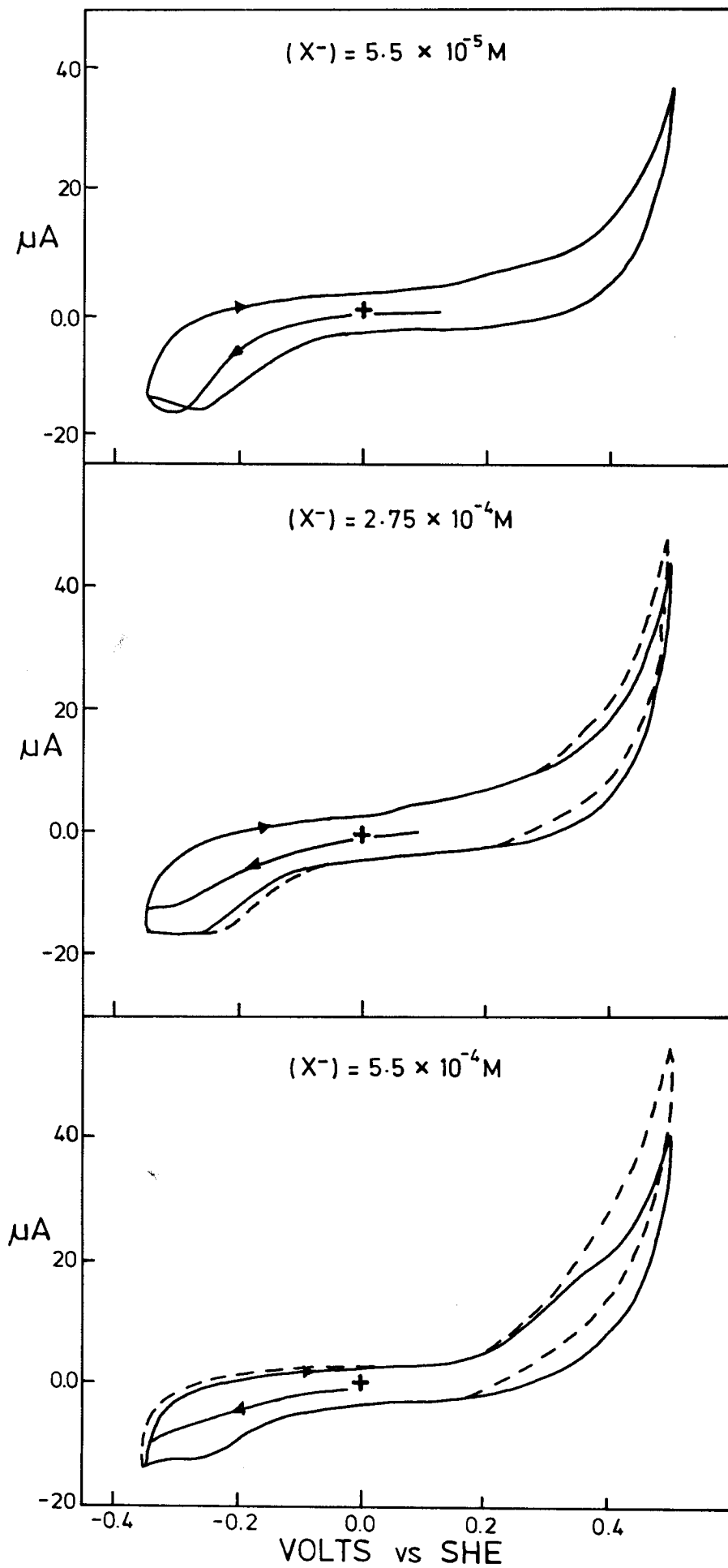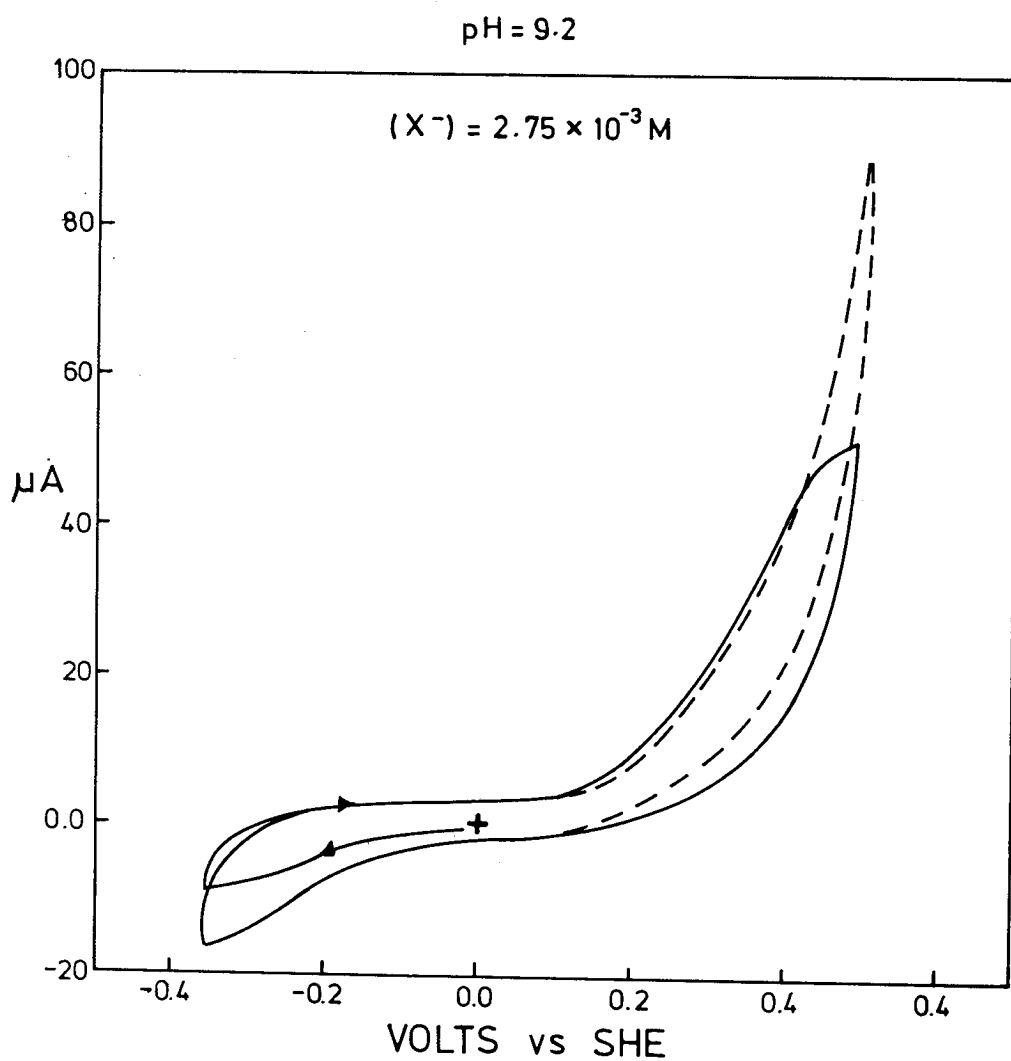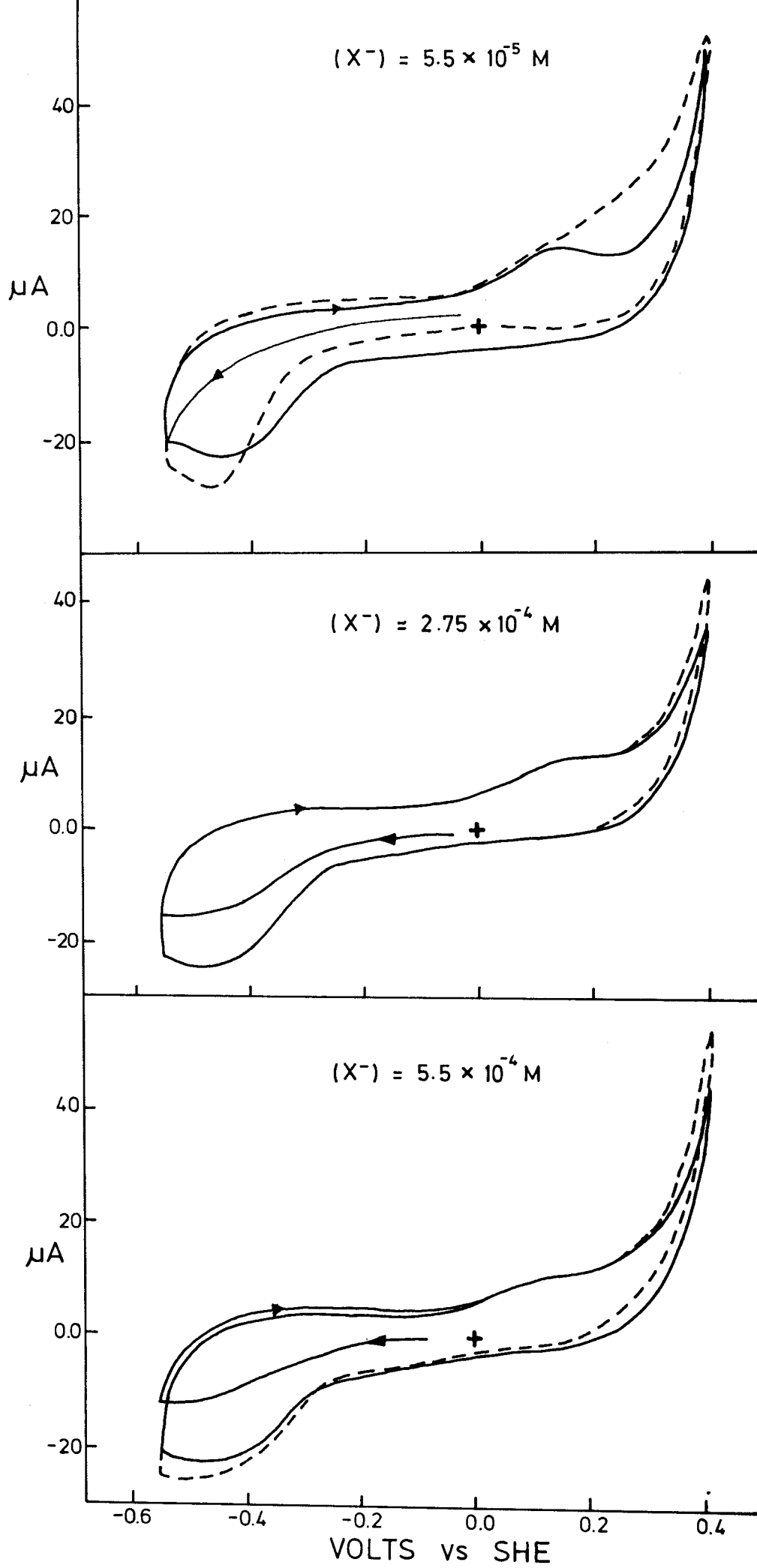$(X^-) = 2.75 \times 10^{-4}$ M

$(X^-) = 5.5 \times 10^{-4}$ M

VOLTS vs SHE
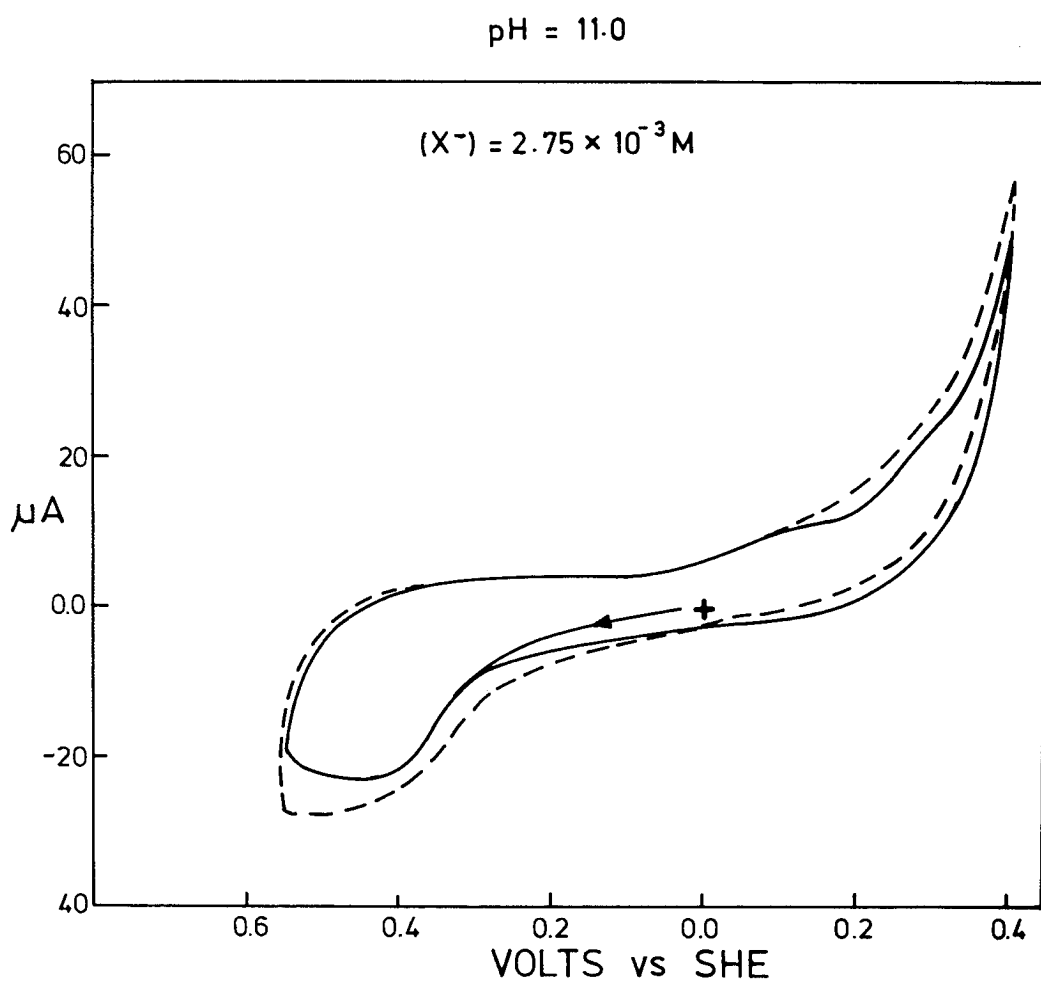
Figure 5.31   Cyclic voltammograms of chalcopyrite in buffer solutions at pH 11.0, containing different concentrations of ethyl xanthate

at about pH 11.0, there is likely to be sufficient di-ethyl dixanthogen formation on the chalcopyrite to render the mineral floatable. This suggests that, the process by which chalcopyrite is rendered hydrophobic does not entirely involve the formation of di-ethyl dixanthogen only. This process is evidently retarded when the pH of the solution is raised. However, the electrode showed some hydrophobic properties as bubbles of nitrogen adhered to the chalcopyrite mineral electrode though not so strongly as at pH 7.0. It appears that when the pH of the solution is increased, the mineral shows a tendency to oxidise forming other surface oxidation products. It is possible that an exchange type of reaction may have occurred between the xanthate ions and the oxidation products to form metal ethyl xanthates.

From the E_h-pH digrams for the **copper-water-xanthate** system as derived by Hepel et al [103] the main phases of interest were cuprous-ethyl xanthate (CuEtX), di-ethyl dixanthogen ($(EtX)_2$) and cupric ethyl xanthate ($Cu(EtX)_2$). The latter is unstable and may decompose into cuprous ethyl xanthate and di-ethyl dixanthogen. Hence in considering another way by which the

chalcopyrite could be rendered hydrophobic, it is important to appreciate the presence of cuprous ethyl xanthate as a possible hydrophobic entity on the mineral surface. There are two possible paths for this to occur:

$$2(\text{EtX})^- \rightleftharpoons (\text{EtX})_2 + 2e^- \dots\dots\dots\dots\dots\dots(5.20)$$

and
$$\text{CuEtX} + (\text{EtX})^- \rightleftharpoons \text{Cu(EtX)}_2 + e^- \dots\dots\dots\dots\dots(5.21)$$

