

## CHAPTER 3 EXPERIMENTAL RESULTS

### 3.1 Construction of the Iodide CWISE

#### 3.1.1 Preparation of AgI

Silver iodide precipitate was yellow powder, which gave 96.84 % yield.

#### 3.1.2 Preparation of coating solution

Table 3.1 Observation characteristics of coating solution

Polymer matrix	Observation characteristics of coating solution	
	Without solvent	With solvent *
1. Epoxy resin	thick, viscous and could be homogenized with AgI with difficulty.	thin, clear and could be homogenized with AgI easily.
2. Hardener of epoxy resin	thick, viscous and could be homogenized with AgI with difficulty.	thin, clear and could be homogenized with AgI easily.
3. Epoxy resin mixed together with its hardener	suddenly hardened in 5 minutes.	hardly dissolved in solvent and could not be homogenized with AgI.
4. PVC	-	thin, clear and easily to homogenized with AgI.

\* = with acetone as solvent except PVC with cyclohexanone as solvent

#### 3.1.3 Preparation of electrodes

From results in 3.1.2, coating solution used was prepared with solvent ; acetone and cyclohexanone.

Table 3.2 Observed characteristics of electrode

Polymer matrix	observed characteristics of electrode
1. Epoxy resin	coated area was in the form of yellow bead and was found to give response by measurement of iodide concentration.
2. Hardener of epoxy resin	coated area was yellow bead and slowly change to greenish-yellow in one night. It was not found to give response by measurement of iodide concentration.
3. Epoxy resin mixed with its hardener	electrode could not be prepared.
4. PVC	coated area was yellow bead and was found to give response to the concentration of iodide.

### 3.2 The investigation of the effect of optimum ratio of silver iodide and epoxy resin

Table 3.3 Electrode slopes of iodide CWISE (E1-E5) in the ratio of 2:1  
(AgI:epoxy resin ) w/w at  $25.0 \pm 0.5$  °C

Electrode number	Electrode slope (mV/decade)
E1	63.8
E2	26.5
E3	24.8
E4	75.9
E5	17.1
$\bar{X}$	41.6
(S.D.) <sub>n</sub>	23.5
%R.S.D.	56.5

Table 3.4 Electrode slopes of iodide CWISE (E6-E10) in the ratio 3:1  
(AgI:epoxy resin ) w/w at  $25.0 \pm 0.5$  °C.

Electrode number	Electrode slope (mV/decade)
E6	54.0
E7	54.5
E8	68.9
E9	52.8
E10	61.9
$\bar{X}$	58.4
(S.D.) <sub>n</sub>	6.1
%R.S.D.	10.4

Table 3.5 Electrode slopes of iodide CWISE (E11-E15) in the ratio 4:1  
AgI:epoxy resin) w/w at  $25.0 \pm 0.5$  °C.

Electrode number	Electrode slope (mV/decade)
E11	38.9
E12	69.3
E13	53.2
E14	59.2
E15	49.1
$\bar{X}$	53.9
(S.D.) <sub>n</sub>	10.1
%R.S.D.	18.7

Table 3.6 Electrode slopes of iodide CWISE(E16-E20) in the ratio 5:1  
(AgI:epoxy resin) w/w at  $25.0 \pm 0.5$  °C.

Electrode number	Electrode slope (mV/decade)
E16	68.2
E17	74.2
E18	56.6
E19	47.2
E20	59.6
$\bar{X}$	61.2
(S.D.) <sub>n</sub>	9.3
%R.S.D.	15.2

Table 3.7 Electrode slopes of iodide CWISE(E21-E25) in the ratio 6:1  
AgI:epoxy resin) w/w at  $25.0 \pm 0.5^\circ\text{C}$ .

Electrode number	Electrode slope (mV/decade)
E21	78.5
E22	81.9
E23	81.5
E24	59.4
E25	93.6
$\bar{X}$	79.0
(S.D.) <sub>n</sub>	11.1
%R.S.D.	14.0

### 3.3 Effect of the membrane thickness on electrode slope of iodide CWISE

Table 3.8 Electrode slope of iodide CWISE in the range of membrane thickness; 0.0080-0.0100 g of coating solution at  $25.0 \pm 0.5$  °C

Electrode number	Membrane thickness (g of coating solution)	Electrode slope (mV/decade)
E26	0.0088	56.6
E27	0.0088	57.7
E28	0.0099	55.7
E29	0.0099	52.4
E30	0.0082	54.3
	$\bar{x}$	55.3
	(S.D.) <sub>n</sub>	1.84
	%R.S.D	3.32

Table 3.9 Electrode slope of iodide CWISE in the range of membrane thickness; 0.0150-0.0250 g of coating solution at  $25.0 \pm 0.5$  °C

