CHAPTER 4

ANODIC STRIPPING ANALYSIS OF INDIUM (III)

The electrochemical behavior of indium in pH 9.3 borate-buffer was studied by a galvanostatic method (61) and by a potentiostatic method (62). The electrochemical determination of In (III) in nitric tartaric acid (pH 10) (63), in nitrate-tartrate and in nitrate-citrate solutions (64), as well as the electrodeposition of In (III) from a Trilon B electrolyte (65) and from an In-polyethylenepolyamine complex solution (66) were proposed. During the deposition of In (III) on a solid electrode in H_2SO_4 and $HClO_4$ solutions, a break in the cathodic process occurred even at a very low polarization; owing to the hydrogen evolution (67). The conditions for simultaneous electrodeposition of indium and tin from perchlorate electrolytes were also studied (68). The deposition of indium from ethylenediaminetetraacetate, and nitrilotriacetate alkali solutions were possible by means of potential sweep voltammetry (69). In addition, the electrochemical concentration of In (III) impurities in GaAs sample on a graphite electrode was declared (44).

The polarographic behavior of In (III) in alkali metal and alkali earth nitrates was studied and a quasireversible process was indicated (70). A catalytic effect of polarographic prewaves of In (III) in M $NaClO_4$ in the presence of 10^{-3}M thiocyanate was observed (71). In the presence of $NaClO_4$, polarographic study of indium in lactate medium shows a 3-electron reversible process, except at low concentration of lactic acid (72). A quasireversible process was also found in the polarographic reduction of In (III) in KNO_3 and in the presence of some monocarboxylic acids, e.g., glycolic, pyruvic, butyric or levulinic acid (73). Indium oxinates in dimethylformamide in the presence of naphthalene gave a well-defined polarographic wave (74). Polarographic behaviors of complexes of In (III) with N-cinnamoyl-N-phenylhydroxylamine (29), with N-phenylcinnamoylhydroxamic acid (30), and with N-benzoylphenylhydroxylaminates (31) were also studied in nonaqueous media. The electrochemical reduction of In (III) on a dropping mercury electrode was studied in the presence of tensioactive substance, e.g., sodium dodecylsulfate, tetrabutylammonium perchlorate and Triton X-305 (75). Moreover, the effect of several terpenes and their derivatives on the reduction of In (III) on the dropping mercury electrode in N HCl, $HClO_4$, H_2SO_4 and formic acid was discussed in reference 33, as well as the polarography of In (III) in aqueous melted $Ca(NO_3)_2\ 4H_2O$, $Ca(NO_3)_2\ 4D_2O$, $LiNO_3$-$3H_2O$ and $CaCl_2\ 6H_2O$ was described in reference 18.

The polarographic determination of indium in triethylenetetramine (76) and in tetraethylenepentamine (77) was discussed. Indium in the indium-phosphorus-selenium system was determined without preliminary separation by a.c. polarography (78), as well as indium in ternary system of mercury-indium-tellurium was determined without prior separation at -0.6 V in 2 M ammonium acetate-2 M acetic acid supporting electrolyte (79). Moreover, indium in a semiconductor type $(In_2Te_3)_x$ - $(Hg_3Te_3)_{1-x}$ was polarographically determined in a HCl supporting electrolyte by the addition method (80). The 10^{-7}- 10^{-6}% indium as trace impurities in lead of special purity was possible to be determined by polarography (81). The applications of polarography in the determination of indium in minerals (82), in doped semiconductors (83, 84), in zinc concentrates and lead cake (85) were reported. By a high harmonic a.c. polarographic technique, 1 X 10^{-4}M In (III) could determined in a 10 fold excess of Cd (II) in 1 M HCl, although their half-wave potentials was only 40 mV different (86). In addition, the complex formation of indium with 2-dimethylaminoethanethiohydrochloride was studied by polarography (87).

The potentiometric titration of indium, in the presence of gallium, in citrate or tartrate solutions, with 8-mercaptoquinoline, sodium diethyldithiocarbamate, and sodium dibutyldithiocarbamate was carried out at a Hg-pool (indicator electrode) vs SCE and Ga 100 fold excess did not interfere in the titration of indium in the presence of fluoride ion (88). The 3.48 X 10^{-4}- 6.88 X 10^{-3}M In (III) was possible to determine by potentiometric titration with dithiocarbamic acid derivatives at pH 6.5 (89). In addition, the automatic potentiometric titration of indium in acetone with a standard solution of KOH in isopropyl alcohol was also proposed (43).