$$\text{Cu}(\text{EtX})_2 + \text{EtX}^- \rightleftharpoons \text{CuEtX} + (\text{EtX})_2 + e^- \dots\dots(5.22)$$
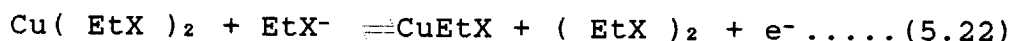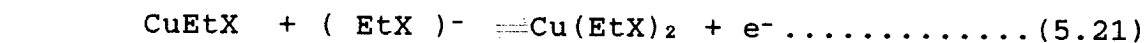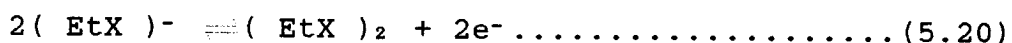
with the cathodic reduction of oxygen being the main cathodic reaction. Figure 5.32 (a), 5.32 (b) and 5.32 (c) show current-time curves for a chalcopyrite electrode held at potentials of 0.1 and 0.3 volts in solutions of pH value of 7.0, 9.2 and 11.0 containing 5.5×10^{-4} M ethyl xanthate. At pH 7.0 the curves show that chemisorption reaction occurred when the electrode was held at a potential of 0.3 volts but not at 0.1 volts as seen from the marked hump on the the curve. This process remarkably slowed down as the potential was held at potentials lower than 0.1 volts. At pH 9.2 and 11.0 the current-time curves did not show any features which could be ascribed to a chemisorption process. This behaviour supports the fact that as the pH of the solution is increased, there is less and less chemisorption of ethyl xanthate on the mineral surface to form di-ethyl dixanthogen. Hence the other hydrophobic entities proposed could have been responsible for making chalcopyrite water repellant.
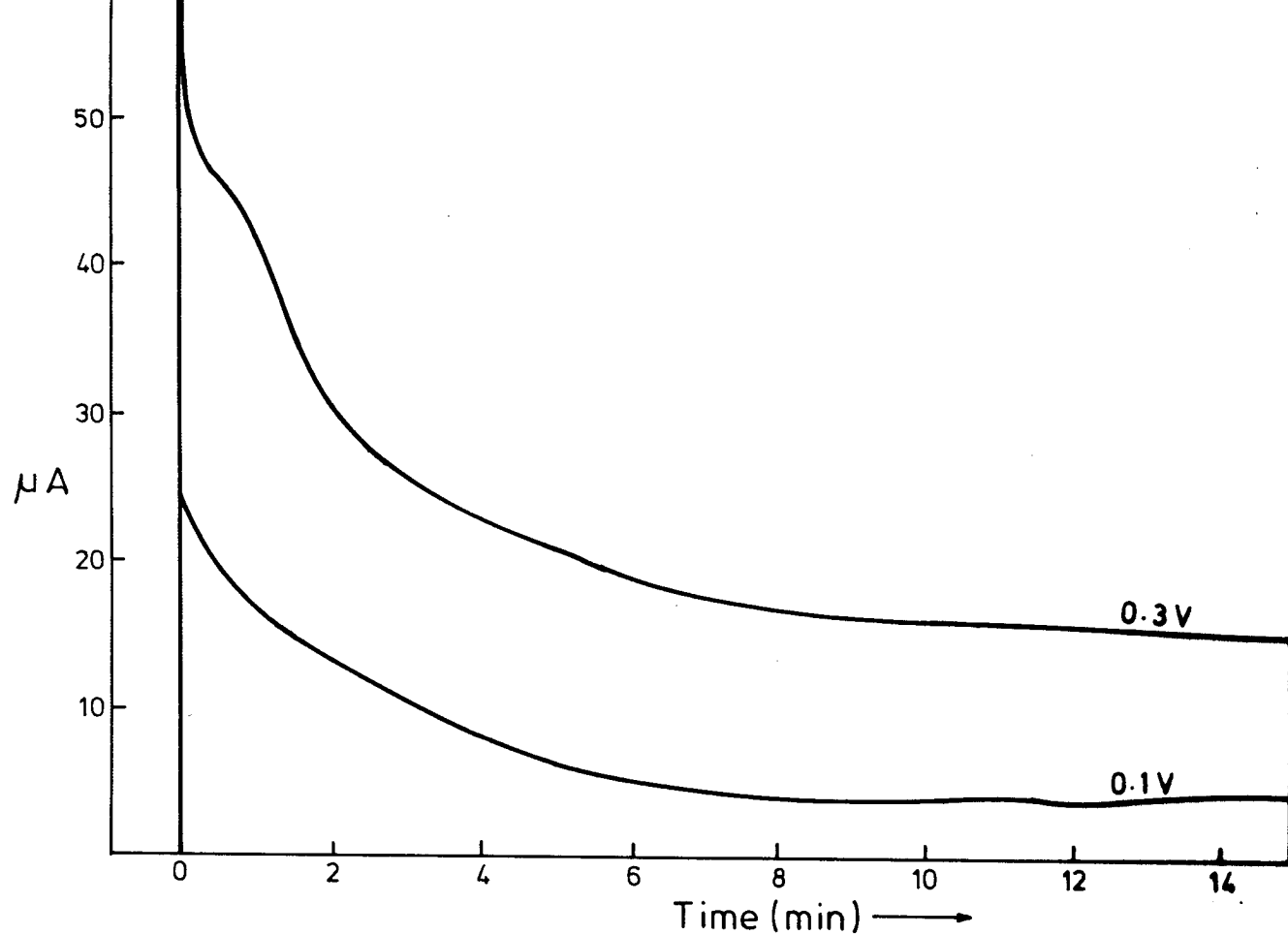
FIGURE 5.32(a): Current-time curves for a chalcopyrite electrode in buffer solutions containing 5.5×10^{-4}M ethyl xanthate at pH 7.0 with the electrode held at 0.1 and 0.3V/vs SHE.
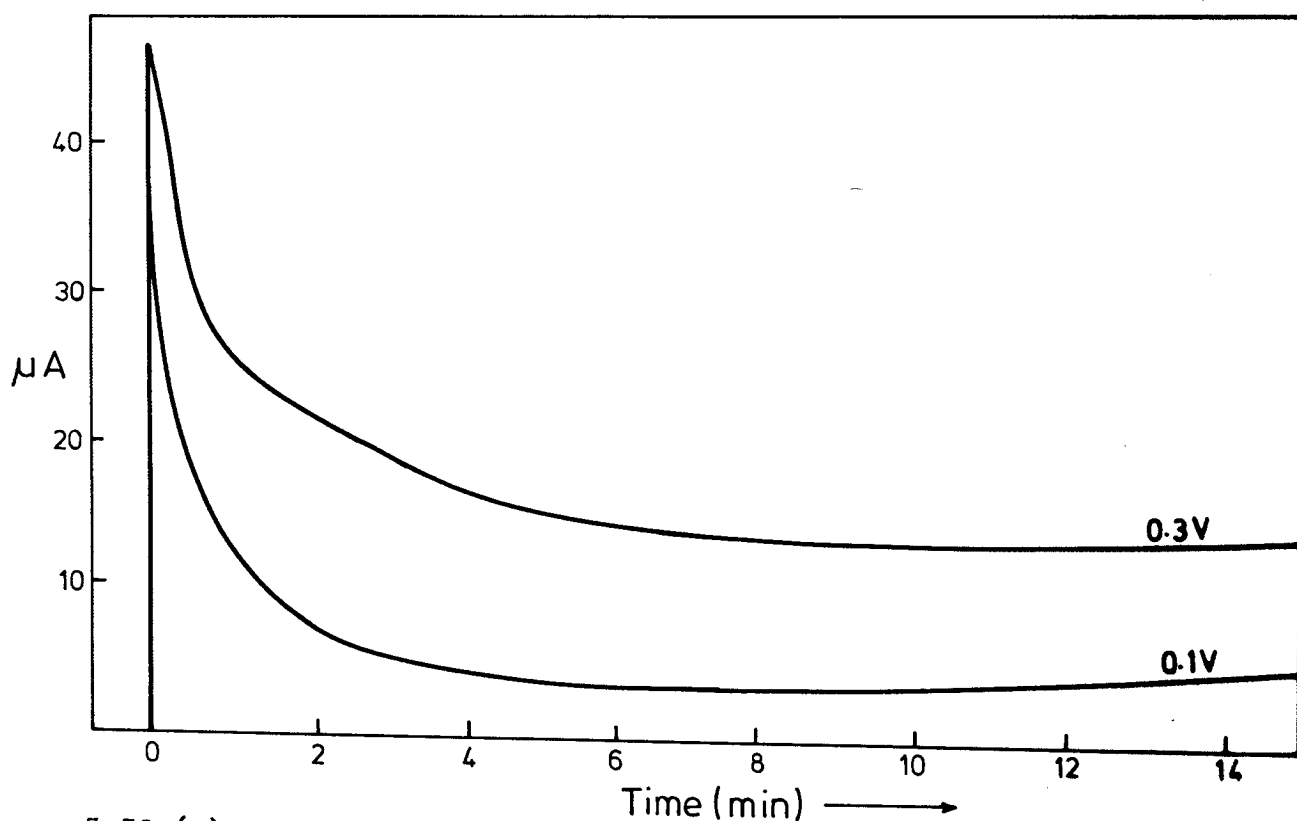
5.32 (b): Current-time curves for a chalcopyrite electrode in buffer solutions at pH 9.2 containing 5.5×10^{-4}M potassium ethyl xanthate with the electrode held at 0.1V and 0.3V vs SHE.

5.2.2.2 THE INTERACTION BETWEEN CHALCOPYRITE, SODIUM CYANIDE AND POTASSIUM ETHYL XANTHATE.

The function of cyanide ions as depressant for chalcopyrite appeared to be associated with a reduction in the rest potentials of the mineral electrode as was earlier seen in rest potential maesurements. That cyanide is capable of reducing the potential of a platinum electrode to a far greater extent in the presence of chalcopyrite than in its absence had been observed by **Heyes** et al.[33] The mechanism of interaction of cyanide and chalcopyrite was described as being obscure, but it was clearly related to the floatability of the mineral. They concluded that, it was the potential rather than the level of cyanide ions which determined the recovery of the mineral.

Figures 5.33, 5.34 and 5.35 show the voltammetric behaviour of chalcopyrite mineral electrode in solutions containing different concentration of sodium cyanide at pH values 7.0, 9.2 and 11.0 respectively.

As the cyanide ion concentrations increased at pH 7.0, the anodic

FIGURE 5.33: Cyclic voltammograms of chalcopyrite in buffer
solutions at pH 7.0 containing varying
concentrations of sodium cyanide.

oxidation of the mineral moved to more cathodic potentials. Under such conditions the tendency of the mineral would be to undergo a dissolution reaction resulting in ions going into the bulk of the solution. However, the ionic species resulting as a result of this enhanced dissolution process will most likely complex with the free cyanide ions in solution to form cyanide complexes on the surface of the mineral which prevents further oxidation of the mineral. This ' passivation' stage is indicative of the region in which the currents were constant soon after the initial oxidation of the mineral as could be seen in Figure 5.33. The cyanide complexes might have oxidised further as the potential was made more anodic, but on the reverse potential sweep, the products of the anodic oxidation process readily reduced back to the original products. Whether the reduction process involved the release of cyanide ions back into solution or a reduced cyanide species on the surface of the mineral is not readily apparent. However, on the positive going scan, an oxidation process was noted to commence at about the same potential and retraced the same path of the voltammograms as the potential reached the upper limit and after being reversed.

When the pH of solution was increased to pH 9.2 as shown in Figure 5.34, the ability of cyanide to reduce the potential of the anodic oxidation of the mineral was more apparent. The

FIGURE 5.34: Cyclic voltammograms of chalcopyrite in buffer solutions at pH 9.2 containing varying concentrations of sodium cyanide.
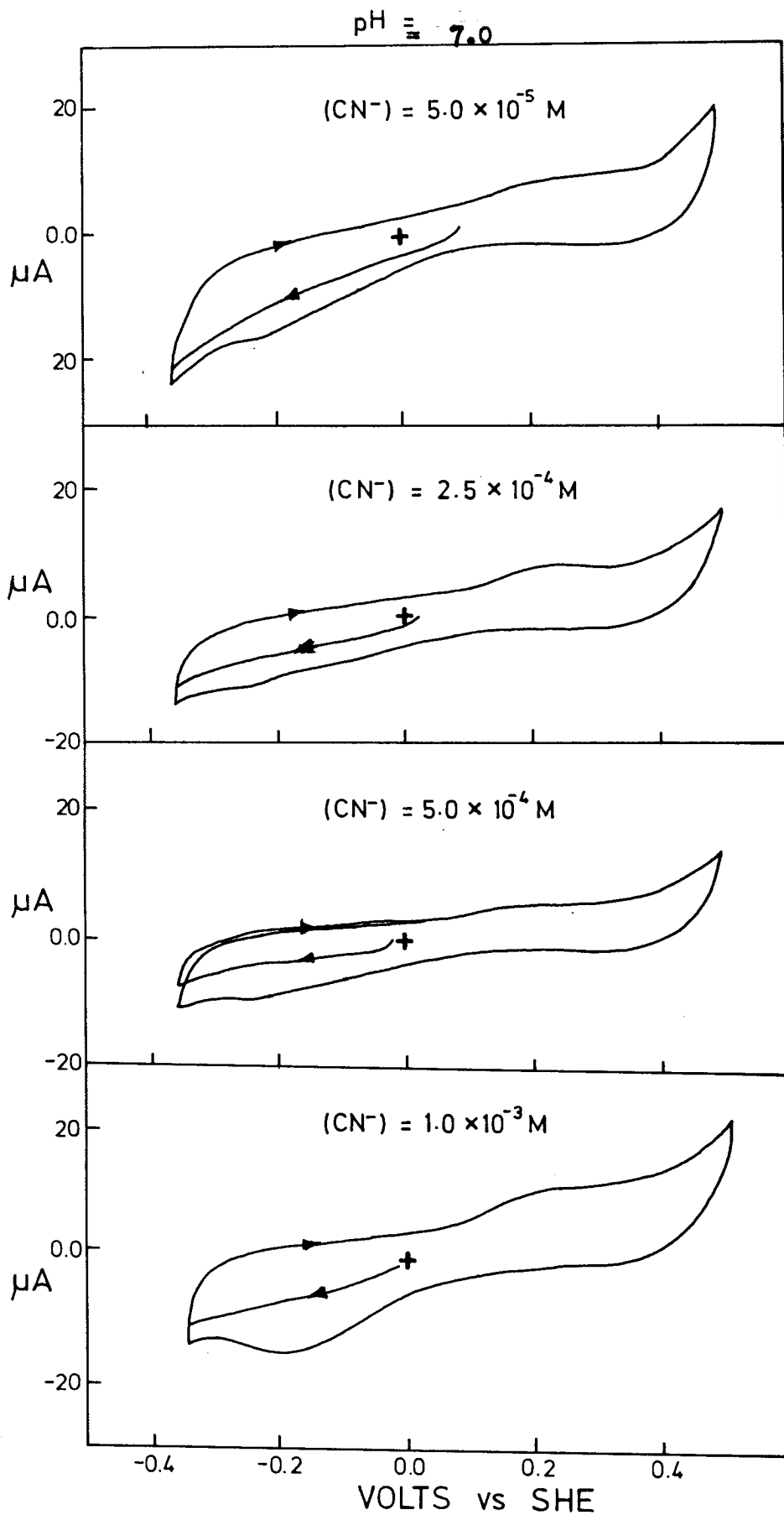
FIGURE 5.34: Cyclic voltammograms of chalcopyrite in buffer
solutions at pH 9.2 containing varying
concentrations of sodium cyanide.

tendency to enhance the anodic oxidation of the mineral was also clearly noticeable as depicted by the increase in the magnitudes of both the anodic and cathodic limiting currents. The processes occurring at this pH value are certainly related to surface cyanide species which remained on the surface of the mineral and are independent of stirring. However, the system does show quite an appreciable degree of reversibility as the voltammograms did not significantly change in successive cycles.

Increasing the pH of the solution to pH 11.0 showed an increased effect of the ability of cyanide to enhance the anodic oxidation of the mineral. The limiting currents increased with cyanide concentrations. This increase in anodic oxidation process could be due to the well established fact about cyanide complexing ability for copper ions. However, in their work Heyes et al[33] concluded that there was no direct relation between the presence of these complexes and the depression of chalcopyrite at least in a system involving the natural floatability of this mineral.

Cyclic voltammetric behaviour of a chalcopyrite mineral electrode in solutions containing different concentrations of sodium cyanide with a constant concentration of potassium ethyl xanthate is shown in Figures 5.36, 5.37 and 5.38 for solutions of pH 7.0, 9.2 and 11.0 respectively.
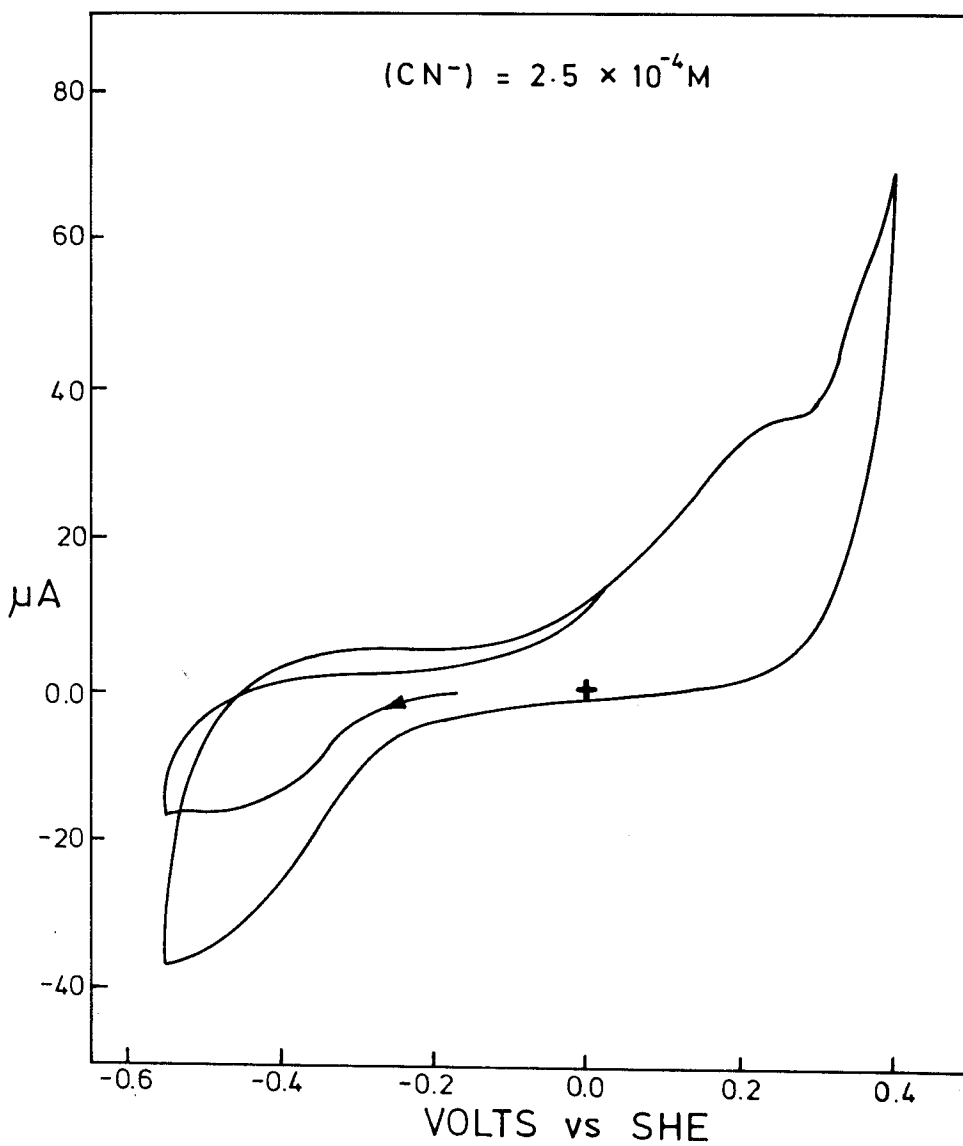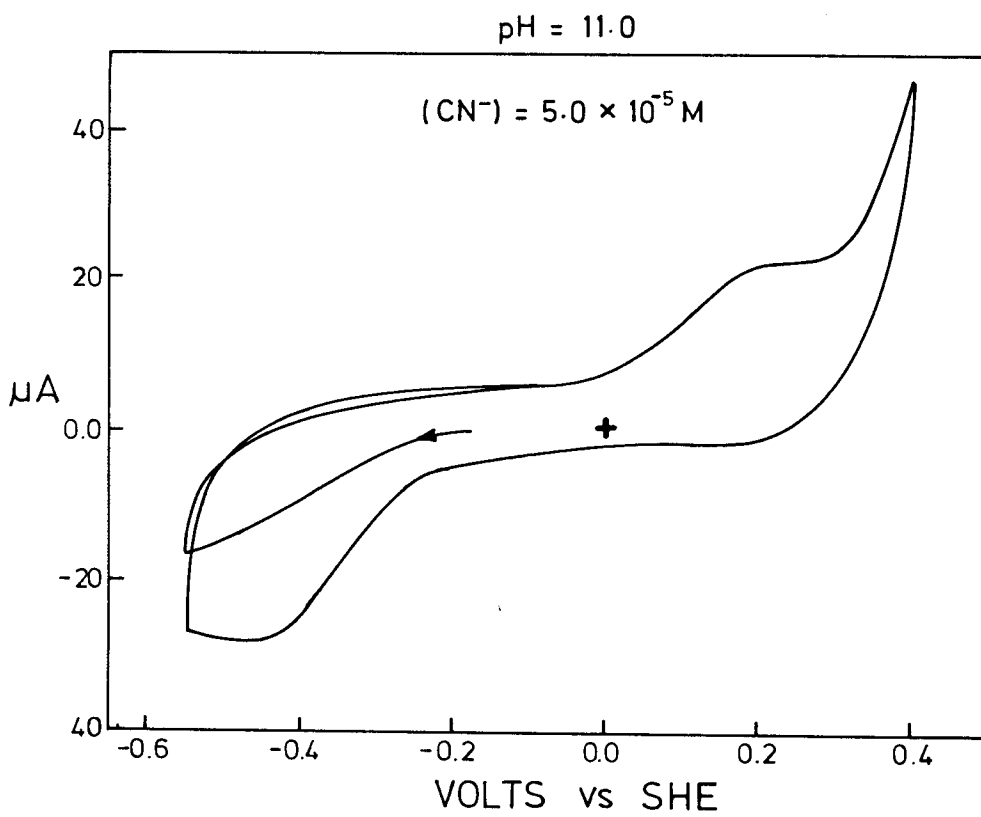
Figure 5.35: Cyclic voltammograms of chalcopyrite in buffer solutions at pH 11.0 containing varying concentrations of sodium cyanide.