Electrode number	Membrane thickness (g of coating solution)	Electrode slope (mV/decade)
E31	0.0200	46.1
E32	0.0195	30.8
E33	0.0200	38.8
E34	0.0235	34.4
E35	0.0154	27.9
	$\bar{x}$	35.6
	(S.D.) <sub>n</sub>	6.39
	%R.S.D	17.9

Table 3.10 Electrode slope of iodide CWISE in the range of membrane thickness; 0.0200-0.0270 g of coating solution at  $25.0 \pm 0.5$  °C

Electrode number	Membrane thickness (g of coating solution)	Electrode slope (mV/decade)
E36	0.0229	57.4
E37	0.0247	56.3
E38	0.0261	59.7
E39	0.0242	56.5
E40	0.0209	56.6
	$\bar{x}$	57.3
	(S.D.) <sub>n</sub>	1.25
	%R.S.D	2.18

### 3.4 Effect of particles size of silver iodide precipitate to electrode slope

#### 3.4.1 Electrode slope of iodide CWISE prepared with 200 mesh particle size of AgI

Table 3.11 First set of electrode slope of iodide CWISE prepared with 200 mesh particle size of AgI at  $25.0 \pm 0.5$  °C

Electrode number	membrane thickness of electrode (g of coating solution)	electrode slope (mV/decade)
E41	0.0208	60.3
E42	0.0234	62.7
E43	0.0282	60.7
E44	0.0228	63.1
E45	0.0231	58.5
$\bar{x}$	0.0237	61.1
(S.D) <sub>n</sub>	$2.44 \times 10^{-3}$	1.68
%R.S.D	10.2	2.75

Table 3.12 Second set of electrode slope of iodide CWISE prepared with 200 mesh particle size of AgI at  $25.0 \pm 0.5$  °C

Electrode number	membrane thickness of electrode (g of coating solution)	electrode slope (mV/decade)
E46	0.0200	46.1
E47	0.0195	30.8
E48	0.0200	38.8
E49	0.0235	34.4
E50	0.0194	27.9
$\bar{x}$	0.0205	35.6
(S.D) <sub>n</sub>	$1.53 \times 10^{-3}$	6.39
%R.S.D	7.46	17.9

### 3.4.2 Electrode slope of iodide CWISE prepared without particles size control of AgI

Table 3.13 First set of electrode slope of iodide CWISE prepared without particle size control of AgI at  $25.0 \pm 0.5$  °C

Electrode number	membrane thickness of electrode (g of coating solution)	electrode slope (mV/decade)
E51	0.0261	59.7
E52	0.0209	56.6
E53	0.0206	55.1
E54	0.0242	56.5
E55	0.0200	57.5
$\bar{x}$	0.0224	57.1
(S.D) <sub>n</sub>	$2.37 \times 10^{-3}$	1.52
%R.S.D	10.6	2.66

Table 3.14 Second set of electrode slope of iodide CWISE prepared without particle size control of AgI at  $25.0 \pm 0.5$  °C

Electrode number	membrane thickness of electrode (g of coating solution)	electrode slope (mV/decade)
E56	0.0207	64.1
E57	0.0186	49.0
E58	0.0247	49.3
E59	0.0213	87.5
E60	0.0214	53.3
$\bar{x}$	0.0213	60.6
(S.D) <sub>n</sub>	$1.96 \times 10^{-3}$	14.5
%R.S.D	9.20	23.9

### 3.5 Comparison of response time of conditioned and un-conditioned of iodide CWISE

#### 3.5.1 Results of un-conditioned iodide CWISE

Table 3.15 Response time of un-conditioned iodide CWISE (E61-E65) in the ratio of 3:1 (Agl:epoxy resin ) w/w in iodide solution  $10^{-3}$  M at  $25.0 \pm 0.5$  °C.

Electrode number	Response time (min)
E61	17.50
E62	22.50
E63	17.50
E64	21.25
E65	17.50

#### 3.5.2 Results of conditioned iodide CWISE

Table 3.16 Response time of conditioned iodide CWISE (E66-E70) in the ratio of 3:1 (Agl:epoxy resin) w/w in iodide solution  $10^{-3}$  M at  $25.0 \pm 0.5$  °C.