The sequential amperometric titration of indium in the mixture of indium and zinc or in the mixture of indium and lead with EDTA was reported (90), as well as the amperometric titration of indium with EDTA in anhydrous acetic acid medium was possible (91). In addition, biamperometric titration of indium with EDTA in a medium of acetic acid-benzene was described in reference 92. The amperometric titrations of indium with thiooxime (93) and with uranil-N, N-diacetic acid (94) were also studied.

Oscillopolarographic reductions of In (III) in absence of a supporting electrolyte (95) as well as in the presence of 0.5 M KCl supporting electrolyte (96) were investigated by Vladimirova. The reversibility of indium reduction in citric acid was studied by oscillopolarographic method (97). Oscillopolarographic determinations of indium in alloys (98), and in nitric and citric acids by using a Cu-plated Pt electrode (99) were examined. Moreover, the effect of NH_2OH-H_2SO_4, complexon I, ethylenediamine sulfate and Na_2SO_4 additives on the oscillopolarographic determination of In (III) in 0.5 M KCl supporting electrolyte was studied (100).

By low noise polarograph, 8 X 10^{-9}M In (III) in acetic acid-sodium acetate buffer was detectable (101). The application of anodic stripping method to practical analysis using the balanced head stationary hanging mercury drop electrode was tested with 10^{-6}M In (III) in various supporting electrolytes(102). Indium (III) in KCl was possible to be determined by anodic potential-step stripping voltammetry with a standard deviation in the peak height measurement of 3% for 0.2 ppm In (III) (49). Application to natural waters, the determination of indium by ASV at hanging mercury drop electrode with differential pulse and a.c. modes, and at the thin film electrode using a rapid d.c. scan was investigated (103). Stripping voltammetry of indium at disproportionate concentration was examined by using the amalgam concentration (56). The occurence of two peaks of indium electrodissolution from a graphite electrode was discussed in reference 104. The determination of indium in aluminum of high purity on a graphite electrode in KCl and KBr solution was proposed (105). The sensitivity for the ASV of indium was improved by using Hg-plated carbon electrode (51). By using a slow dropping mercury electrode in anodic stripping alternating current voltammetry, the sensitivity permitted was higher than that obtained with anodic stripping direct current voltammetry (106). In addition, anodic stripping chronopotentiometry on a glassy carbon disk electrode was especially useful for analysis of In (III) in metal mixtures such as In-Cd (107) and Cd-Pb-In (108).

In the present study, the conditions for anodic stripping analysis of In (III) and the sensitivity of In (III) in the electrolyte chosen are reported.

4.1 Evaluation of electrolyte

Due to the best anodic stripping voltammogram of Tl (I) obtained in 0.1 M KNO_3, 0.1 M KCl and acetate buffer at pH 5.0 (see CHAPTER 3) and In (III) could be determined in 1 M HCl supporting electrolyte (86), the cathodic voltammetric behavior of In (III) was studied in 0.1 M KNO_3, 0.1 M KCl, acetate buffer at pH 5.0 and 1 M HCl. The cathodic voltammetric data of 1.00 X 10^{-3}M In (III) in each supporting electrolyte mentioned are listed in Table 4.1 and its voltammogram is shown in Figure 4.1. The anodic voltammetric behaviors of 1.00 X 10^{-4}M In (III) in 0.1 M KNO_3, 0.1 M KCl, acetate buffer at pH 5.0 and 1 M HCl were also tested. A well defined anodic peak of indium was given in the supporting electrolyte as 0.1 M KCl, 1 M HCl and acetate buffer at pH 5.0. However, no anodic peak of indium in 0.1 M KNO_3 was obtained. To obtain the optimum concentration of each electrolyte, the ASV of In (III) in KCl, HCl and acetate buffer were studied in detail.

Table 4.1 The cathodic voltammetric behavior of 1.00 X 10^{-3}M In (III) in various supporting electrolytes.