pH = 11.0

(CN⁻) = 5.0 × 10⁻⁴ M
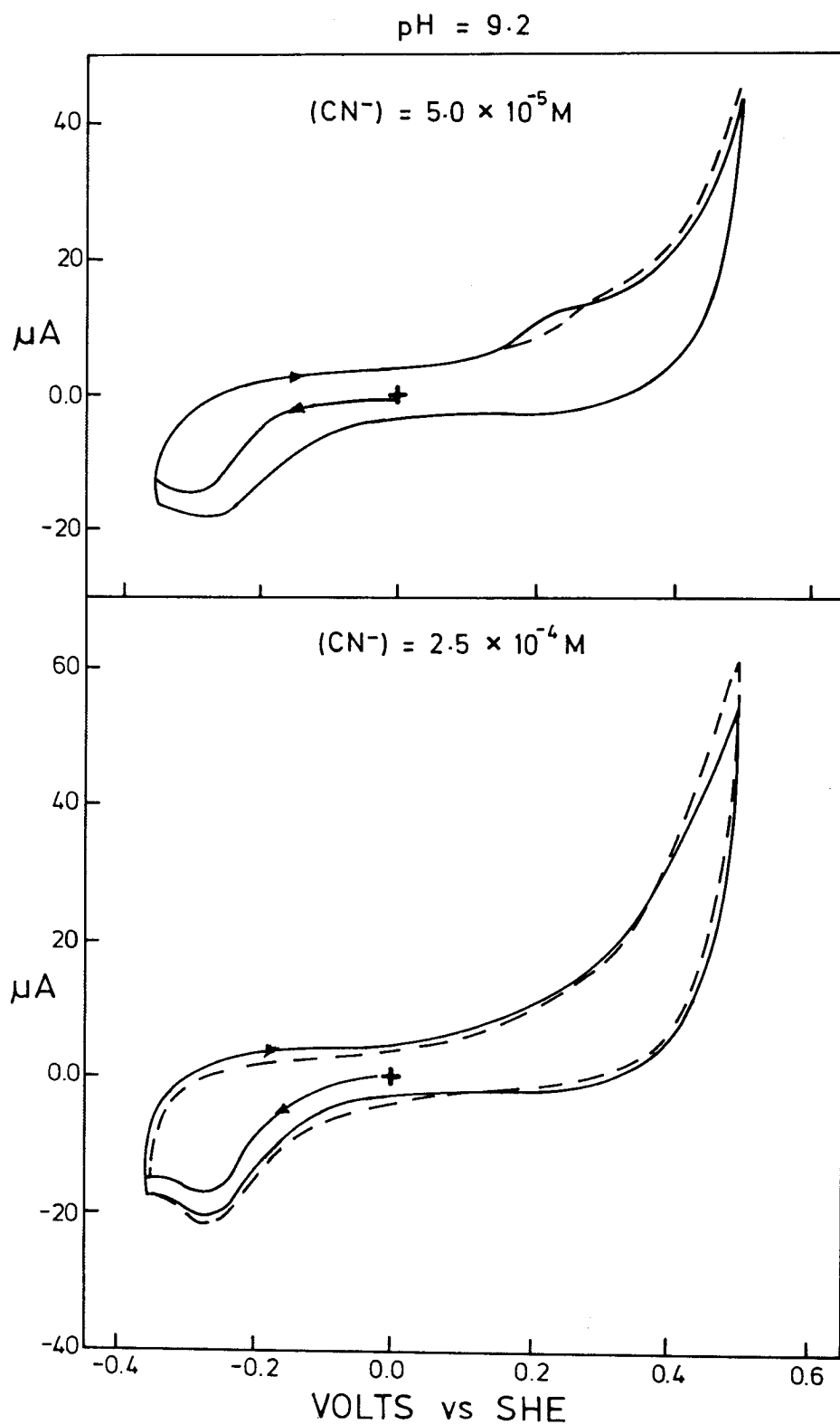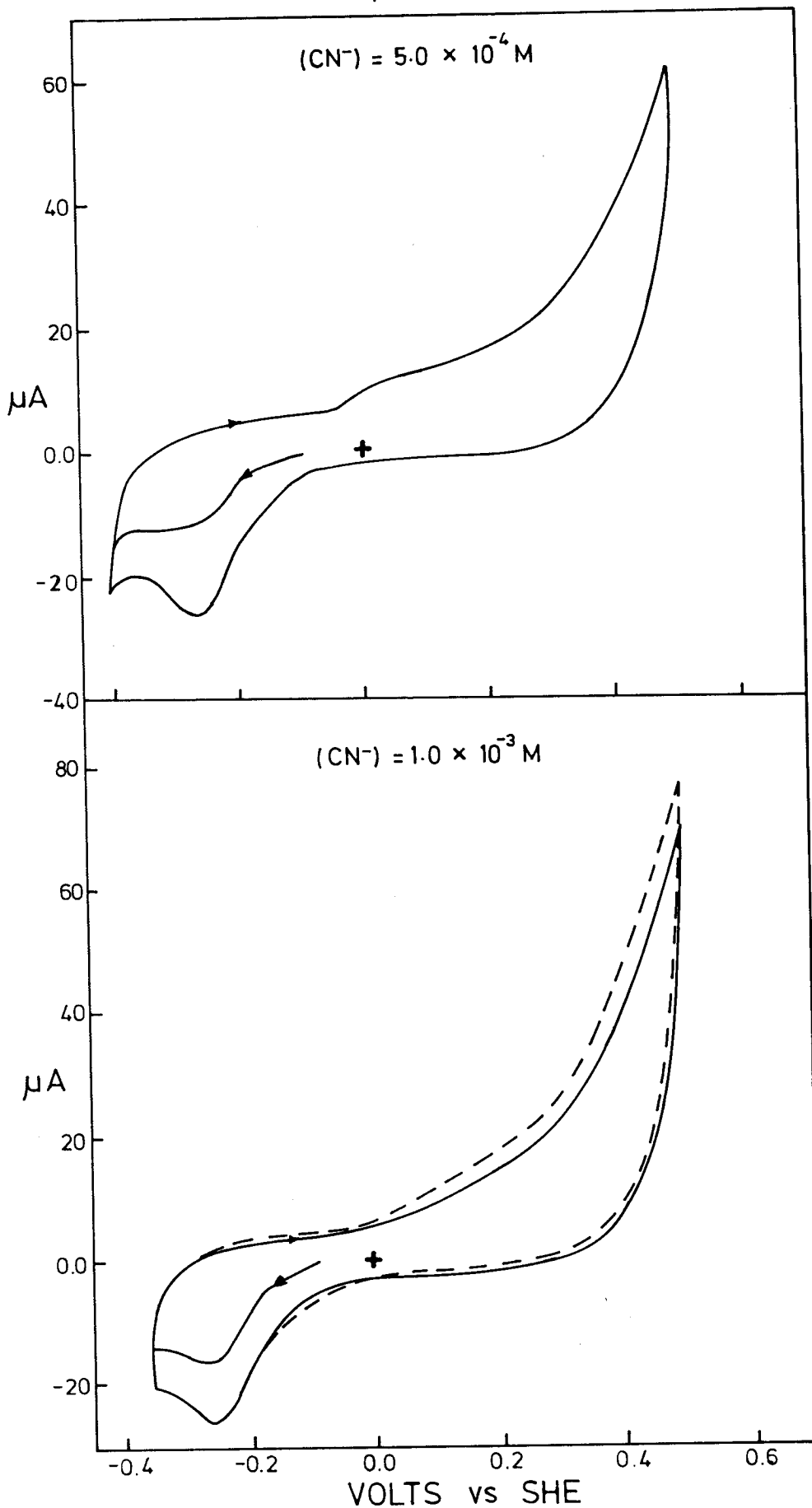
FIGURE 5.35: Cyclic voltammograms of chalcopyrite in buffer solutions at pH 11.0 containing varying concentrations of sodium cyanide.

CONSTANT XANTHATE

$(X^-) = 5.5 \times 10^{-4}$ M

$(CN^-) = 5.0 \times 10^{-5}$ M

$(CN^-) = 2.5 \times 10^{-4}$ M

$(CN^-) = 5.0 \times 10^{-4}$ M

$(CN^-) = 1.0 \times 10^{-3}$ M

μA
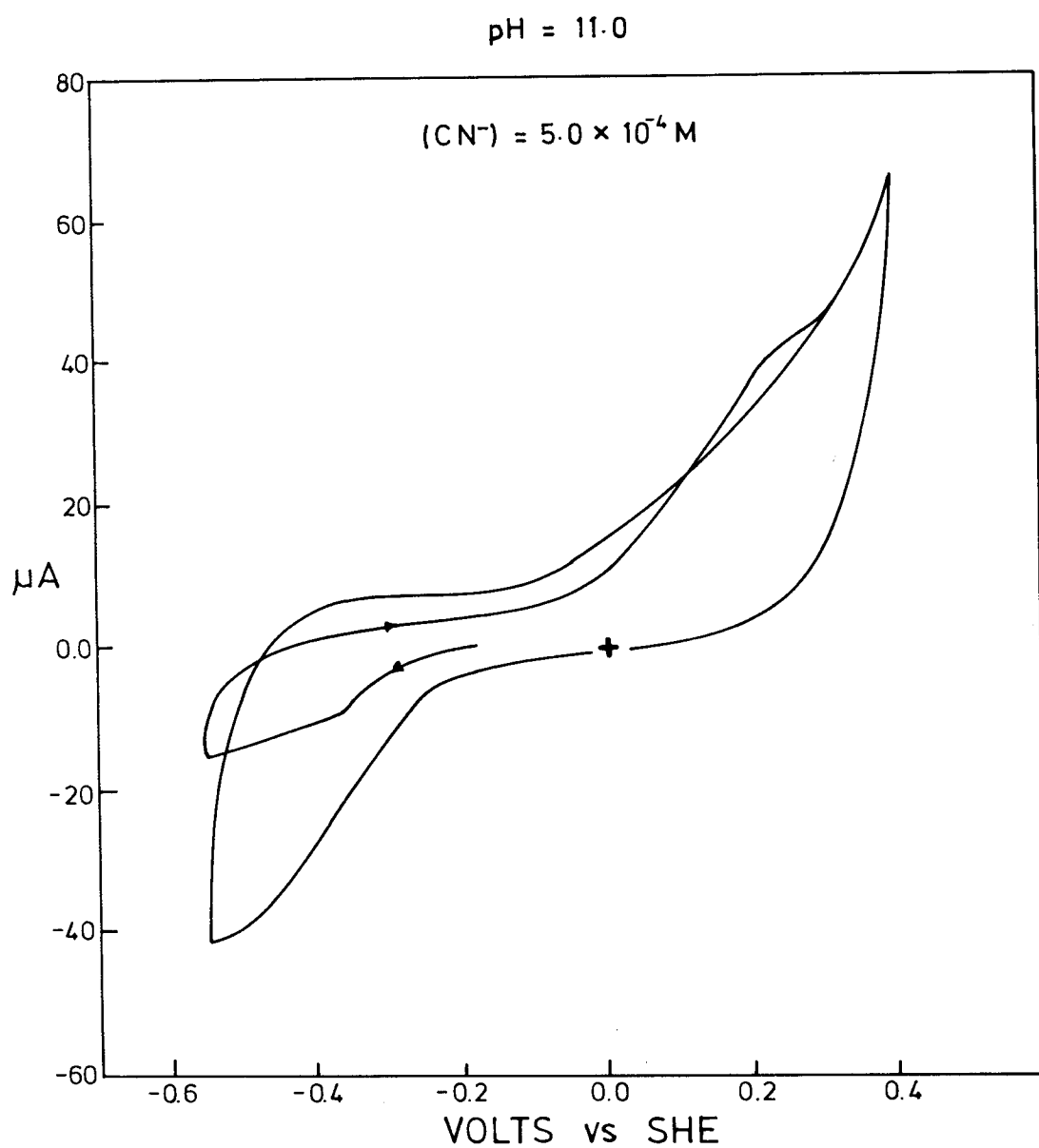
VOLTS vs SHE

FIGURE 5:36: Cyclic voltammograms of chalcopyrite in buffer
solutions at pH 7.0 containing a constant
amount of ethyl xanthate with different concentrations
of sodium cyanide.

The voltammograms in Figure 5.36 did not show that at a constant ethyl xanthate addition a similar process as when there was no xanthate occurred as the cyanide concentration increased. If anything, the major observable feature was the suppression of both the oxidation of the mineral and ethyl xanthate. However, as the cyanide concentration increased, the oxidation of the mineral took precedence. The bubble attachment ability of the mineral rapidly decreased with the increasing cyanide concentration. No observable attachment of bubbles was seen at a cyanide concentration of $5.0 \times 10^{-4} M$. The resulting cyanide complex as the cyanide concentration increased was therefore hydrophilic in nature and could cause the depression of chalcopyrite in a flotation pulp. There could be some ethyl xanthate ions which adsorbed on the surface of the mineral but did not oxidise to form di-ethyl dixanthogen. The only other process by which the mineral surface could acquire some hydrophobicity is by the formation of a metal xanthate most likely **cuprous ethyl xanthate.**[104] However, though this is recognised as being an important hydrophobic species in copper flotation, it was not verified that it's role was similar to that of lead ethyl xanthate which is responsible for the hydrophobicity in the galena- xanthate system. This behaviour was also observed by **Poling et al.**[106]

pH = 9·2

CONSTANT XANTHATE

$(X^-) = 5.5 \times 10^{-4} M$

$(CN^-) = 5.0 \times 10^{-5} M$

$(X^-) = 5.5 \times 10^{-4} M$

$(CN^-) = 2.5 \times 10^{-4} M$

VOLTS vs SHE
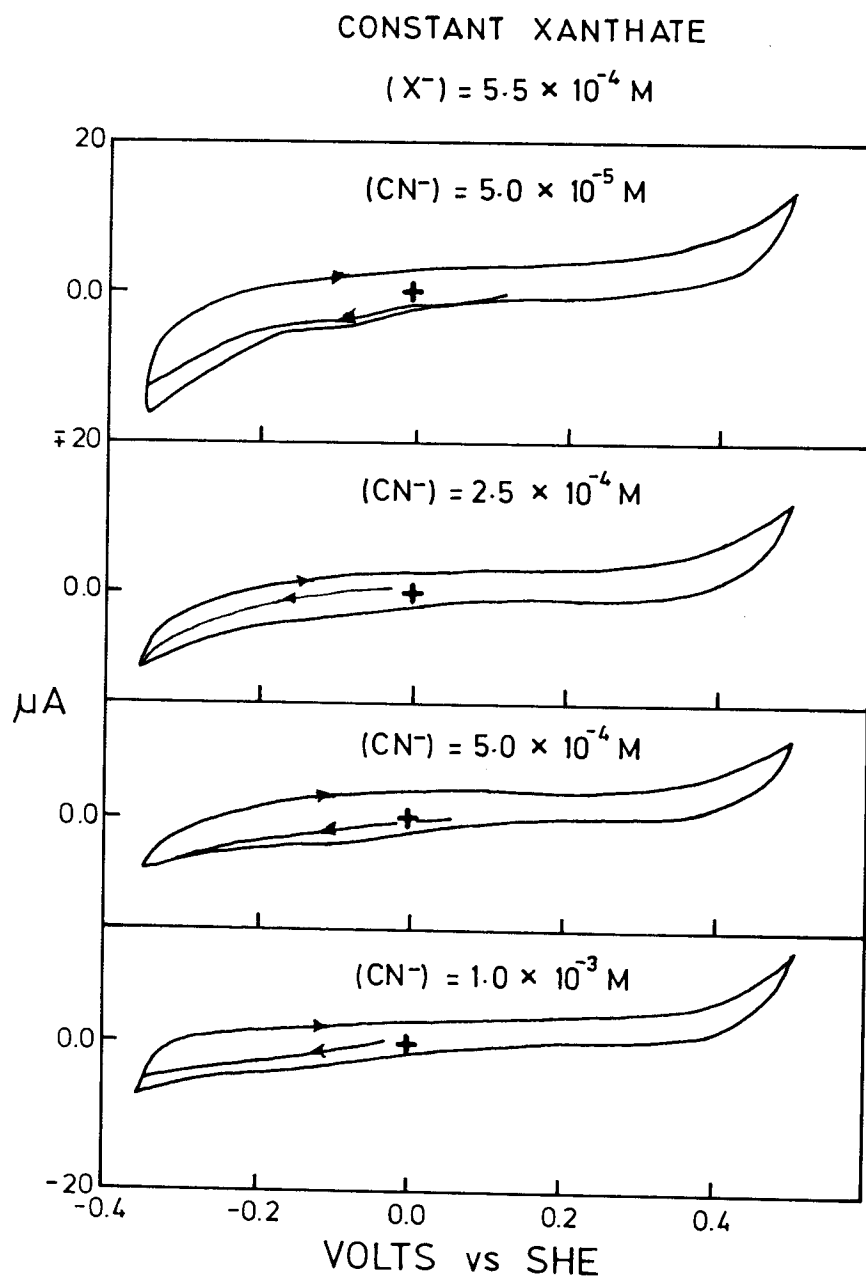
FIGURE 5:37: Cyclic voltammograms of chalcopyrite in buffer solutions at pH 9.2 containing a constant amount of ethyl xanthate with different concentrations of sodium cyanide.
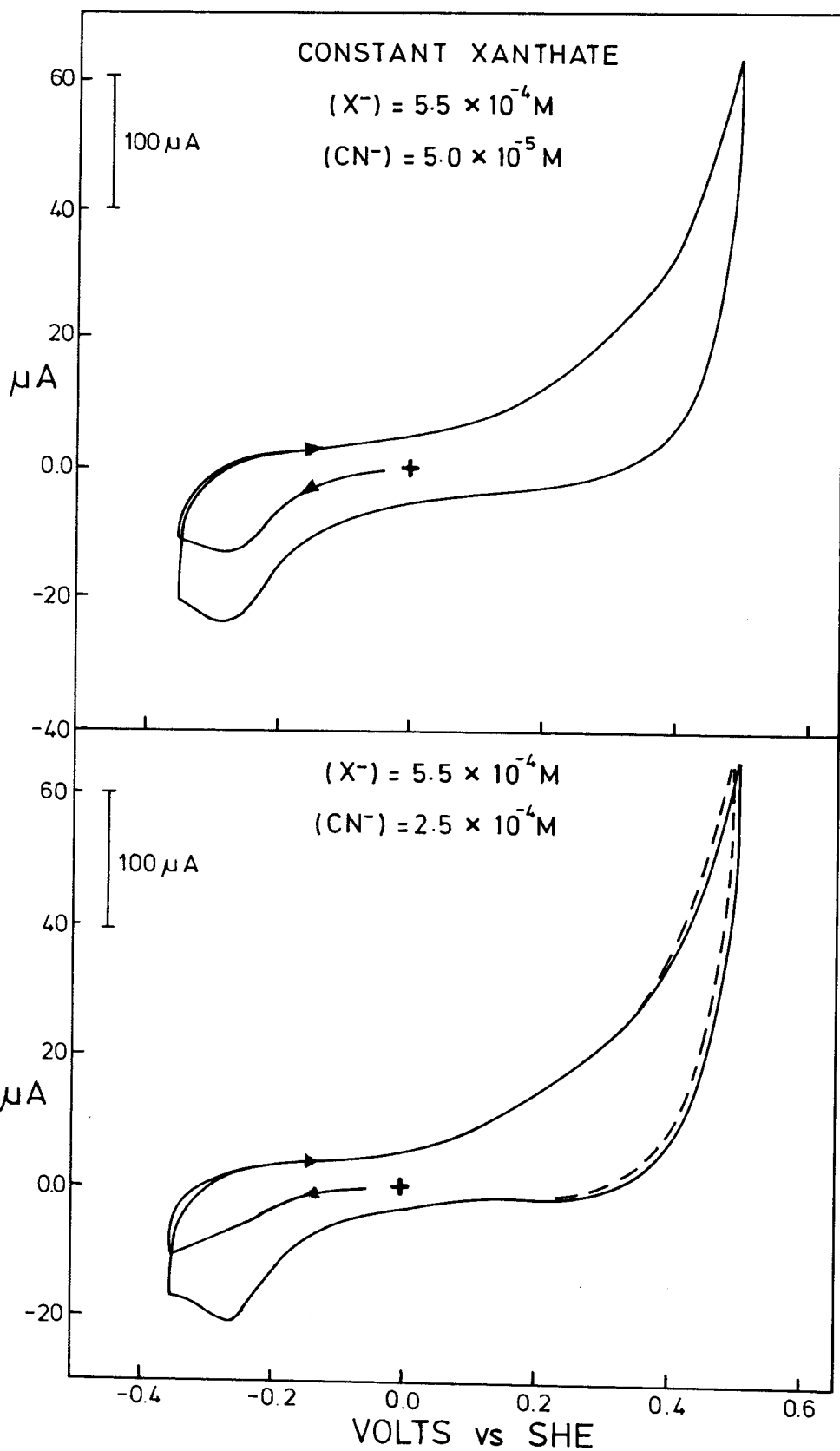
The voltammograms in Figure 5.37 suggested that it is likely that ethyl xanthate oxidation occurred alongsides with the anodic oxidation of the mineral. Furthermore, it appeared like that during the anodic oxidation there was competition between the oxidation of ethyl xanthate and cyanide ions. Significant bubble attachment was observed to at a cyanide concentration of 5.0 x 10^{-4}M. At lower cyanide concentration it is likely that the anodic oxidation process was such that the oxidation of ethyl xanthate to form surface hydrophobic species was favoured. The situation is different when cyanide was present well in excess of ethyl xanthate ions. Clearly the potential at which anodic oxidation began shifted to less anodic (more cathodic)potentials. This was attributed to cyanide interaction with the mineral surface. Thus this process was expected to be more favourable than ethyl xanthate oxidation as the cyanide concentration increased. Under these conditions, the mixed potential system was assumed to be that of the mineral surface oxidation and oxygen reduction leaving hydrophilic species on the surface of the mineral. This would explain the weak bubble attachment at this solution pH.

FIGURE 5.38: Cyclic voltammograms for chalcopyrite in a buffer solution at pH 9.2 containing a constant amount of cyanide with different concentrations of ethyl xanthate.

In Figure 5.38, the cyanide concentration was kept constant while that of potassium ethyl xanthate was increased to assess how the relative variation would affect the voltammetric behaviour of the mineral at pH 9.2. Clearly as the ethyl xanthate concentration was increased to $5.5 \times 10^{-3} M$, the anodic potential moved into the region where the oxidation of ethyl xanthate was possible. Indeed, bubbles were seen to adhere to the electrode when toe potentials were held well above the values reported for the anodic current flow. This observation collaborated with the view that under these experimental conditions anodic oxidation occurred as a competitive reaction as outlined above.

Figure 5.39 shows cyclic voltammograms for chalcopyrite at pH 11.0 with varying concentrations of cyanide at a constant concentration of ethyl xanthate. The potential for the oxidation of this mineral was further shifted to more cathodic potentials making it a more favourable process than the ethyl xanthate oxidation. Again as was observed at other pH values, anodic oxidation of the mineral accounted for the voltammetric currents as the cyanide concentration increased. At reasonably low cyanide concentration, the voltammetric behaviour appeared to be a compromise between the effect of both ethyl xanthate and cyanide.In fact, at low cyanide concentration, the ethyl xanthate oxidation was the main anodic reaction which accounted for the
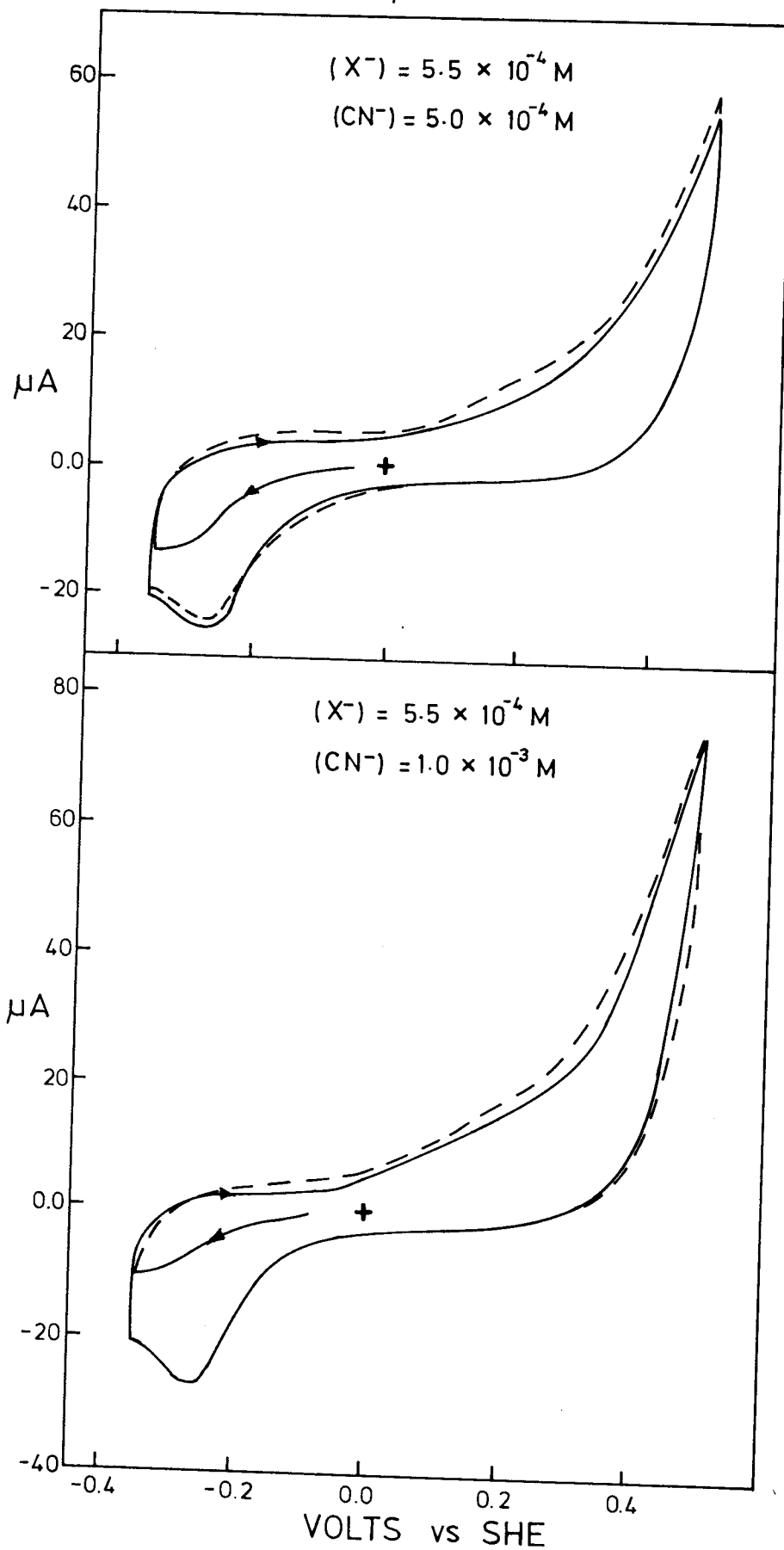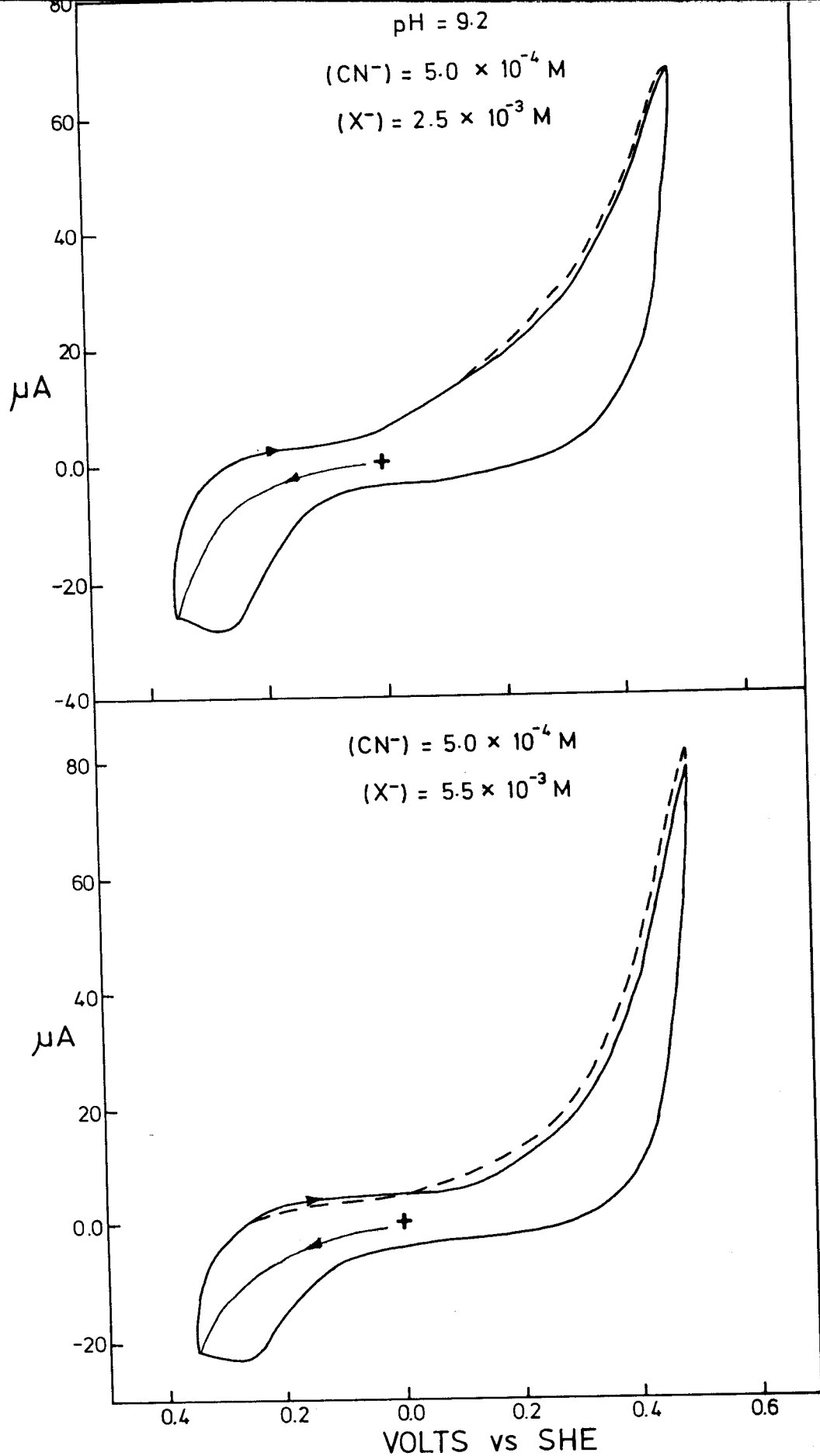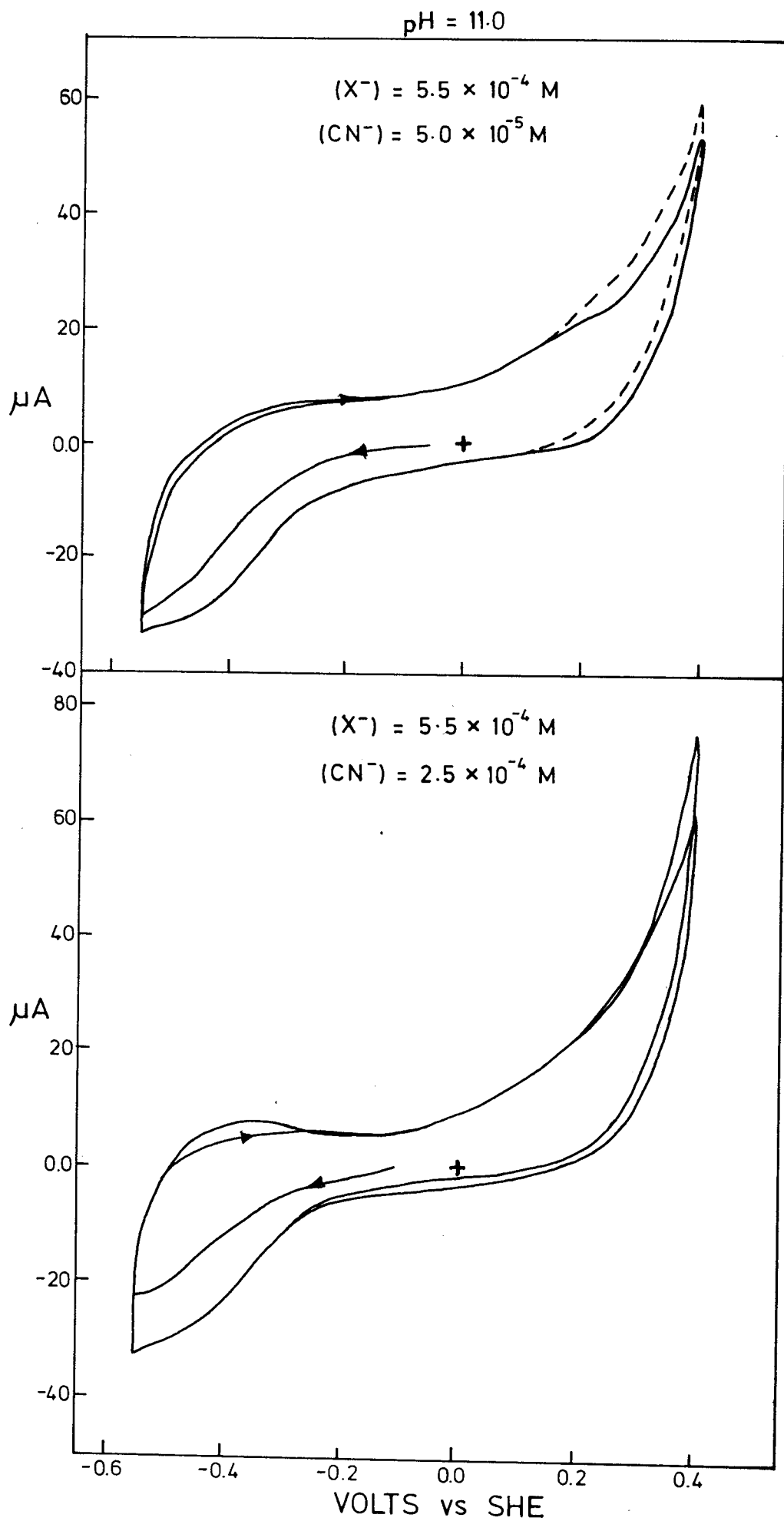
Figure 5.39
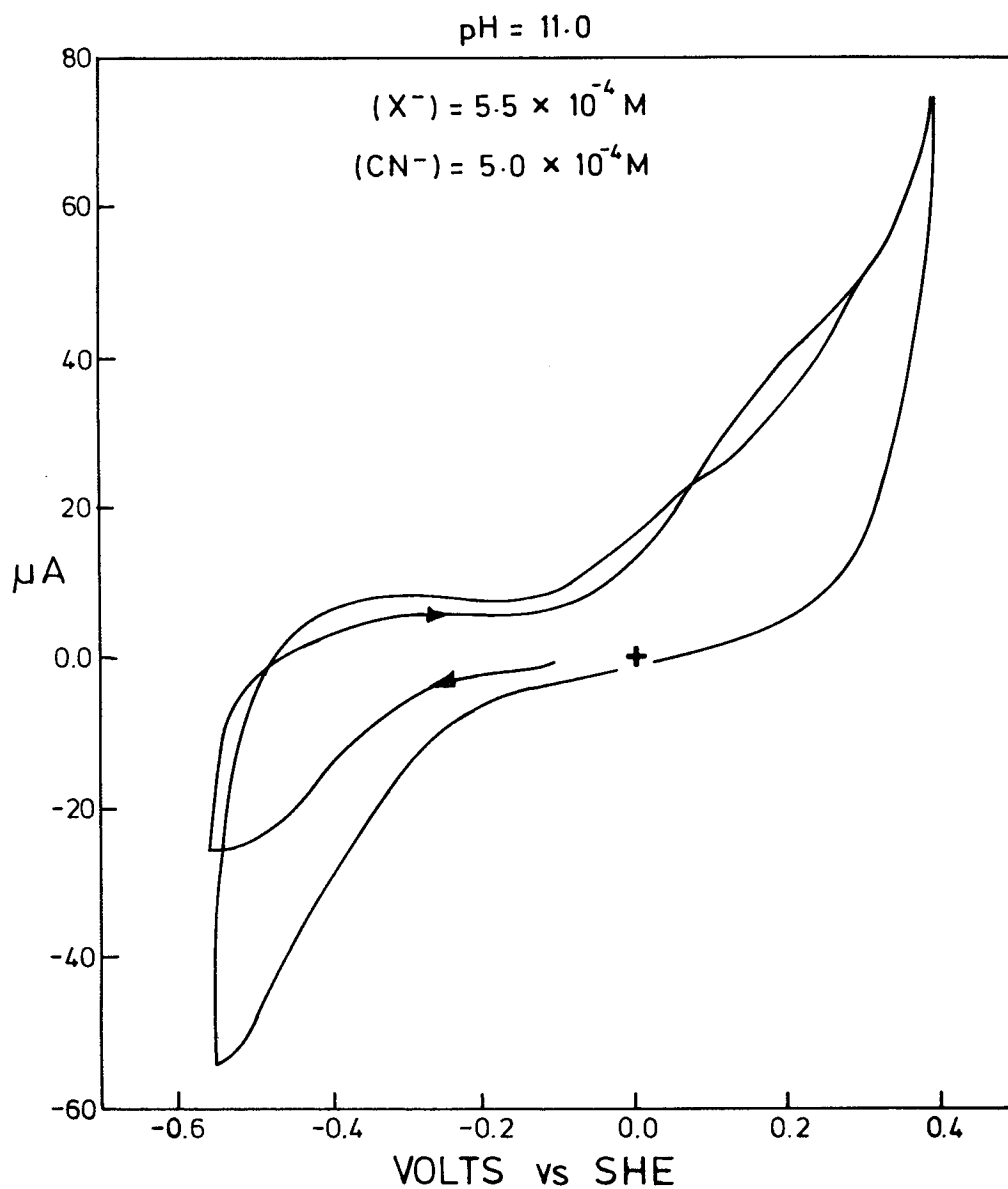
FIGURE 5.39: Cyclic voltammograms for chalcopyrite in a buffer solution at pH 11.0 containing a constant amount of ethyl xanthate with different concentrations of cyanide.

observed anodic response of the mineral electrode. Although the amount of ethyl xanthate oxidation products were probably restricted to a few monolayers, they did impart some hydrophobicity to the mineral electrode enabling it to weakly hold nitrogen bubbles when introduced in the cell.

In Figure 5.38 there was some indications that as the ethyl xanthate concentration increased, the anodic process due to cyanide oxidation was progressively replaced with the ethyl xanthate oxidation reaction. At sufficiently high concentration of ethyl xanthate, the effect of cyanide complexing reactions would probably be rendered ineffective.

The mode of depression of chalcopyrite by cyanide from the electrochemical point of view, would be one which involved the introduction of another anodic reaction which is more favourable than that of the collector oxidation. THis process would lead to the formation of surface species which tend to inhibit ethyl xanthate attachment to the mineral surface. The fact that anodic oxidation of the mineral in cyanide containing solutions occurred at lower potentials than that of ethyl xanthate oxidation, suggested that the depression action of cyanide on chalcopyrite is similar to that of alkali on pyrite. This behaviour was also noted by **Wark** **et al**[105] who correlated the reduction in the potential of a copper electrode in cyanide solutions with the depression of chalcopyrite.

5.2.3 EFFECT OF USING A LONG CHAIN HYDROCARBON COLLECTOR SUCH AS POTASSIUM AMYL XANTHATE.

In order to assess the role of less specific long chain xanthate collectors in flotation characteristics of carrollite and chalcopyrite mineral electrodes, potassium amyl xanthate was also employed in the study of their voltammetric behaviour using the same techniques.

The voltammetric behaviour of a carrollite electrode immersed in deoxygenated solutions containing various concentrations of amyl xanthate is shown in Figure 5.40 for a solution at pH 7.0. The corresponding response in solutions of various concentrations of cyanide with a constant addition of amyl xanthate is shown in Figure 5.41.

The main feature in Figure 5.40 is the shift in the xanthate oxidation curve to less anodic potentials. As the xanthate concentrations increased, this became quite apparent. Judging from the limiting anodic currents passed, it appeared like the reactions occurring on the mineral electrode proceeded with ease when compared with that obtained in the presence of ethyl xanthate (refer to Figure 5.19). The electrode was made sufficiently water repellant and bubble readily stuck to the mineral electrode.