Supporting electrolyte	$E_{p,c}$ V	$i_{p,c}$ μa
0.1 M KNO_3	-0.93	16.0
0.1 M KCl	-0.98	17.5
acetate buffer pH 5.0	-0.95	17.0
1 M HCl	-1.10	8.0

4.1.1 potassium chloride

The voltammetric reduction of In (III) in 0.1 M KCl supporting electrolyte occurred at -0.98 V (see Table 4.1), therefore the electrodeposition potential of In (III) was set at -1.0 V. The ASV of In (III) in varied KCl concentration was investigated and the results are shown in Table 4.2. From Table 4.2, the anodic peak

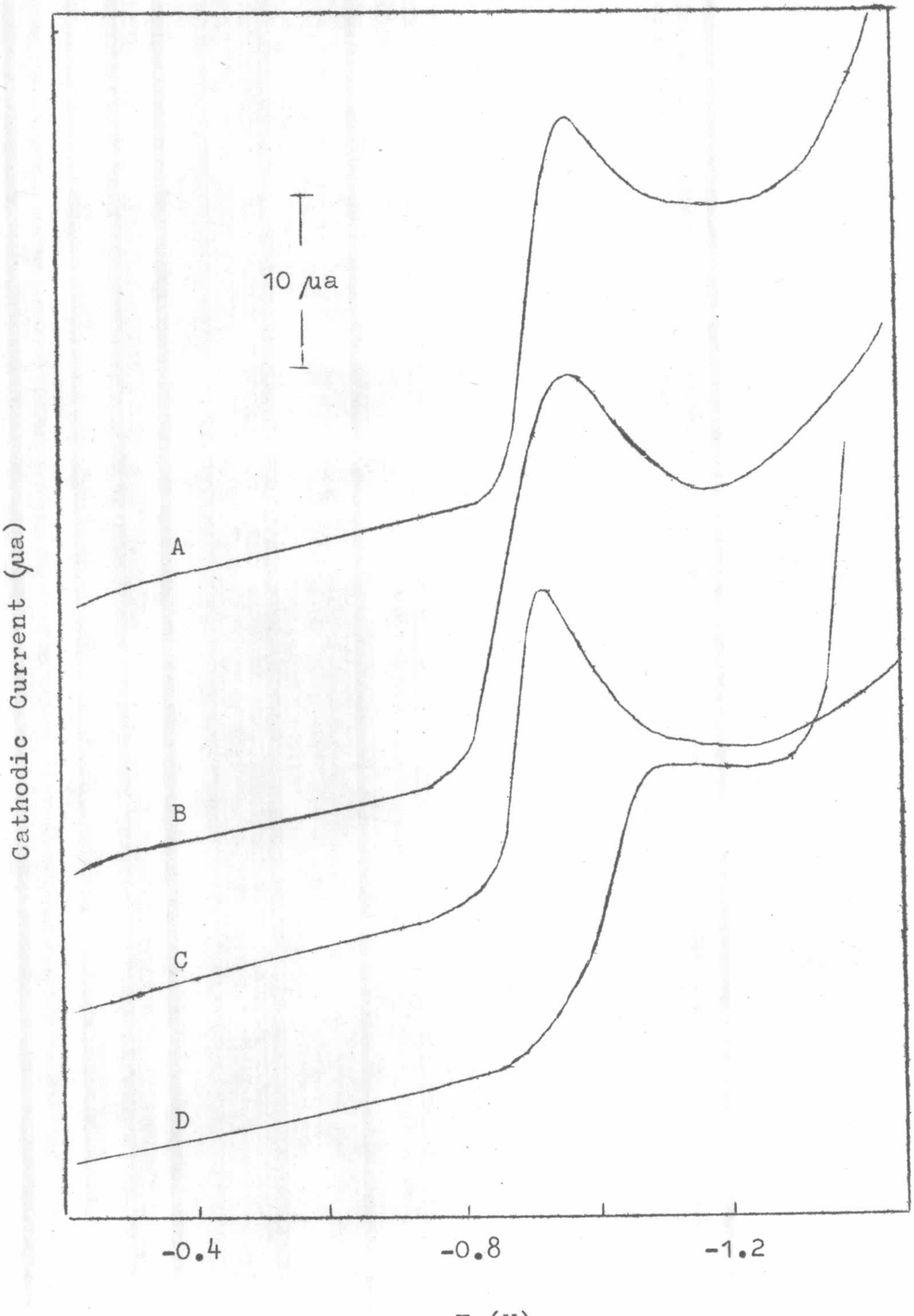

Figure 4.1 Cathodic voltammograms of 1.00 X 10^{-3}M In (III) in the following supporting electrolyte: A) acetate buffer at pH 5.0, B) 0.1 M KCl, C) 0.1 M KNO_3, and D) 1 M HCl

current increases as the concentration of KCl increases. Thus, the ASV of In (III) in 0.10 - 0.50 M KCl is possible and a well-defined anodic peak of indium is obtained (see Figure 4.2).