When cyanide was added as shown in Figure 5.41, the process of anodic oxidation of amyl xanthate was considerably slowed down at even low concentrations of cyanide. However, this effect appeared to diminish as the concentration of cyanide increased. The

XANTHATE

KAX = 5.5×10^{-5} M

KAX = 5.5×10^{-4} M

KAX = 2.75×10^{-3} M
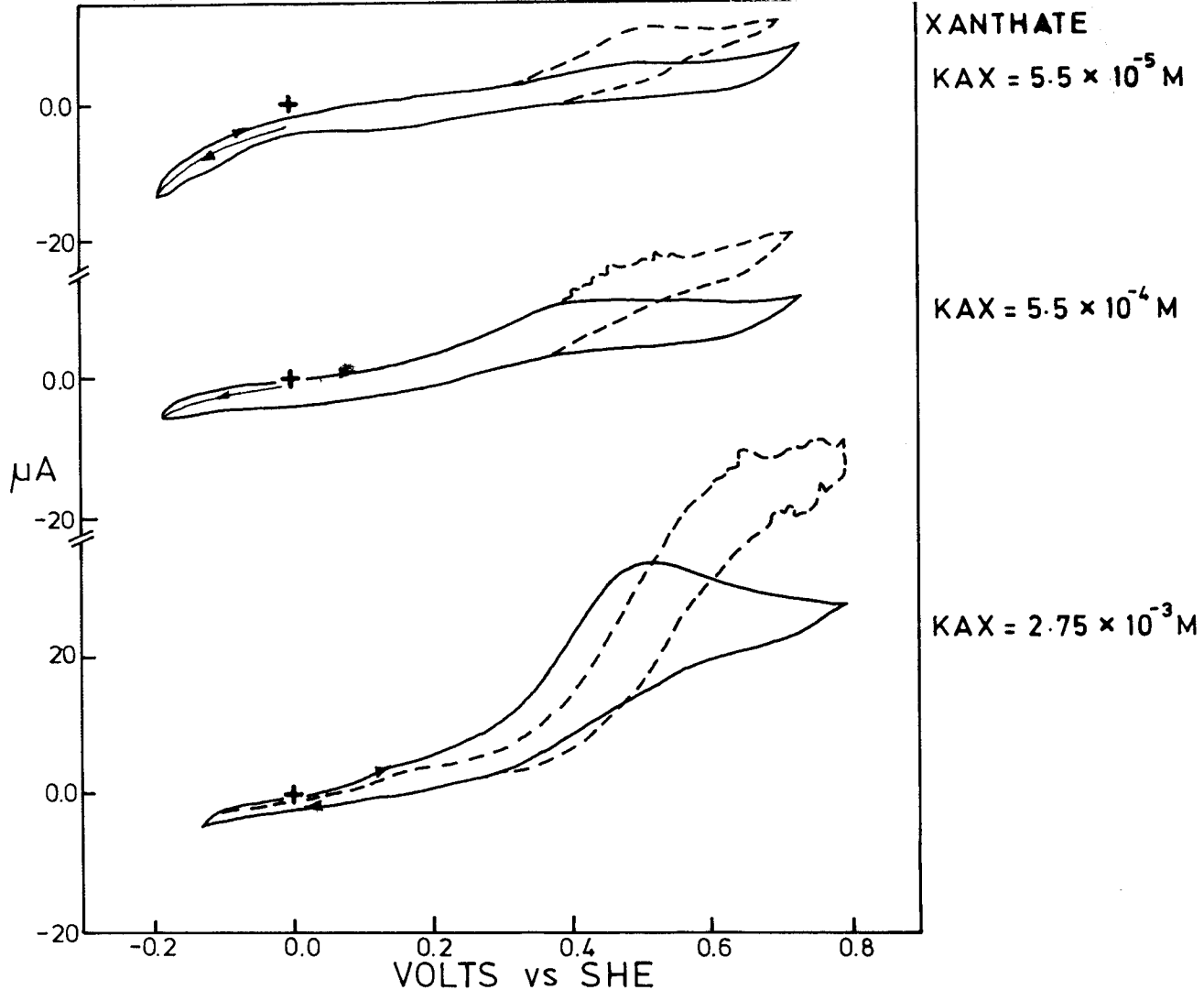
Figure 5.40:   Cyclic voltammograms of carrollite in aqueous
solutions containing varying concentrations of
potassium amyl xanthate at pH 7.0 .

KAX = 2.75×10^{-3} M
$(CN^-) = 5.0 \times 10^{-5}$ M

KAX = 2.75×10^{-3} M
$(CN^-) = 2.5 \times 10^{-4}$ M
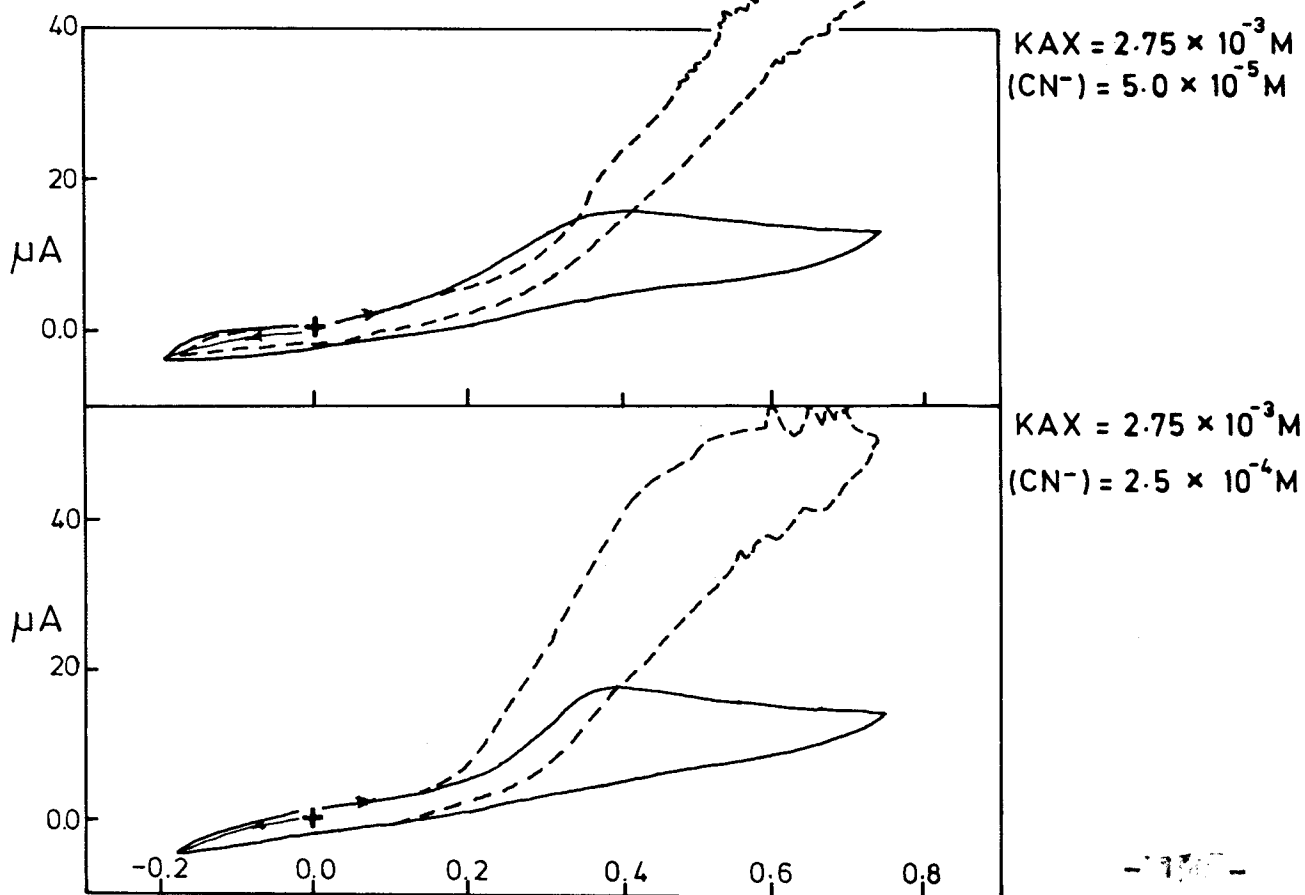
FIGURE 5.41: Cyclic voltammograms of carrollite in aqueous
solutions at pH 7.0 containing various
concentrations of cyanide with a constant addition
of amyl xanthate.

voltammograms also show that the anodic process was shifted to more anodic potentails at which the electrode showed only weak bubble attachment properties. As cyanide concentration increased, the anodic oxidation of the mineral would probably have dominated and because of this the electrode was expected to have remained hydrophilic.

Figure 5.42, show the voltammograms of a carrollite mineral electrode in amyl xanthate at pH 9.2. The ease with which the amyl xanthate could be oxidised on the mineral seemed to have diminished. However, at high amyl xanthate concentration, the anodic wave appeared to commence at about the same potentials as that observed at pH 7.0. Bubbles showed strong attachment to the mineral electrode. This was due to hydrophobic species which formed on the surface of the mineral.

Figure 5.43, shows the voltammetric behaviour of the carrollite mineral electrode in a solution at pH 9.2, containing a constant amyl xanthate concentration with varying concentration of cyanide. There was enhanced oxidation of the mineral in the presence of cyanide. this resulted in the mineral electrode becoming water 'loving'.

The voltammetric behaviour of a carrollite mineral electrode immersed in various concentrations of potassium amyl xanthate at pH 11.0 is shown in Figure 5.44. The anodic current flow occurred at a potential which could be identified with amyl xanthate oxidation. The anodic current peak increased with amyl xanthate

FIGURE 5.43: Cyclic voltammograms of carrollite in aqueous solutions at pH 9.2 containing varying concentrations of cyanide and constant amyl xanthate content.

KAX = 5.5 × 10⁻⁵ M

KAX = 5.5 × 10⁻⁴ M

KAX = 2.75 × 10⁻³ M

VOLTS vs SHE

169
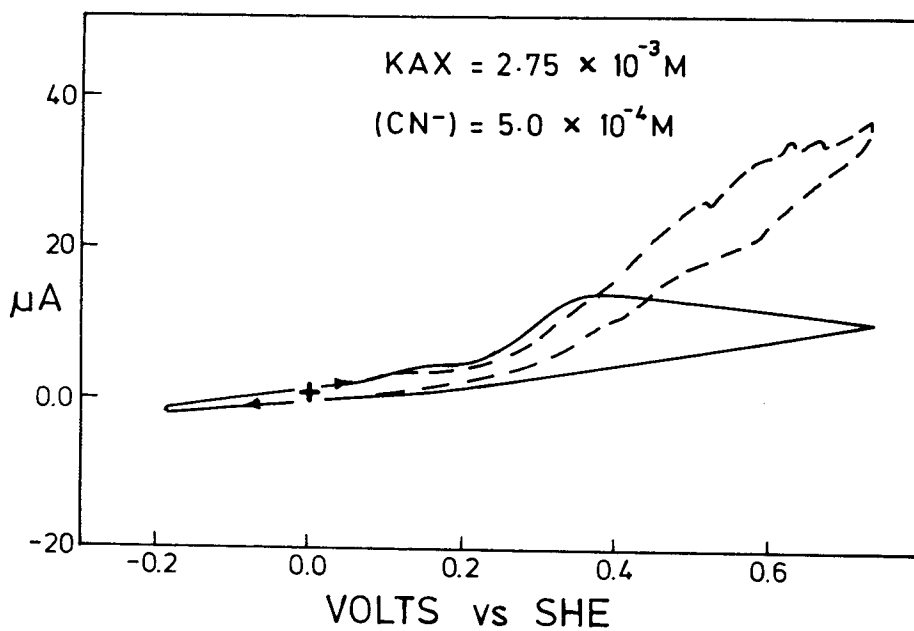
FIGURE 5.44: Cyclic voltammograms of enargite in aqueous solutions at pH 11.0 containing varying concentrations of amyl xanthate.

concentration. The anodic currents due to the oxidation of xanthate were greatly inhibited by small concentrations of cyanide, while the oxidation of the mineral appeared to have been enhanced. This can be seen in Figure 5.45 which shows the voltammograms of carrollite in various concentrations of cyanide at a constant concentration of amyl xanthate. Similar behaviour had also been observed when ethyl xanthate was used. Although oxidation of the mineral was dominant, there was also some oxidation of amyl xanthate. This reaction was, however, so slow that it did not produce sufficient hydrophobicity to support bubble attachment on the electrode. The depression of carrollite seemed to be greatly enhanced at high pH values of solutions. It is possible that hydroxyl ions did play a significant role in effecting this depressant action. The fact that even at high cyanide concentrations weak bubble attachment was observed, however, implied that some hydrophobic species were still available on the mineral surface and would lead to some flotation in actual flotation practice.

The voltammetric behaviour of a chalcopyrite mineral electrode immersed in a solution at pH 7.0, containing varying concentration of amyl xanthate is shown in Figure 5.46 . The anodic currents showed that this collector did not readily oxidise on this mineral as was the case with ethyl xanthate. The effect of cyanide addition is shown in Figure 5.47. At fist sight,

FIGURE 5.45   Cyclic voltammograms of carrollite in aqueous solutions at pH11.0 containing varying concentrations of amyl xanthate.

KAX = 2.75 × 10^{-3} M
(CN⁻) = 2.5 × 10^{-4} M

VOLTS vs SHE

KAX = 2.75 × 10^{-3} M
(CN⁻) = 5.0 × 10^{-4} M

VOLTS vs SHE

FIGURE 5.45 : Cyclic voltammograms of carrollite in aqueous
solutions at pH11.0 containing varying
concentrations of amyl xanthate.

FIGURE 5.46: Cyclic voltammograms of chalcopyrite in aqueous solutions at pH 7.0 containing varying concentrations of amyl xanthate.
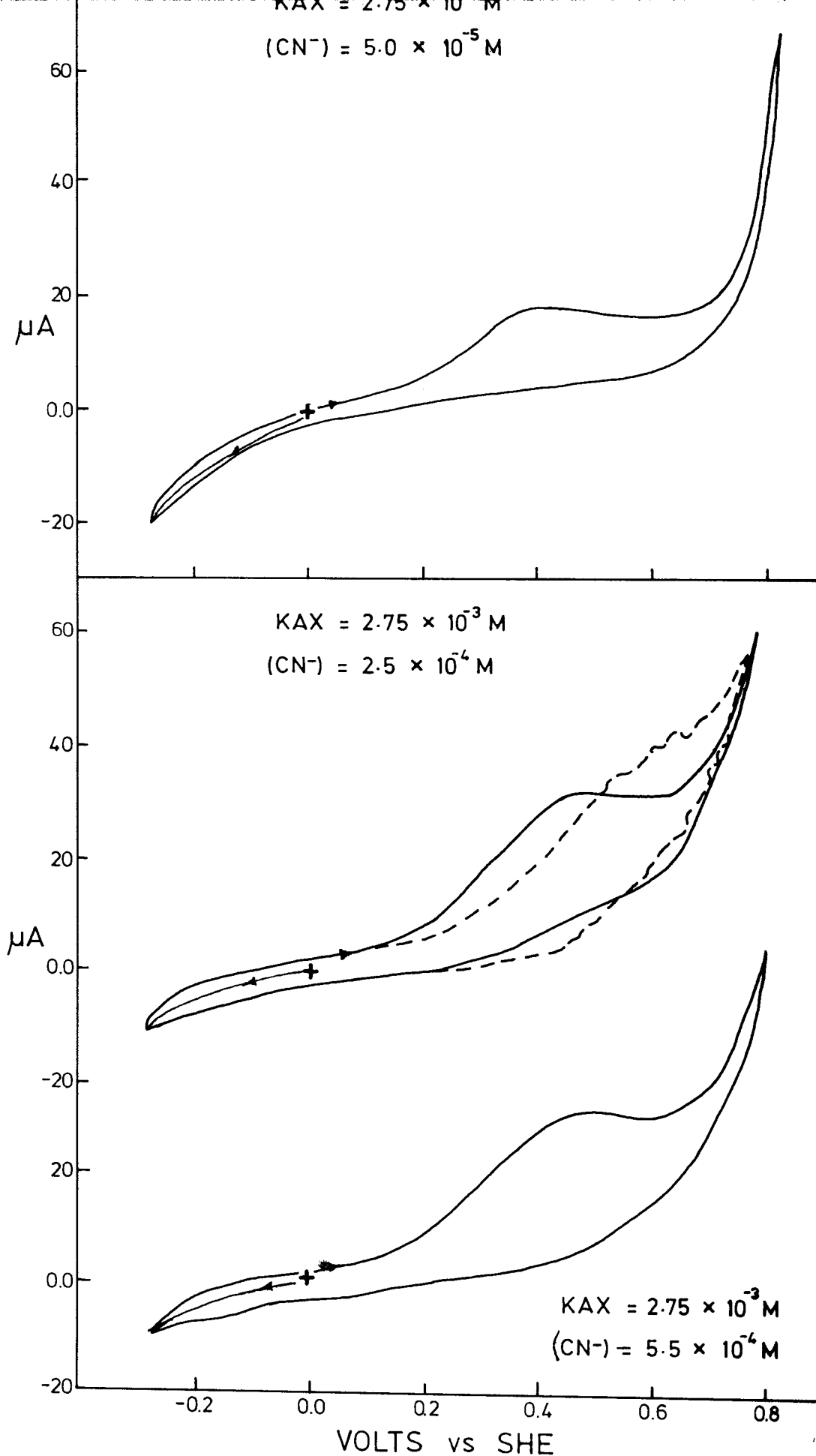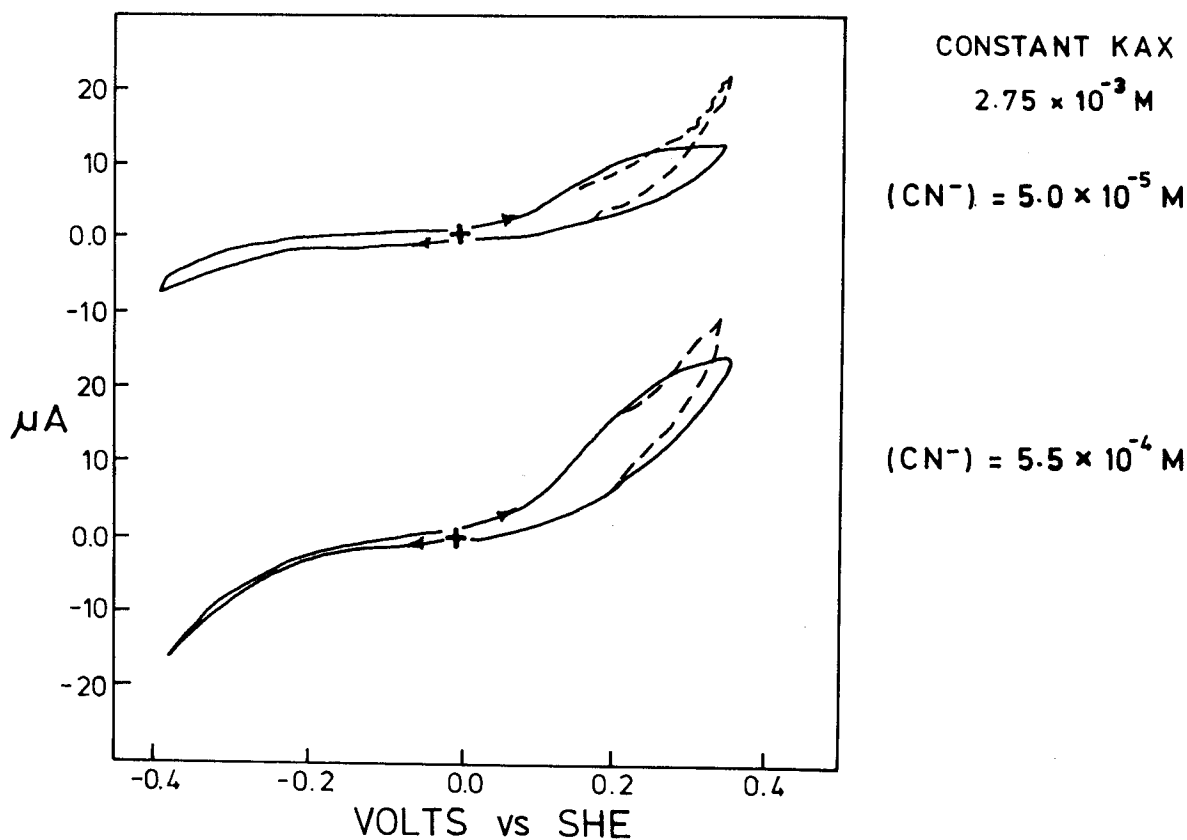

FIGURE 5.47: Cyclic voltammograms of chalcopyrite in aqueous solutions at pH 7.0 containing varying concentration of sodium cyanide with a constant concentration of amyl xanthate.

it appears that, the main effect of cyanide was to enhance the anodic process, which could be due to the complexing capability of cyanide of any ionic species which readily formed cyanide complexes. The reduction of whatever cyanide products formed during the anodic potential sweep, appeared obscure. No evident reduction peaks could be assigned to the reduction process. however, on making the electrode more anodic on the positive scan the voltammetry retracted with no appearance of additional peaks. This implied that the product of anodic oxidation was reduced on the negative scan. The nature of the product on the mineral electrode is hydrophilic in type, since no noticeable bubble attachment occurred on the electrode surface.