4.1.2 hydrochloric acid

Corresponding to the cathodic peak of In (III) was observed at -1.10 V in 1.0 M HCl (see Table 4.1), the electrodeposition potential of In (III) at -1.10 V was employed. In HCl medium, a well-defined anodic peak of In (III) is obtained in various concentrations of HCl supporting electrolyte, 0.1 M - 3.0 M HCl (see Figure 4.2). The anodic stripping voltammetric data of 1.00 X 10^{-4} M In (III) in each concentration of HCl studied are presented in Table 4.3. As the concentration of HCl increases the anodic peak current produced

Table 4.2 The ASV behavior of 1.00 X 10^{-4} M In (III) in various concentrations of KCl supporting electrolyte using a 5 minute deposition at -1.0 V.

Conc. of KCl M	$E_{p,a}$ V	$i_{p,a}$ * µa
0.05	-0.63	19.50 ± 0.50
0.10	-0.64	41.30 ± 1.90
0.50	-0.68	68.00 ± 2.00

* average anodic peak current ± average deviation of more than 2 trials.

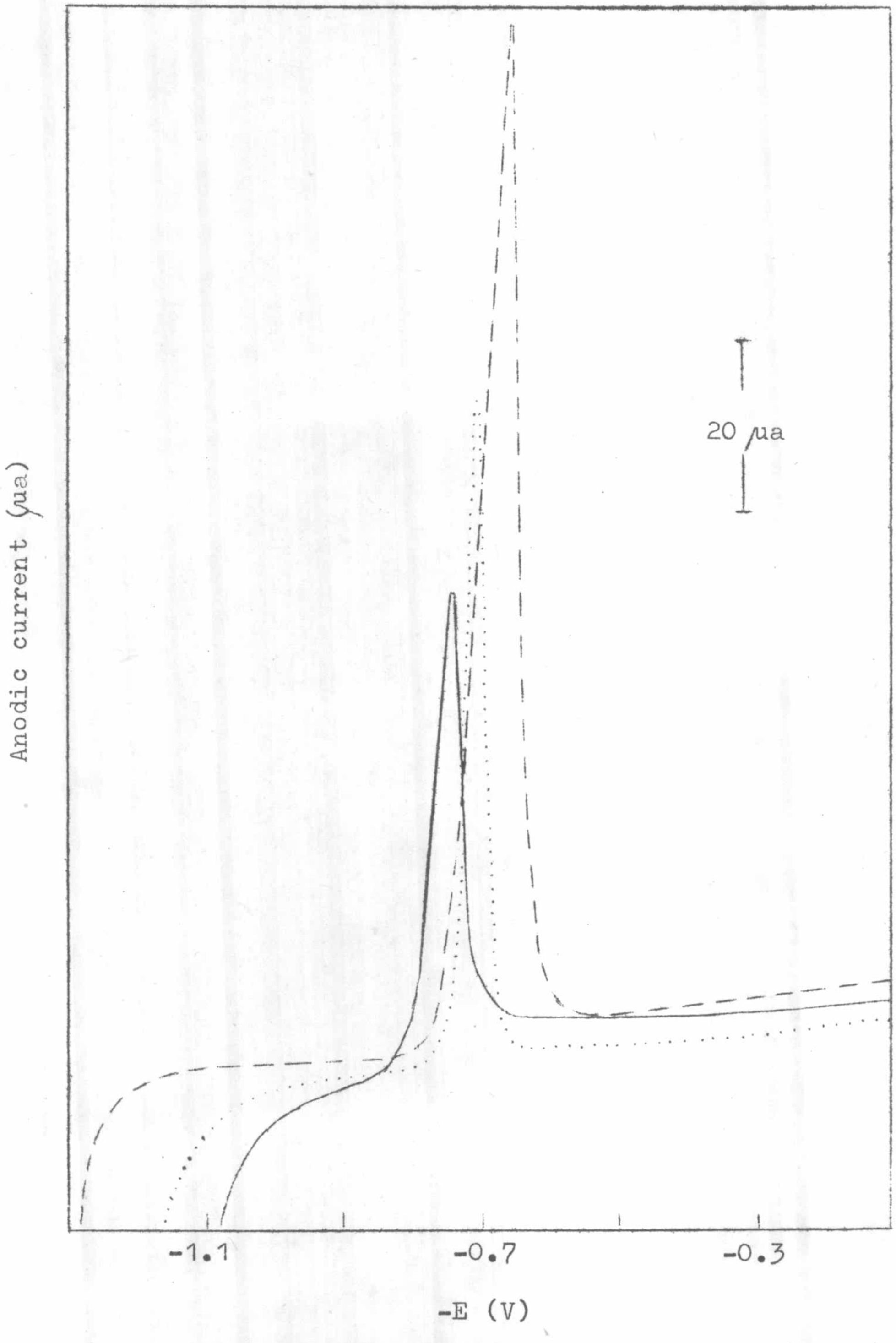

Figure 4.2 Anodic voltammograms of 1.00 X 10^{-4}M In (III) with a 5 minute deposition at -1.0 V in 0.1 M KCl (____), and in acetate buffer at pH 5.0 (-----) and at -1.1 V in 2 M HCl (....)

Table 4.3 The ASV data of 1.00×10^{-4} M In (III) in various concentrations of HCl supporting electrolyte using a 5 minute deposition at -1.1 V.

Conc. of HCl M	$E_{p,a}$ V	$i_{p,a}^{*}$ µa
0.1	-0.52	2.00 ± 0.01
0.5	-0.67	52.00 ± 2.01
1.0	-0.68	40.33 ± 2.82
2.0	-0.70	72.80 ± 1.60
3.0	-0.73	74.33 ± 2.44

* average anodic peak current ± average deviation of more than 3 trials.

increases (see Table 4.3). However, a hydrogen evolution was noticed during the electrodeposition of In (III) in higher HCl concentrations (1.0 M - 3.0 M). Thus, the concentration higher than 0.5 M HCl should be avoided and the suitable HCl content for ASV of In (III) is recommended at 0.5 M HCl.

4.1.3 acetate buffer

The cathodic voltammogram of In (III) showed a peak in acetate buffer at ca. -0.95 V (see Table 4.1), thus the ASV of In (III) was investigated by using the electrodeposition potential of -1.0 V. The anodic stripping voltammetric data of In (III) in various pH of acetate buffer system obtained are listed in Table 4.4 and the plot of anodic peak current vs pH of test solution is shown in Figure 4.3. It is seen that the optimum pH of acetate buffer is 5.0 which gives the maximum value in anodic peak current.

Therefore the best anodic stripping voltammogram of In (III) is obtained in 0.5 M KCl, 0.5 M HCl and acetate buffer pH 5.0. Using the same condition such as concentration of In (III), deposition time and stirring rate, the ASV of In (III) in acetate buffer pH 5.0 gives a higher anodic peak current than in the other two supporting electrolytes (see Tables 4.2, 4.3 and 4.4). The chloride concentration higher than 0.5 M was not used since In (III) could form chloride complexes with excess chloride (2). Thus, acetate buffer pH 5.0 was used as an appropriate supporting electrolyte for the ASV of In (III) by this study.

Table 4.4 The ASV behavior of In (III) in acetate buffers, using a deposition of 1.00 X 10^{-4} M In (III) for 5 minutes at -1.0 V.

pH	$E_{p,a}$ V	$i_{p,a}^{*}$ µa
4.0	-0.61	83.56 ± 2.63
4.6	-0.62	95.50 ± 1.01
4.8	-0.64	99.98 ± 0.75
5.0	-0.64	110.64 ± 2.52
5.2	-0.66	85.00 ± 2.60
5.6	-0.69	58.90 ± 1.72

* average anodic peak current ± average deviation of more than 3 trials.