The voltammetric behaviour of chalcopyrite in solution of pH valve 9.2 containing similar concentration, the voltammetric response was due mostly to the mineral oxidation. The anodic peak observed at about 0.6V was due to further oxidation of the mineral probably by reaction(5.18). The reduction peak observed at about-0.15V could be due to the reduction of the oxidation product. As the xanthate concentration increased, there was an oxidation.This anodic wave shifted to more negative potentials in compatibility with the xanthate/dixanthogen couple as the xanthate
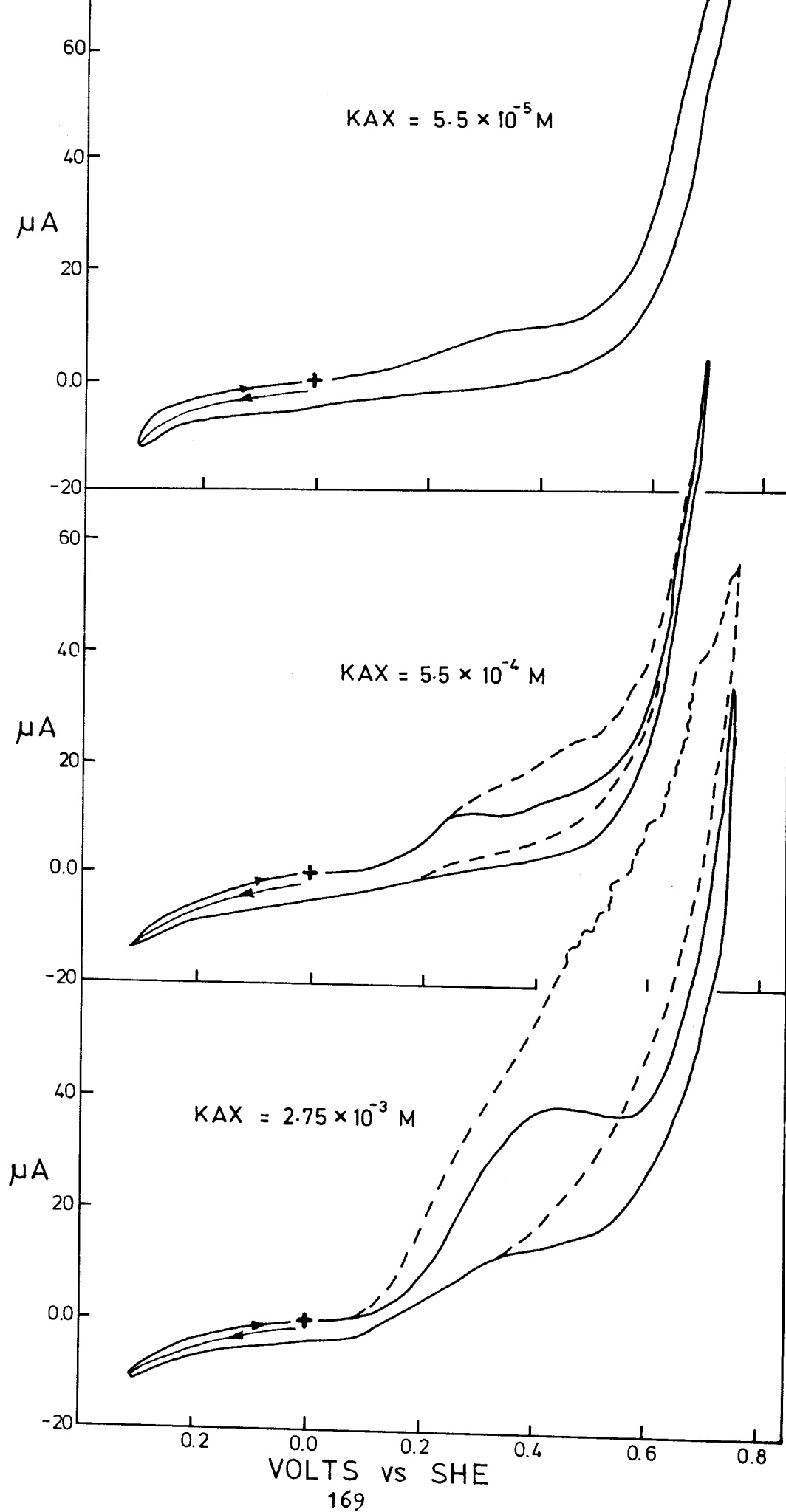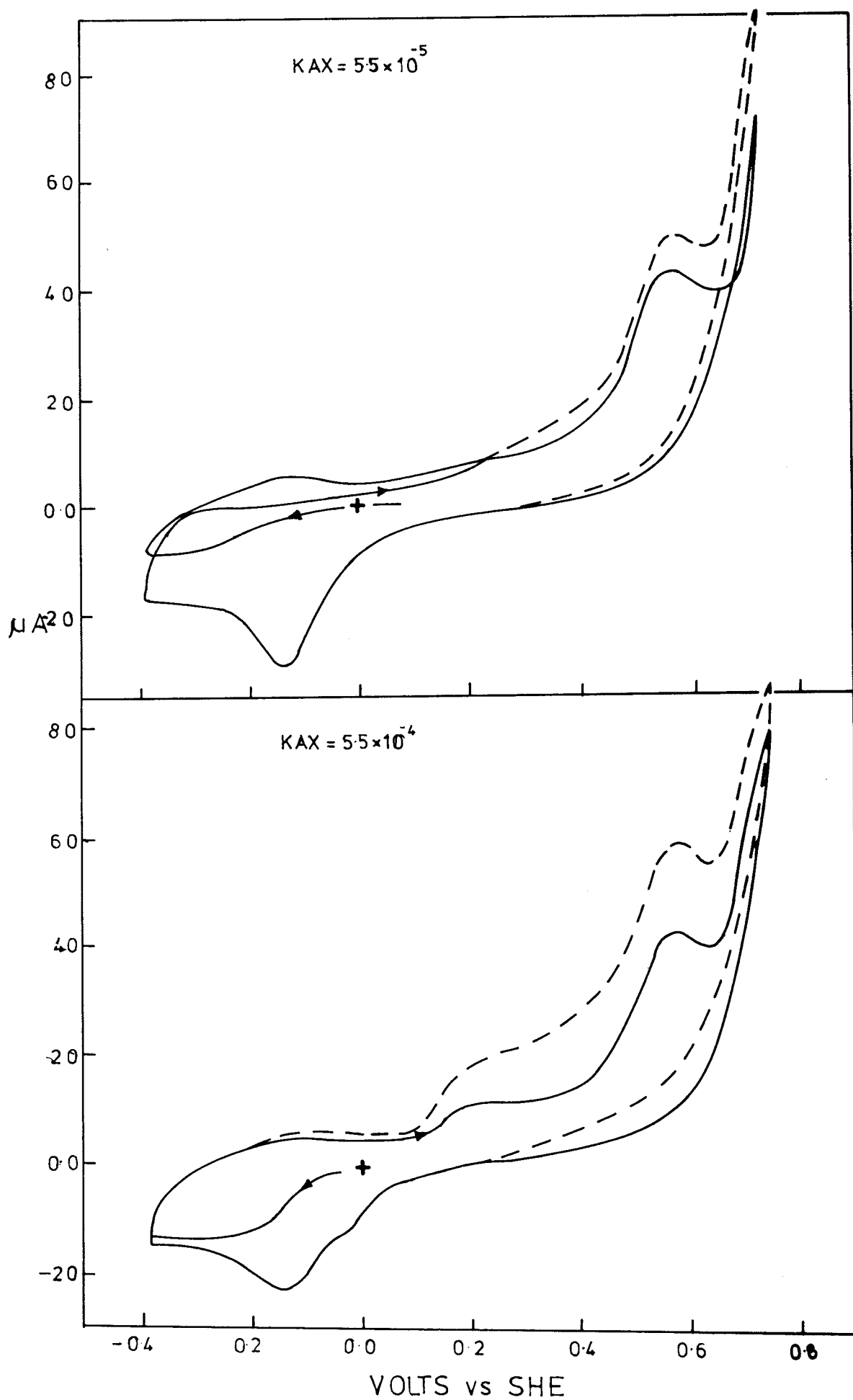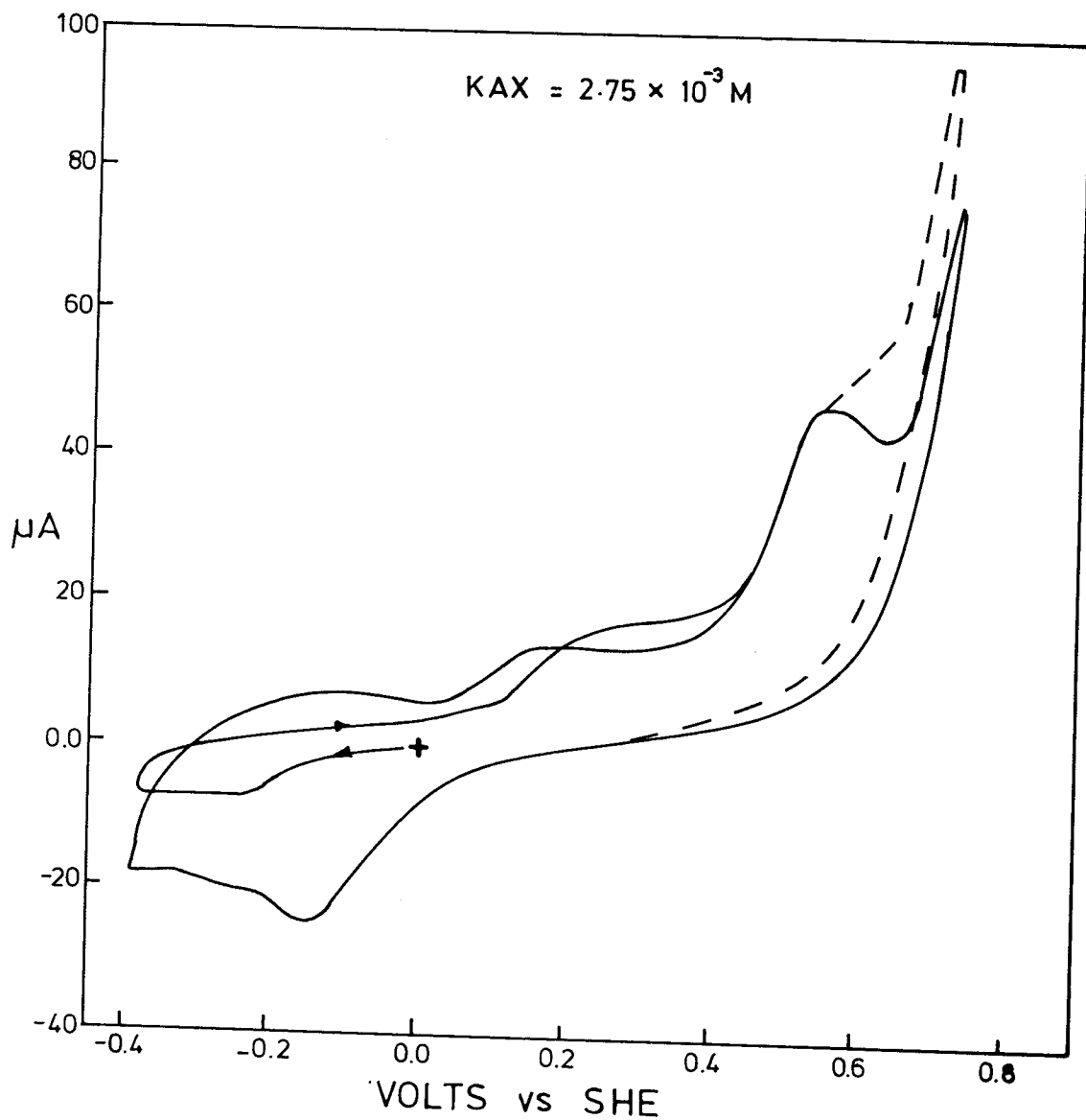
Figure 5.48

FIGURE 5.48; Cyclic voltammograms of chalcopyrite in aqueous
solutions at pH 9.2 containing varying
concentrations of amyl xanthate.

concentration increased. However, bubbles of nitrogen still showed weak attachment on the mineral electrode. The oxidation reaction may have therefore resulted in products which were not necessarily hydrophobic. When cyanide was added, the anodic wave assumed to be due to xanthate oxidation was completely eliminated at about 5.0×10^{-4} M cyanide concentration as in Figure 5.49 shows. The peak which was assigned to further oxidation of the mineral increased with cyanide concentration. The anodic wave due to the anodic oxidation of the mineral was decreased to lower potentials so that it occurred faster than the oxidation of amyl xanthate.