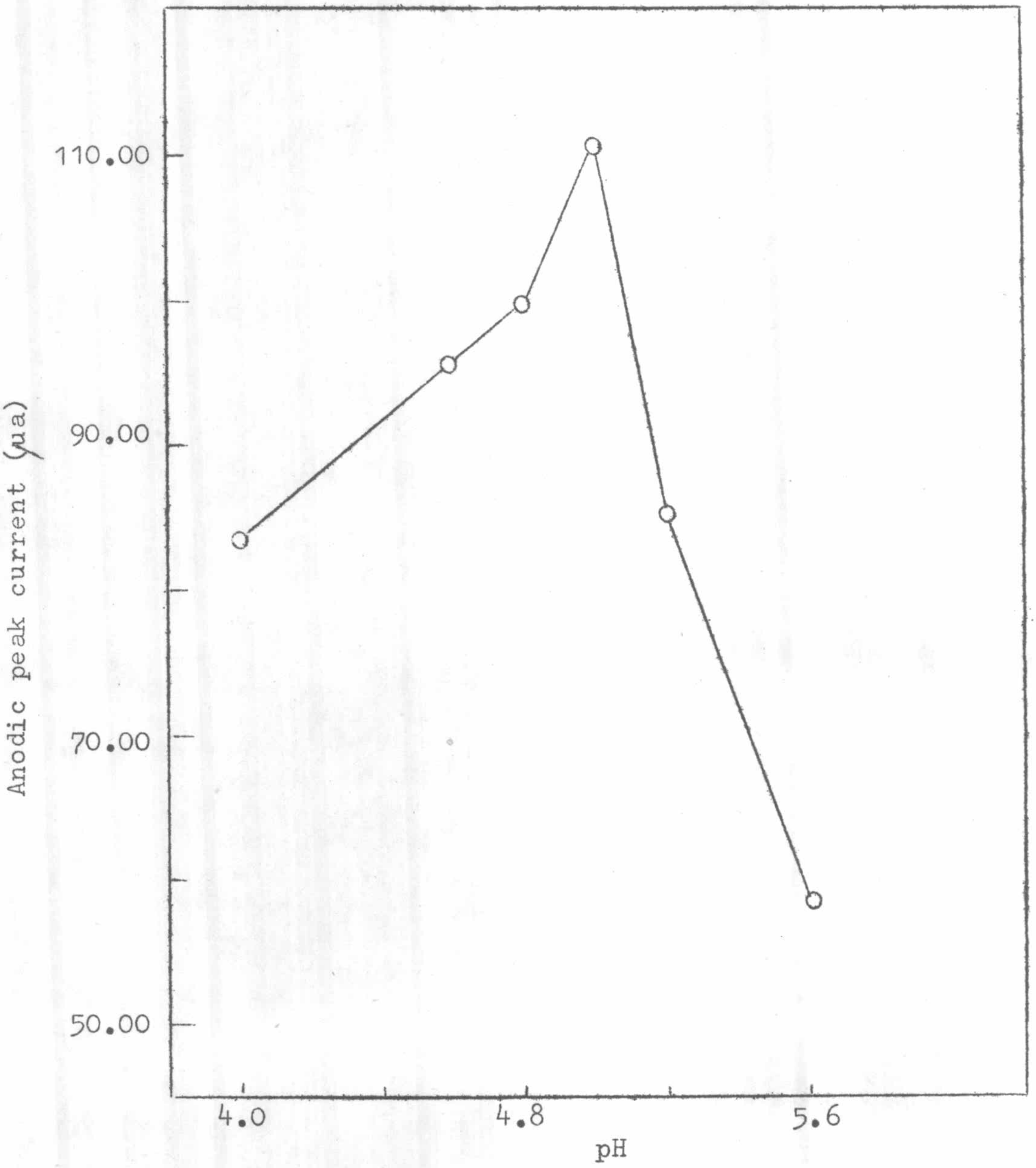

Figure 4.3 The effect of pH on the anodic peak current of In (III); 1.00 X 10^{-4}M In (III) in acetate buffer with a 5 minute deposition at -1.0 V.

4.2 Stripping analysis

Conditions for the anodic stripping analysis of In (III) in acetate buffer pH 5.0 and its sensitivity are reported in Table 4.5. The cathodic and anodic voltammogram obtained are illustrated in Figure 4.4. The linear dependence of anodic peak current on concentration is obtained in the range of $1.00 \times 10^{-4} - 1.00 \times 10^{-5}$ M In (III) and $1.00 \times 10^{-5} - 1.00 \times 10^{-6}$ M In (III) with the deposition time of 3 and 10 minutes; respectively, as seen in Figure 4.5. A 20 minute deposition was investigated for the ASV of $1.00 \times 10^{-6} - 1.00 \times 10^{-7}$ M In (III) in acetate buffer pH 5.0 and the anodic stripping peak current yielded was not reproducible. This nonreproducibility of the anodic stripping peak current may be explained by the adsorption of In metal on the GCE taking into account in a longer deposition time (20 minutes). It has been reported that an adsorption of In metal on the graphite electrode occurred in the electrooxidation of indium by inversed voltammetry (104). Thus, the detection limit of this study is 1.00×10^{-6} M In (III).

Table 4.5 Conditions for electrodeposition of indium (III) and data of anodic stripping analysis of indium in acetate buffer pH 5.0 (0.0472 M acetic acid - 0.1128 M sodium acetate).

Deposition		Conc. of In(III) (M)	$E_{p, a}$ (V)	$i^*_{p, a}$ (µa)	Detection limit (M)
Potential (V)	time (min)				
-1.0	3	1.01×10^{-4}	-0.65	88.50 ± 4.90	
		8.08×10^{-5}	-0.67	79.27 ± 0.18	
		6.06×10^{-5}	-0.68	55.15 ± 3.98	
		4.04×10^{-5}	-0.70	38.48 ± 1.58	
		2.02×10^{-5}	-0.71	21.14 ± 1.63	
		1.01×10^{-5}	-0.72	14.42 ± 0.46	
-1.0	10	1.01×10^{-5}	-0.69	34.35 ± 1.65	
		8.08×10^{-6}	-0.70	31.38 ± 1.34	
		6.06×10^{-6}	-0.71	21.95 ± 1.82	
		4.04×10^{-6}	-0.72	16.70 ± 1.14	
		2.02×10^{-6}	-0.73	9.71 ± 0.75	
		1.01×10^{-6}	-0.74	1.61 ± 0.13	1.01×10^{-6}

* average anodic peak current ± average deviation of more than 5 trials.

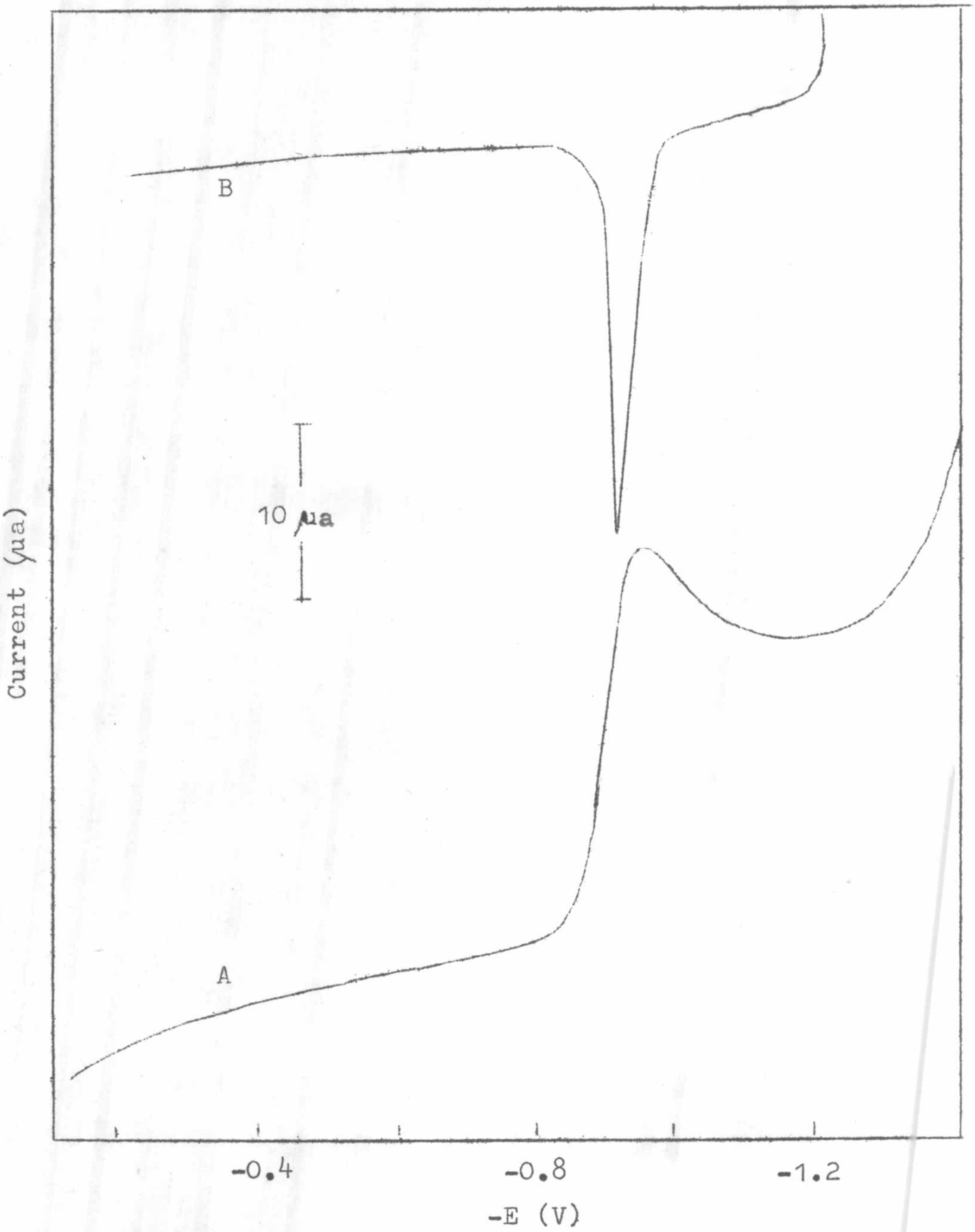

Figure 4.4 Voltammograms of indium in acetate buffer pH 5.0 (0.0472 M acetic acid -0.1128 M sodium acetate) : A) cathodic voltammogram of 1.00 X 10^{-3}M In (III) and B) anodic voltammogram of 2.02 X 10^{-4}M In (III) with a 3 minute deposition at -1.0 V.