Figure 5.50 show cyclic voltammograms of a chalcopyrite mineral electrode in a solution at pH 11.0 with different concentrations of amyl xanthate. The anodic oxidation of the mineral was replaced by a xanthate oxidation wave and the electrode became sufficiently water repellant at higher amyl xanthate concentrations to give strong bubble attachment.
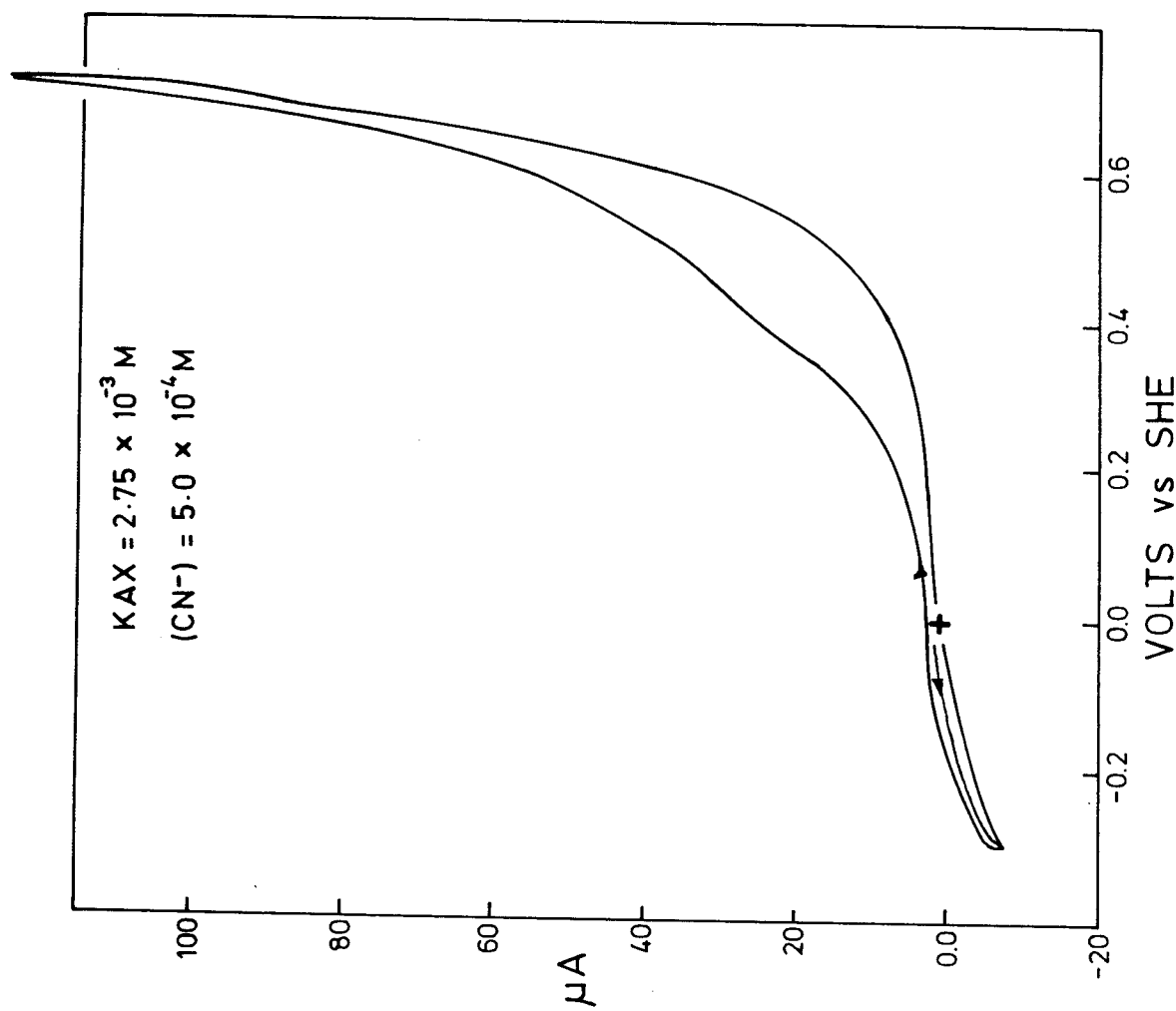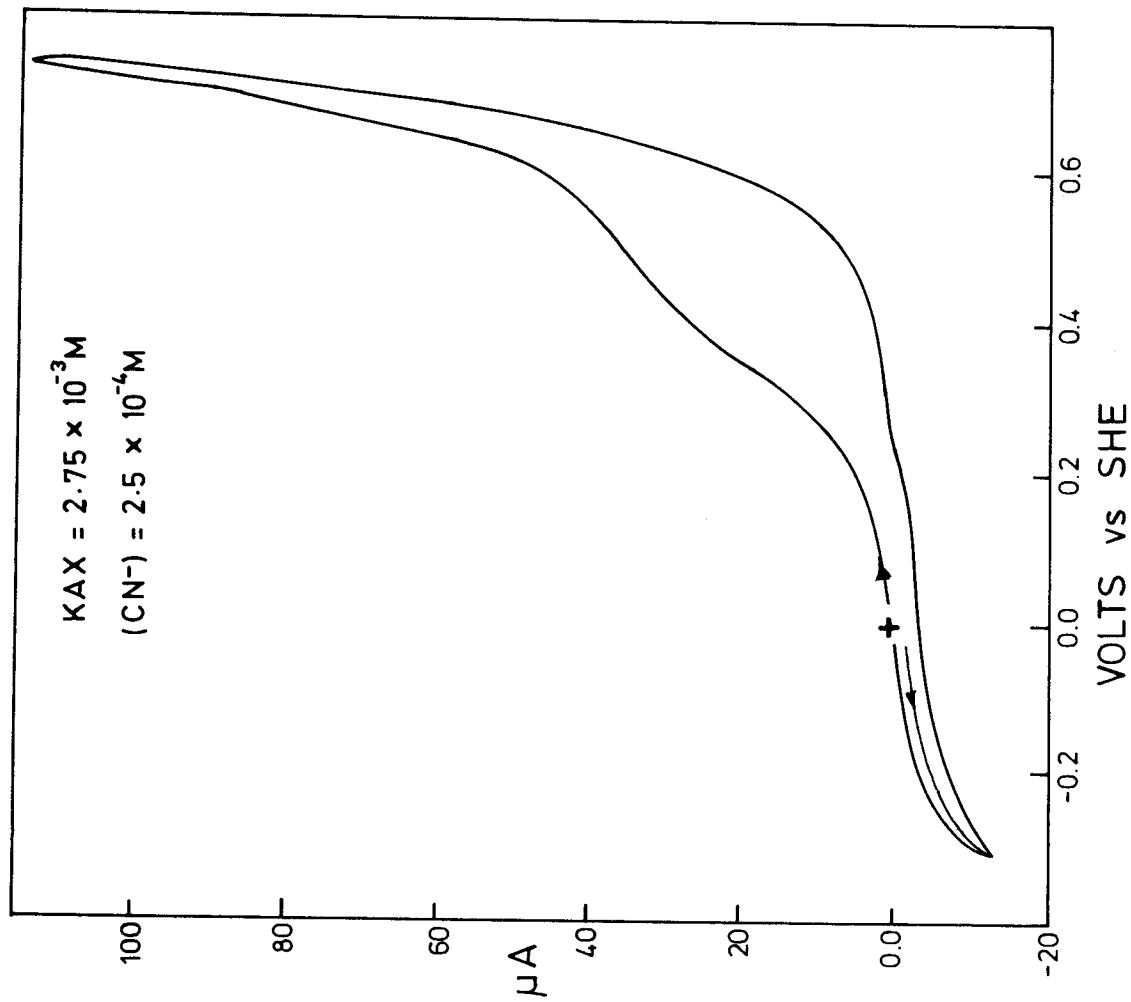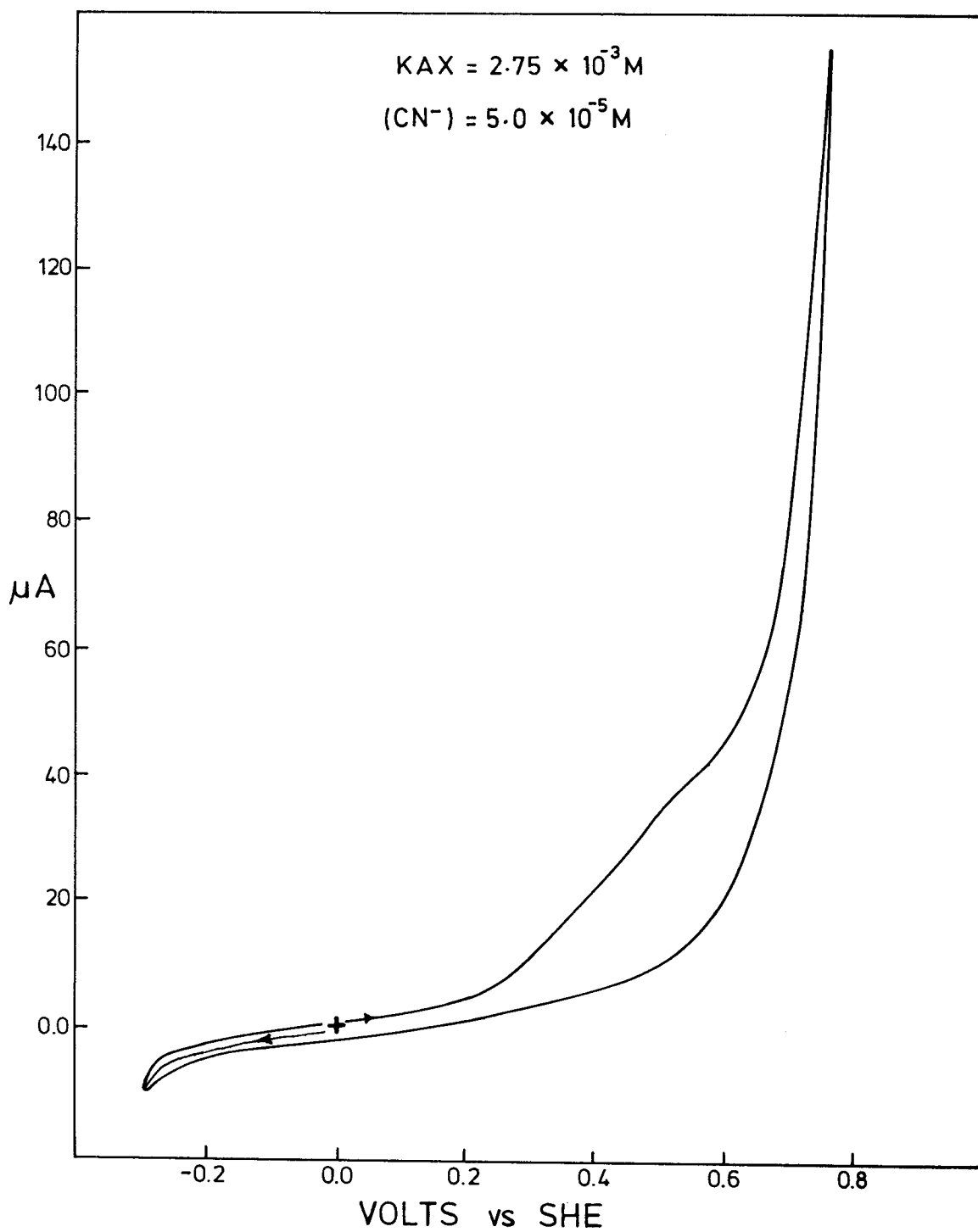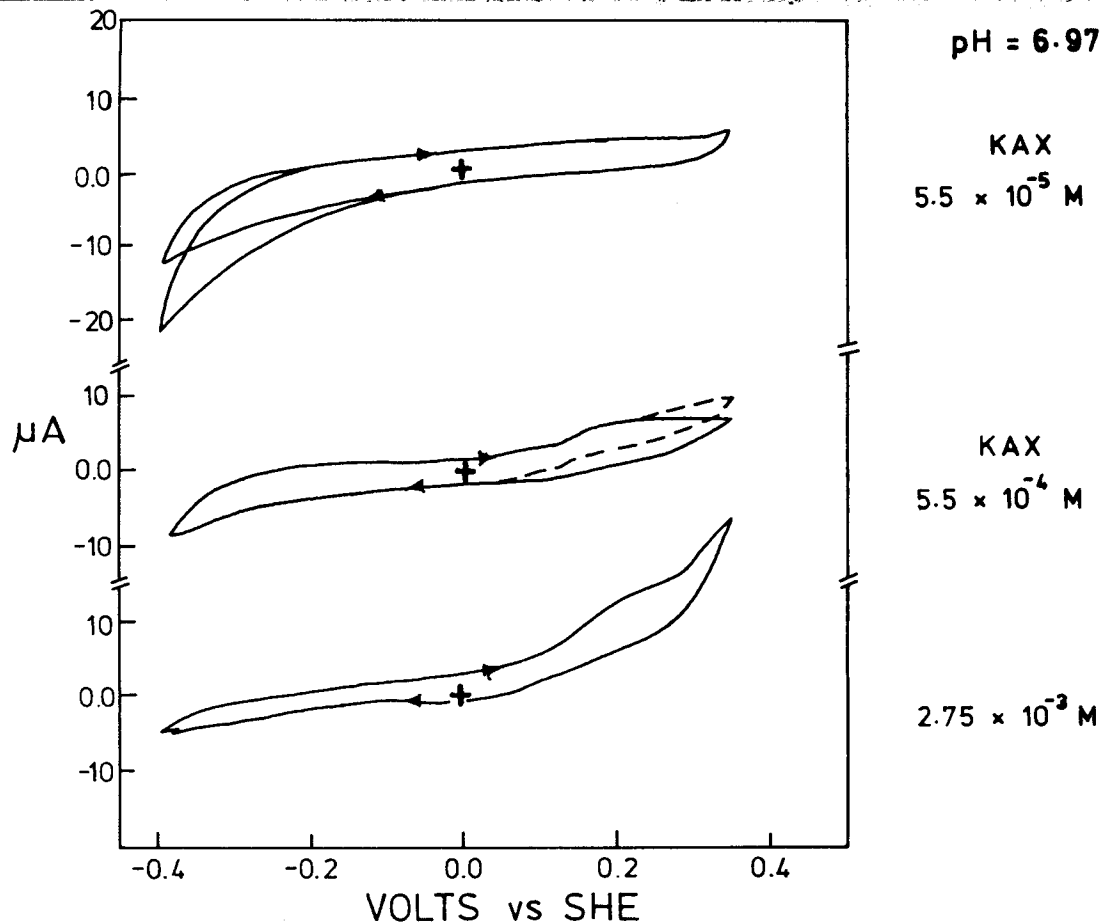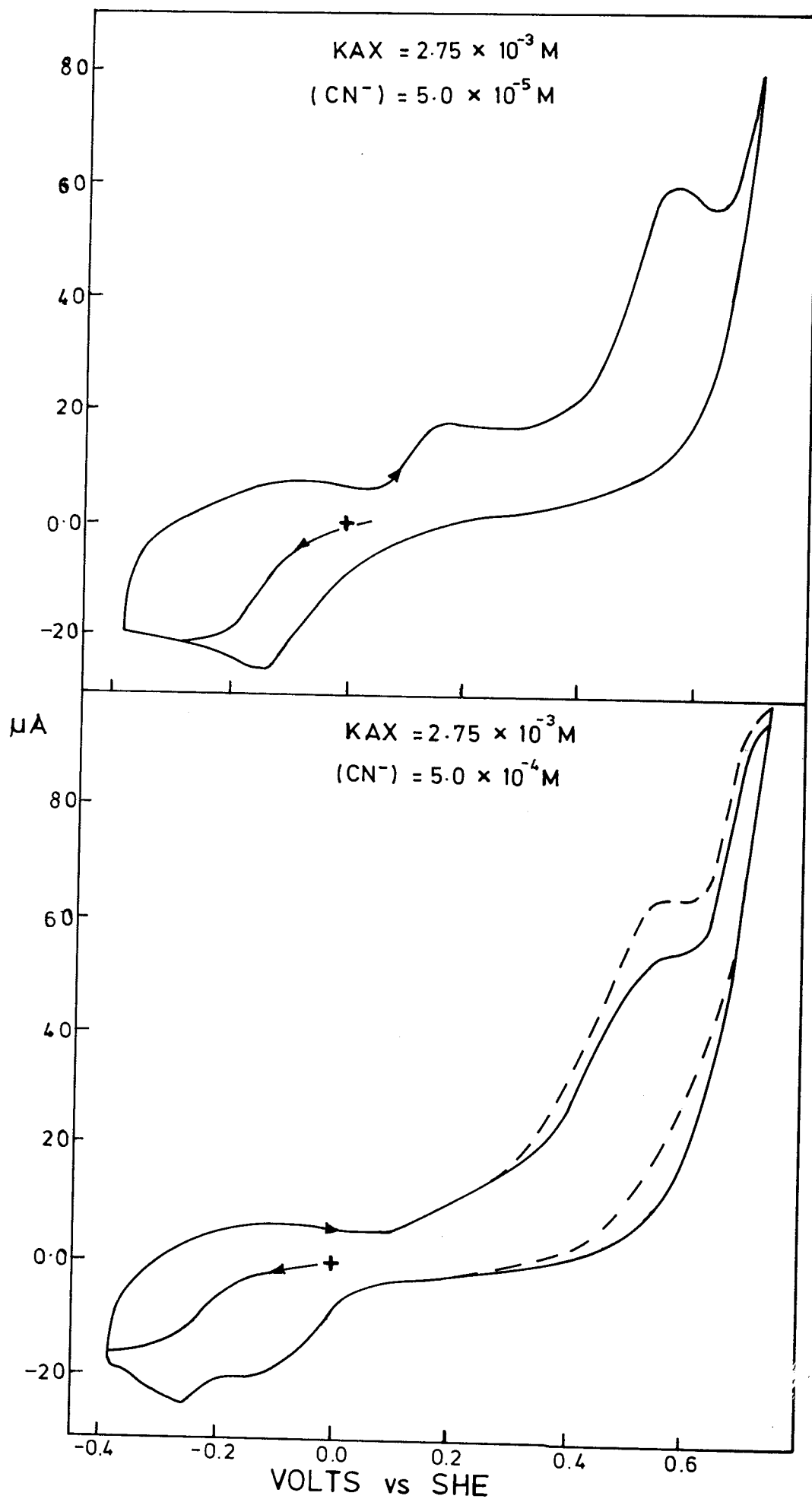
Figure 5.49
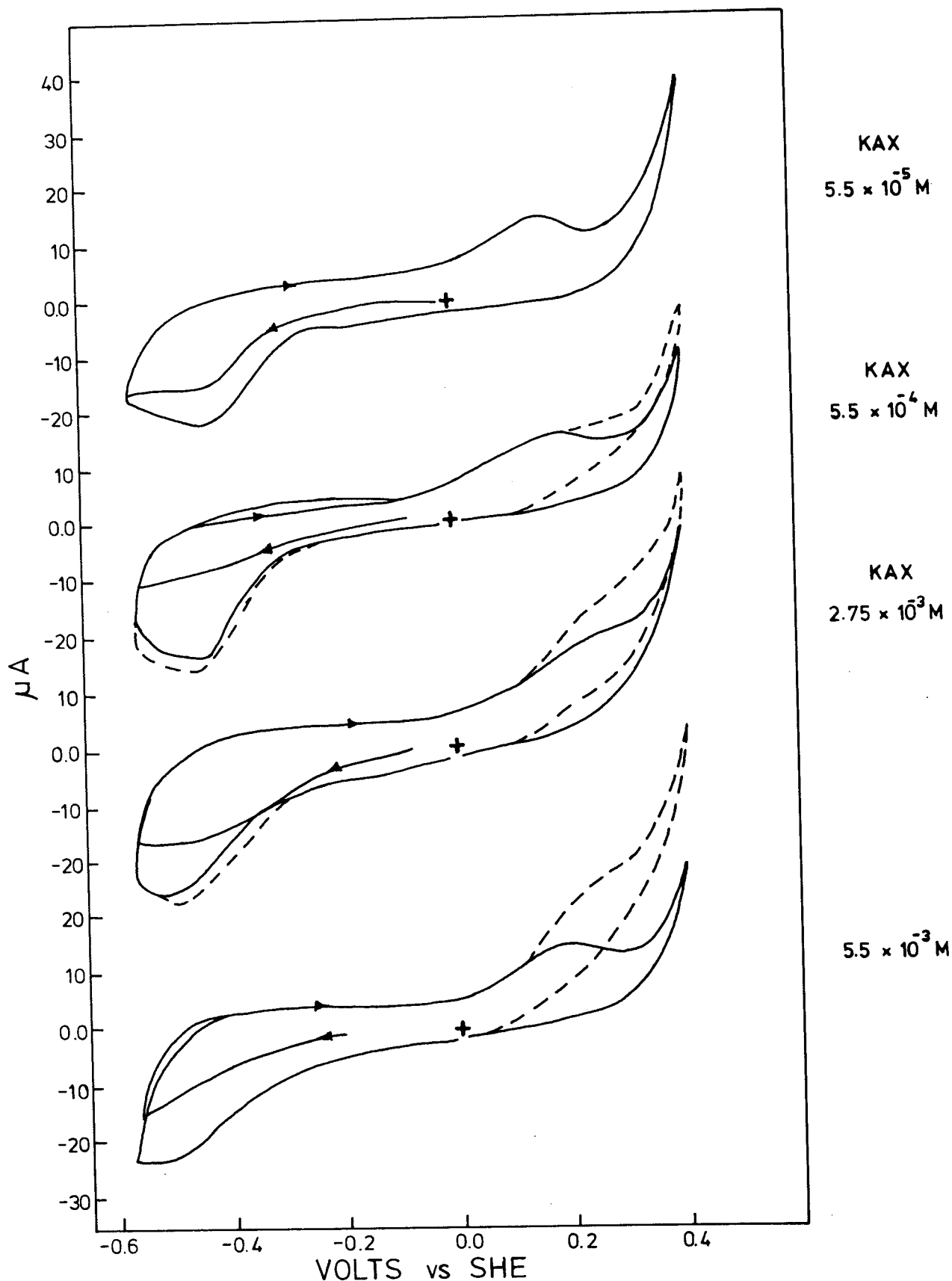
FIGURE 5.50: Cyclic Voltammograms of chalcopyrite in aqueous solutions at pH 11.0 containing varying concentrations of amyl xanthate.
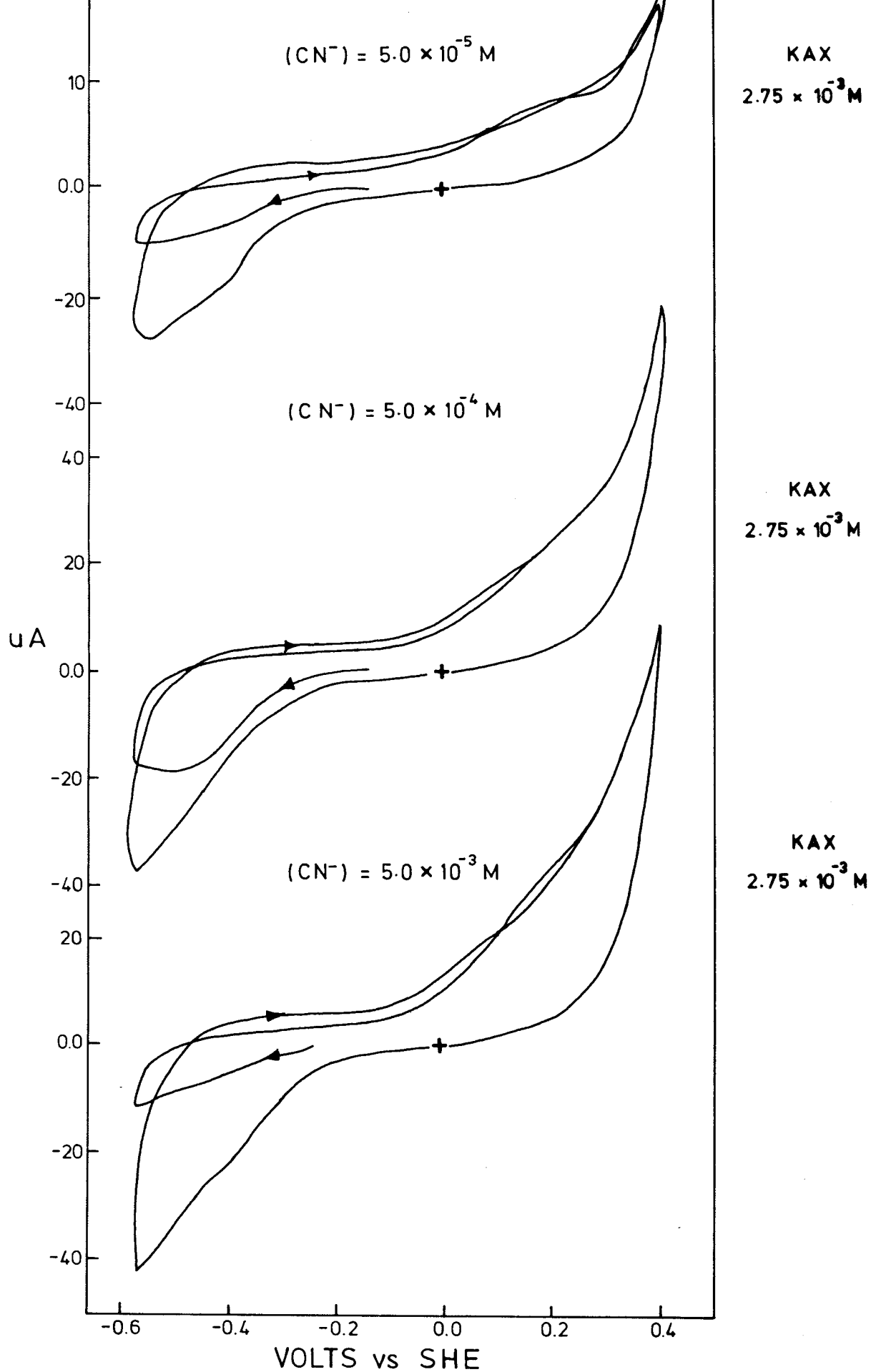
FIGURE 5.51: Cyclic voltammograms of chalcopyrite in aqueous solutions at pH 11.0 containing varying concentrations of sodium cyanide with a constant concentration of amyl xanthate.

The effect of cyanide addition is shown in Figure 5.51 which clearly show that cyanide enhanced the oxidation of the mineral. The mechanism by which cyanide prevented amyl xanthate oxidation is therefore by making the anodic oxidation of the mineral more favourable than that of xanthate oxidation. This behaviour was also observed in the case of ethyl xanthate.

CONCLUSIONS AND SUMMARY

6.0   SUMMARY AND CONCLUSIONS.

This study attempted to understand the electrochemical behaviour of carrollite and chalcopyrite with a view of predicting their flotation responses. The investigations in this study included mineralogical analyses of both minerals, rest potential measurements in the presence and absence of reagents (xanthate and cyanide), infrared spectroscopic measurements of extracts from the mineral particles and cyclic voltammetric studies of both minerals (carrollite and chalcopyrite) in the presence and absence of reagents. From the results obtained the following conclusions were drawn:

Mineralogical analyses
Carrollite mineral

The carrollite mineral used was fairly pure with a composition of 89.6% $CuCo_2S_4$, 8.2% $CuFeS_2$ and 2.2% siliceous gangue minerals. Chalcopyrite was distributed as an impurity in the matrix at assorted spots and occurred with pyrite. Linnaeite was present in very small proportions and electron micro probe analysis revealed that the carrollite mineral was high cobalt phase with coarse grains.

Chalcopyrite mineral

Unlike the carrollite mineral, the chalcopyrite mineral was moderately contaminated with pyrite. It's composition was 75.1% $CuFeS_2$, 19.5% FeS_2, 1.7% Cu_2S and 3.2% gangue minerals. The presence of bismuth sulphide and bismuth - silver alloy was revealed by electron micro probe analysis.

The mineralogical composition of the minerals determined the subsequent electrochemical behaviour. Although it would have been meaningful to conduct the investigations using pure minerals due to their more precise nature of the electrochemical behaviour, it was considered that the presence of the above impurities made comparisons to practical copper- cobalt separations more realistic.

Rest potential measurements in the absence of xanthate and cyanide.

In general the rest potential of both minerals were influenced by a number of factors such as :

i)   the nature of the solution (pH of the solution and the presence and absence of reagents).

ii) the type of aeration gas(nitrogen or oxygen).

iii) the pretreatment procedure particularly in the case of

chalcopyrite and

iv) the duration of the experiment.

The measured rest potentials depended mostly on the subsequent stable species formed on the surface of the mineral. In acidic media, ionic metal species were the stable species whilst hydroxides/oxides were the stable species in alkaline media. The potential recorded in oxygen saturated solutions were generally higher than those recorded in nitrogen saturated solutions for both mineral electrodes. This lead to the conclusion that the main role of oxygen was to enhance the rate of dissolution of the mineral in acidic media. This led to more ions in solution and resulted in higher rest potentials as depicted by the analogy of the Nerst equation. However the role of oxygen in alkaline media was obscure. Increase in the pH of the solution led to a corresponding decrease in the measured rest potentials for both minerals. This shift in the potential could only be accounted for by way of assigned the value to some most stable species which would have formed on the surface of the mineral in analogy to the domain represented by E_h - pH digrams.In interpreting the measured rest potentials in terms of a Nerst type of equation it is important to include an extra term for the chemical potential of the metal to account for the sulphide in the form of the metal. The processes by which these rest potentials are attained were fairly reversible . This was arrived at by assessing the time the electrodes re-attained their rest potential after undergoing perturbation which was almost immediately after this was stopped.

Rest potential measurement in the presence of xanthate and cyanide.

Carrollite electrode.

The rapid decrease in the measured rest potential of the carrollite electrode was observed at near neutral and high solution pH of 7.0 and 11.0 as the ethyl xanthate concentration was increased. This was due to the ready formation of di-ethyl dixanthogen on the carrollite mineral electrode at these solution pH values. Infrared spectra confirmed this findings and pointed to the fact that there was relatively more di-ethyl dixanthogen formed at pH 9.2 than at pH 7.0. There was no di-ethyl dixanthogen detected at pH 11.0. The formation of di-ethyl dixanthogen probably proceeded by a chemisorption process and there was weak bubble attachment of nitrogen at pH value of 7.2 as compared to strong bubble attachment at pH 9.2. This further supported the evidence that there was more di-ethyl dixanthogen formed at pH 9.2 than at pH 7.0. In the presence of cyanide ions, there was a rapid decrease in the measured rest potential with both the increase in the pH of the solution and cyanide concentration at a given ethyl xanthate concentration. However, the relatively higher measured potentials at a solution of pH 9.2 in comparison with those obtained at pH 7.0 and 11.0 showed that there was a possibility of di-ethyl dixanthogen formation at this solution pH. This could not readily be revealed by infrared spectroscopic measurements.

Chalcopyrite electrode.

Chalcopyrite mineral electrode showed similar behaviour to that of carrollite mineral electrode. It also registered rapid decrease in the measured rest potentials at pH values of 7.0 and 11.0 which implied that di-ethyl dixanthogen formed less readily in these solutions. However, the potentials measured at pH 9.2 showed that di-ethyl dixanthogen was likely to have formed. Infrared spectrum confirmed the presence of di-ethyl dixanthogen at pH 9.2. In the presence of cyanide ions, the mineral electrode showed a drastic decrease in the measured rest potential at pH 11.0 with increase in cyanide concentration. Infrared spectrum showed that at this solution pH there was little di-ethyl dixanthogen and that most of the ethyl xanthate remained in its' original form. The presence of pyrite in the chalcopyrite mineral electrode influenced the measured rest potentials of the electrode more especially in the presence of cyanide ions at pH 11.0. At high cyanide concentrations the magnitude of the measured rest potentials showed that there was no di-ethyl dixanthogen formation. This was latter confirmed by lack of adequate bubble attachment. Pyrite galvanically prevented the chalcopyrite electrode from reacting with the ethyl xanthate to form di-ethyl dixanthogen on the chalcopyrite mineral electrode.

Effect of using amyl xanthate.

There was a large decrease in the measured rest potential on the carrollite electrode at pH 9.2 indicating the readiness with which di-amyl dixanthogen formed on this mineral at the pH of the solution. Similarly this was also observed on the chalcopyrite electrode at pH values of 7.0 and 9.2. In general, both minerals showed evidence of good bubble attachment properties at these pH values thus confirming the presence of di-amyl dixanthogen. In the presence of cyanide ions, at pH 11.0, there was a large decrease in potential of both minerals. Di-amyl dixanthogen did not form under such conditions, its is possible that other xanthate compounds might have formed on the chalcopyrite electrode at it atleast showed good bubble attachment properties.

Cyclic voltammetry using a carrollite mineral electrode.

The main oxidation products of carrollite were either Co^{2+} and Cu^{2+} ions in acidic media and $Co(OH)_2$ and CuS in alkaline media. Sulphur or other sulphur species other than the SO_4^{2-} ions were products of these oxidation processes in both media. The cobalt in the surface zone of the mineral probably completely oxidised

before any copper-cobalt-oxygen species were formed. The carrollite mineral surface was reasonably stable in air so that it remained relatively un oxidised prior to use. Since the reactions occurring on the carrollite mineral surface showed a great degree of reversibility in alkaline media, it was concluded that the reaction products under these conditions were insoluble surface products rather that ionic species.

In the presence of ethyl xanthate, di-ethyl dixanthogen was the predominant xanthate oxidation product for the entire pH range covered. However, sufficient amounts were only produced at pH value of 9.2 to render the electrode hydrophobic. This resulted in strong bubble attachment. The presence of cyanide ions greatly inhibited the ethyl xanthate oxidation to di-ethyl dixanthogen at pH 11.0. The inhibition of ethyl xanthate oxidation occurred through the formation of a surface cobalt cyanide species which remained insoluble on the surface of the mineral and did not appreciably change within the potential limits of the experiments. This was deduced from the reversibility of the voltammograms. This inhibition of the oxidation of ethyl xanthate was also dependent on the concentration of cyanide and increased with both the pH of the solution and cyanide concentration.

Cyclic voltammetry using a chalcopyrite mineral electrode.

On the chalcopyrite mineral electrode the main oxidation products were Fe^{2+} and Cu^{2+} ions in acidic media and $Fe(OH)_3$ and CuS in alkaline media. In view of the results from recent XPS studies, a metal - deficient sulphide rather than a stoichiometric sulphide cannot be ruled out as one of the oxidation products. The chalcopyrite mineral electrode unlike that of carrollite under went some oxidation during grinding and transfer to the electrochemical cell. It can be concluded therefore that chalcopyrite is relatively unstable in air. The reactions occurring on the chalcopyrite mineral were reasonably reversible due to the reversibility of the voltammograms. Like in the case of carrollite were the cobalt was completely removed from the surface zone , iron in the surface zone was probably completely oxidised before any copper-iron-oxygen species were formed.

In the presence of ethyl xanthate, di-ethyl dixanthogen formed on the chalcopyrite mineral electrode at lower pH values of 7.0 and 9.2. At higher solution pH of 11.0, copper ethyl xanthate was probably the stable hydrophobic species. When both ethyl xanthate and cyanide ions were present, ethyl xanthate oxidation was inhibited with increase in both the pH of the solution and cyanide concentration. However, at pH 11.0 the resultant copper ethyl xanthate rendered the chalcopyrite mineral electrode

sufficiently hydrophobic to give strong bubble attachment.

Cyclic voltammetry in the presence of amyl xanthate.

Similar behaviour as for ethyl xanthate was observed for both minerals when amyl xanthate was used as a collector. However, the ease with which di-amyl dixanthogen formation occurred was enhanced for both minerals with increase in the pH of the solutions and amyl xanthate concentrations. In the presence of cyanide ions, the suppression of di-amyl dixanthogen formation for both minerals was similar and related to the introduction of an anodic reaction which occurred faster than the amyl xanthate oxidation reaction. It was possible that an ion exchange reaction might have occurred between the free amyl xanthate ions and the oxidised chalcopyrite mineral electrode at pH 11.0 resulting in the formation of copper amyl xanthate. This may have led to the chalcopyrite mineral electrode hydrophobic whilst that of carrollite remained hydrophilic.

SUGGESTED THEORETICAL FLOTATION ROUTES.

On the basis of the data obtained, it is possible to propose the following theoretical flotation routes:

a)   At pH 7.0 and 9.2, there is formation of dixanthogen on both mineral. However, at pH 7.0 dixanthogen formed more readily on the chalcopyrite mineral rather than on the carrollite particles. The chalcopyrite mineral particles will therefore be relatively more hydrophobic and can be floated off at about neutral pH leaving carrollite mineral particles. This is especially so, if sparing concentrations of xanthate are used. It is important to note that such a route would require an optimum critical xanthate addition, below which only chalcopyrite would float,but above it both chalcopyrite and carrollite would float.

b)   The present practice of floating chalcopyrite in the segregation circuit at pH 11.0 appears justifiable. This is because at this pH value and in the presence of cyanide ions ,the oxidation of xanthate to dixanthogen is greatly inhibited on both minerals. Nevertheless, the presence of

copper xanthate on the chalcopyrite renders it hydrophobic. This lead to the preferntial flotation of chalcopyrite leaving carrollite behind. However, high cyanide concentrations apparently results in an ion exchange type of reaction between the metal xanthate and the cyanide ion to form surface cyanide complexes which are hydrophilic. This could lead to poor separation between chalcopyrite and carrollite. An optimisation of cyanide addition would improve the separation process at this pH value.

c) The presence of pyrite in the chalcopyrite leads to the formation of ferric ferrocyanide complexes in cyanide containing solutions as the pulp pH is increased. The presence of these complexes lead to the chalcopyrite surface remaining hydrophilic. Also of interest is that cobalt which occur as cobaltiferous pyrite in cobalt replaces iron in the pyrite matrix lattice. This would be expected to behave in a similar manner to pyrite. Thus, the proportion of pyrite in the chalcopyrite requires to be closely monitored as increasing amounts drastically affect the floatability of the mineral. It has been assumed that in the absence of pyrite in the chalcopyrite, the latter would not be expected to be extensively hydrophilic even at pH 11.0. Future work should therefore, address the presence of pyrite in this system. Specifically, a correlation between the proportion of pyrite in chalcopyrite and the latter's electrochemical behaviour should be attempted. On the basis of the results

obtained, the correlation could be extended to flotation experiments.

APPENDIX

Table 5.1 (a)   Open circuit potentials of carrollite
as a function of pH

pH	Measured potential	(Volts vs SHE)
	Nitrogen (N_2)	Oxygen (O_2)
4.6	0.369	0.426
7.0	0.335	0.389
9.2	0.258	0.324
11.0	0.216	0.269
13.0	0.096	0.151

Table 5.1 (b)   Open circiut potentials of chalcopyrite
function of pH.

pH	Measured potential	(Volts vs SHE)
	Nitrogen (N_2)	Oxygen (O_2)
1.0	0.507	0.582
4.6	0.342	0.392
7.0	0.278	0.313
9.2	0.133	0.292
11.0	-0.049	0.124
13.0	0.036	0.101

Table 5.2 (a)   Open circuit potentials of carrollite as a
function of pH in solutions containing
different concentrations of potassium ethyl
in nitrogen atmosphere

KEx Concentration mole/dm^3	pH 7.0	9.2	11.0 (Nitrogen atmosphere)	*ER(Calculated
	Potentials (Volts vs SHE)			
0	0.335	0.258	0.216	-
5.5×10^{-5}	0.251	0.216	0.192	0.19
2.75×10^{-4}	0.201	0.203	0.184	0.15
5.5×10^{-4}	0.166	0.182	0.143	0.13
2.7×10^{-3}	0.133	0.145	0.112	0.09

Table 5.2 (b)   Open circuit potentials of carrollite as a
function of pH in solutions containing
different concentrations of potassium ethyl
xanthate in oxygen atmosphere

| KEX concentration mole dm^{-3} | pH | | | (Oxygen atmosphere) |
| | 7.0 | 9.2 | 11.0 | *ER(calculated Volts vs SHE |
	Volts vs SHE			
5.5x10^{-5}	0.270	0.252	0.156	0.19
2.75x10^{-4}	0.210	0.250	0.136	0.15
5.5x10^{-4}	0.170	0.214	0.131	0.13
2.75 10^{-3}	0.142	0.204	0.141	0.09
5.5x10^{-3}	--	-	0.133	0.07

*ER refers to the calculated equilibrim potential for the
xanthate/dixanthogen redox couple as given by IUPAC and as
derived by Tokada and Majima (82)

Table 5.2 (c) Open circuit potentials of carrollite as a
function of pH in solutions with different
concentrations of sodium cyanide

Sodium cyanide concentration mole dm^{-3})	pH 7.0	9.2	(Oxygen atmosphere) 11.0
5.0×10^{-5}	0.280	0.247	0.166
2.5×10^{-4}	0.270	–	0.120
5.0×10^{-4}	0.268	0.179	-0.004
1.0×10^{-3}	0.228	0.048	-0.076

Table 5.2 (d) Open circuit potentials of carrollite as a
funciton of pH in solution with different
concentration of sodium cyanide with a constant
dosage of potassium ethyl xanthate in oxygen
atmosphere

Sodium cyanide concentration moles dm^{-3})	pH 7.0	9.2	Volts vs SHE 11.0	Constant xanthate (X-)=5.5*10-4M
5.0×10^{-5}	0.197	0.091	0.142	
2.5×10^{-4}	0.053	0.105	0.110	
5.0×10^{-4}	0.037	0.113	0.081	0.13
1.0×10^{-3}	-0.097	0.097	0.028	

Table 5.3 (a)   Open circuit potentials of chalcopyrite as a
                function of pH in solutions containing
                different concentrations of potassium ethyl
                xanthate in nitrogen atmsphere

| | pH | | (Nitrogen) Volts vs SHE | |
KE concen- mol dm⁻³	7.0	9.2	11.0	ER calcu- lated
5.5×10^{-5}	0.062	0.122	-0.131	0.19
2.75×10^{-4}	0.042	0.074	-0.174	0.15
5.5×10^{-4}	0.004	0.034	-0.196	0.13
2.75×10^{-3}	0.044	0.012	-0.219	0.07
0	0.278	0.133	-0.049	

Table 5.3 (b)   Open circuit potentials of chalcopyrite as a
function of pH in solutions containing
different concentrations of potassium ethyl
xanthate in oxygen atmosphere

KEX concen-tration mol dm⁻³	pH (oxygen) 7.0	9.2	11.0	ER calcu-lated
	Volts vs SHE			
$.5 \times 10^{-5}$	0.106	0.143	0.091	0.19
$.75 \times 10^{-4}$	0.117	0.132	0.068	0.15
$.5 \times 10^{-4}$	0.083	0.101	0.052	0.13
$.75 \times 10^{-3}$	0.098	0.093	0.029	0.07
0	0.313	0.292	0.124	

Table 5.3 (c)   Open circuit potentials of chalcopyrite as a
function of pH in solution containing
different concentrations of sodium cyanide

Sodium cyanide concentration dm⁻³	pH oxygen 7.0	9.2	11.0
	Volts vs SHE		
$\times 10^{-5}$	0.114	0.103	-0.061
$\times 10^{-4}$	0.109	0.087	-0.093
$\times 10^{-4}$	0.082	0.066	-0.122
$\times 10^{-3}$	0.057	0.061	-0.173

Table 5.3 (d) Open circuit potentails of chalcopyrite as a
function of pH in solution containing
different concentration of sodium cyanide
with a constant dosage of potassium ethyl
xanthate in oxygen atmosphere.

Sodium cyande concentration mol/dm³	pH (oxygen) $(X^-) = 5.5 \times 10^{-4}M$		
	7.0	9.2	11.0
	Volts vs SHE		
6×10^{-5}	0.122	0.112	0.020
5×10^{-4}	0.103	0.083	-0.032
0×10^{-4}	0.084	0.072	-0.77
9×10^{-3}	0.045	0.041	-0.115

Table 5.4 (a): Rest potentials of a carrollite electrode in
solutions of varying concentrations of potassium amyl xanthate
saturated with nitrogen

X concentration moles/dm³	pH (nitrogen)			E* calculated
	7.0	9.2	11.0	
			Volts Vs SHE	
5.5×10^{-5}	0.149	0.103	0.150	0.111
5.5×10^{-4}	0.070	0.045	0.090	0.050
2.75×10^{-3}	0.042	0.022	0.085	0.010

Table 5.4 (b): Rest potentials of a carrollite electrode in solutions of varying concentrations of potassium amyl xanthate saturated with oxygen.

KAX concentration moles/dm^{-3}	pH (oxygen)			E* calculated
	7.0	9.2 Volts Vs SHE	11.0	
5.5 x 10	0.179	0.114	0.189	0.110
5.5 x 10	0.106	0.086	0.122	0.050
2.75 x 10	0.089	0.044	0.125	0.010

E* is calculated on the basis of the relation derived by Majima and Takeda for which the xanthate/di-amyl dixanthogen redox is given as:

$$E = -0.140 - 0.059 \log (X^-) \dots\dots\dots\dots\dots(5.4)$$

Table 5.4 (c): Rest potentials of a carrollite electrode in solutions of varying concentrations of cyanide at constant concentrations of amyl xanthate

Sodium cyanide concentration mole/dm^{-3}	pH (oxygen)			KAX (X$^-$) = 2.75 x 10^{-3}
	7.0	9.2	11.0	
5.0 x 10^{-5}	0.047	0.097	0.118	
2.5 x 10^{-4}	0.045	0.066	0.081	
5.0 x 10^{-4}	0.042	0.042	0.031	0.05
1.0 x 10^{-3}	-	-	0.05	

Table 5.5(a): Rest potentials of a chalcopyrite electrode in solutions of varying concentrations of potassium amyl xanthate with saturated nitrogen.

KAX concentration moles/dm $^{-3}$	pH (nitrogen)			E_R calculated
	7.0	9.2 Volts Vs SHE	11.0	
5.5×10^{-5}	0.046	0.037	0.007	0.110
5.5×10^{-4}	0.005	0.033	-0.083	0.050
2.75×10^{-3}	-0.005	0.00	-0.089	0.010

Table 5.5(b): Rest potentials of a chalcopyrite electrode in solutions of varying concentrations of potassium amyl xanthate with saturated oxygen.

KAX concentration moles/dm $^{-3}$	pH (oxygen)			E_R calculated
	7.0	9.2 Volts Vs SHE	11.0	
5.5×10^{-5}	0.175	0.117	0.031	0.110
5.5×10^{-4}	0.085	0.044	0.018	0.050
2.75×10^{-3}	0.035	0.042	0.007	0.010

Table 5.5 (c): Rest potentials of a chalcopyrite electrode in
solutions of a constant amyl xanthate concentration of cyanide.

Sodium cyanide concentration moles/dm^{-3}	pH (oxygen)			KAX $(X^-) = 2.75 \times 10^{-3}$
	7.0	9.2	11.0	
5.0×10^{-5}	0.046	0.053	-0.107	
2.5×10^{-4}	0.038	+0.044	-0.116	0.05
5.5×10^{-4}	—	+0.032	-0.120	

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