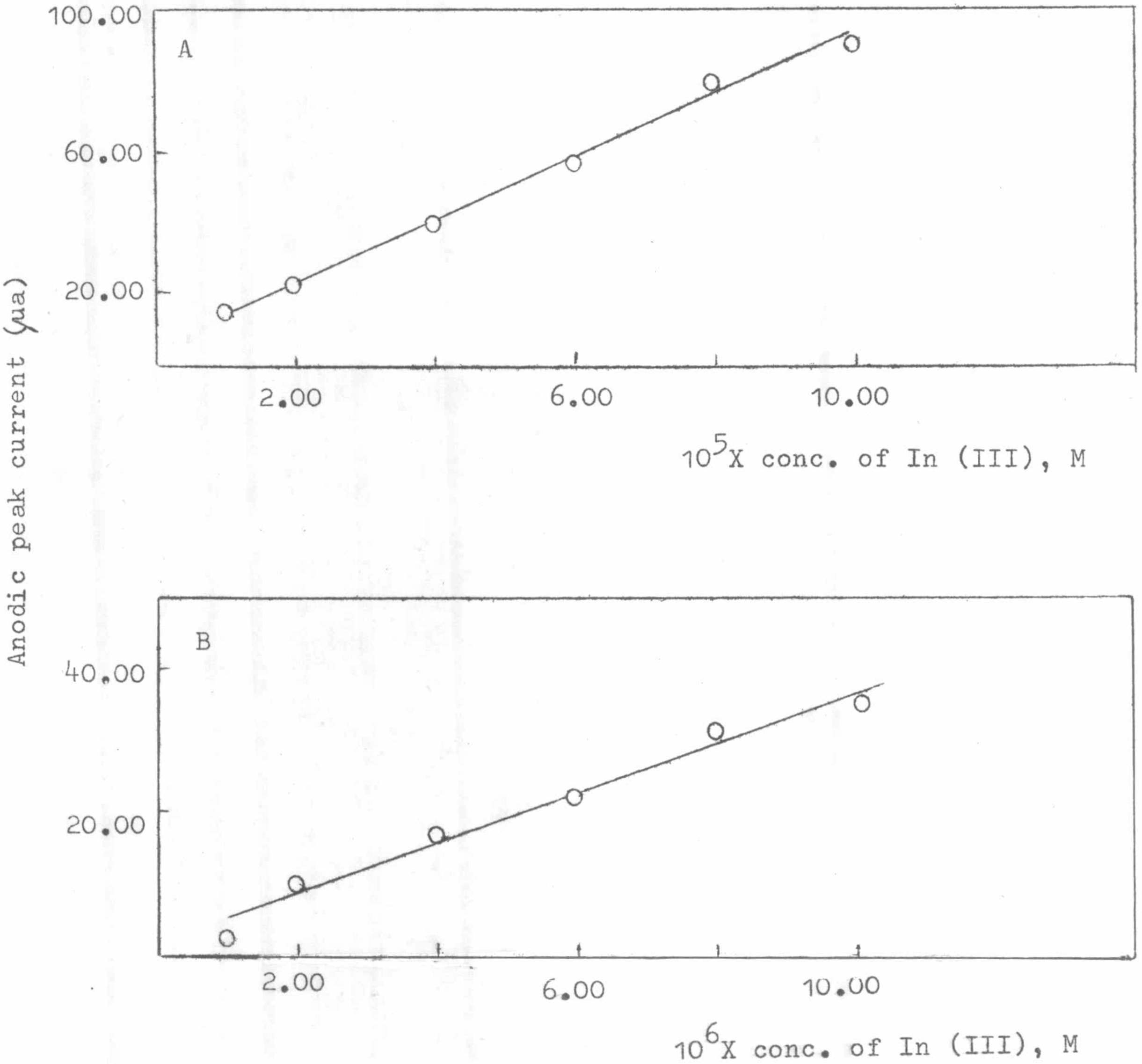

Figure 4.5 The linear dependence of anodic peak current on concentration for the anodic stripping analysis of In (III) in acetate buffer pH 5.0 using electrodeposition time of A) 3 minutes B) 10 minutes The lines drawn are calculated least squares lines.