Electrode number	Response time (min)
E66	5.00
E67	2.00
E68	2.50
E69	7.50
E70	2.50

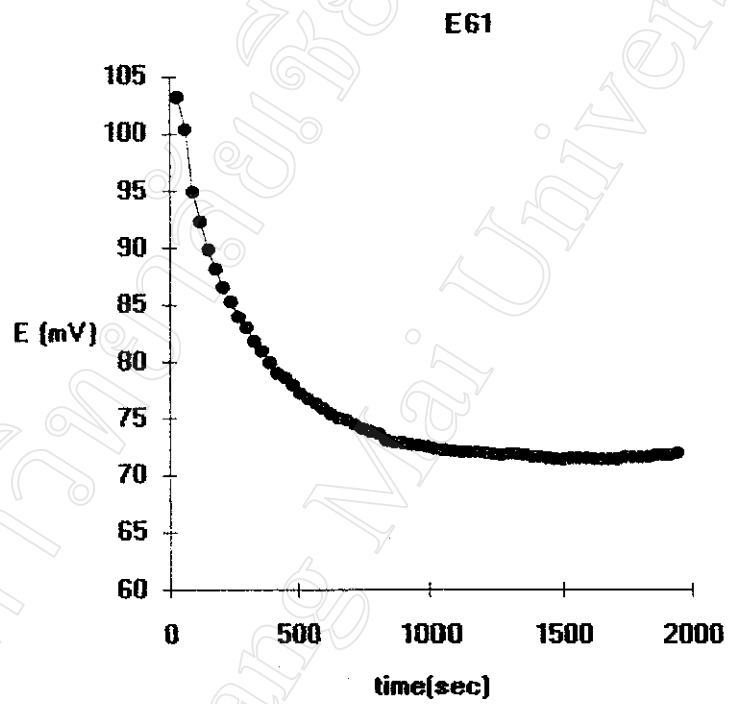


Figure 3.1 Response curve for estimation of response time of un-conditioned iodide CWISE (E61)

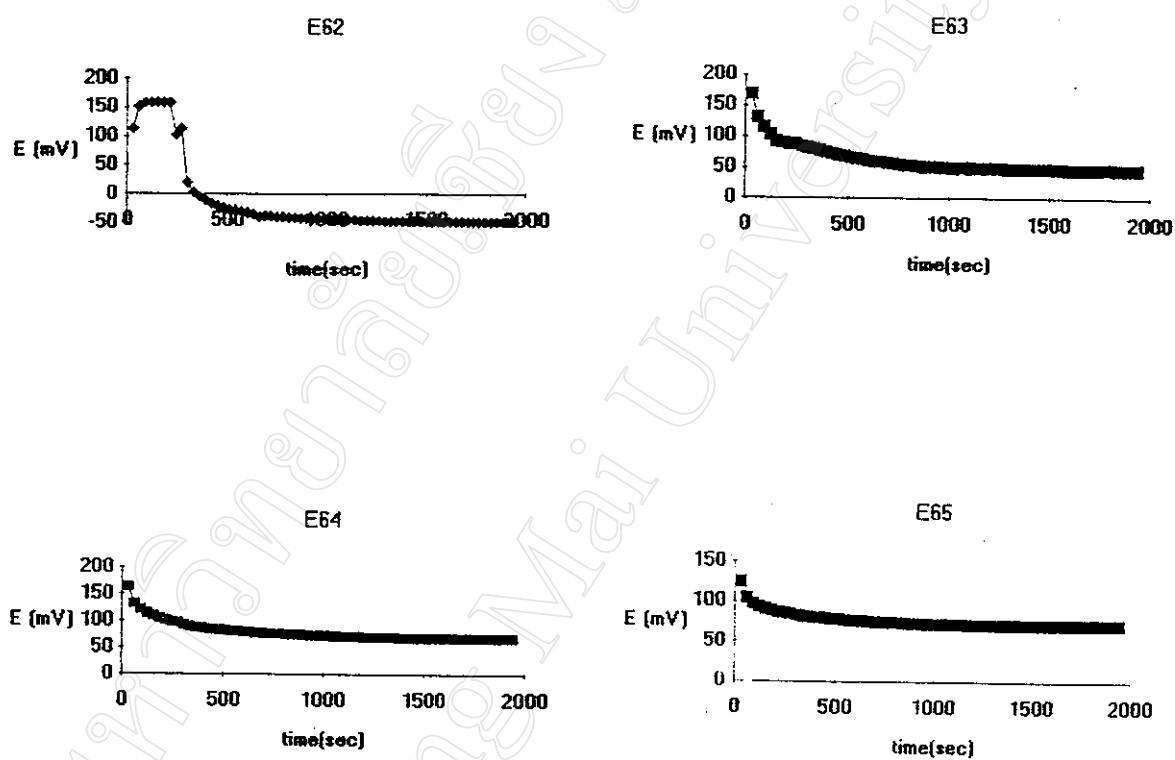


Figure 3.2 Response curve for estimation of response time of un-conditioned iodide CWISE (E62-65)

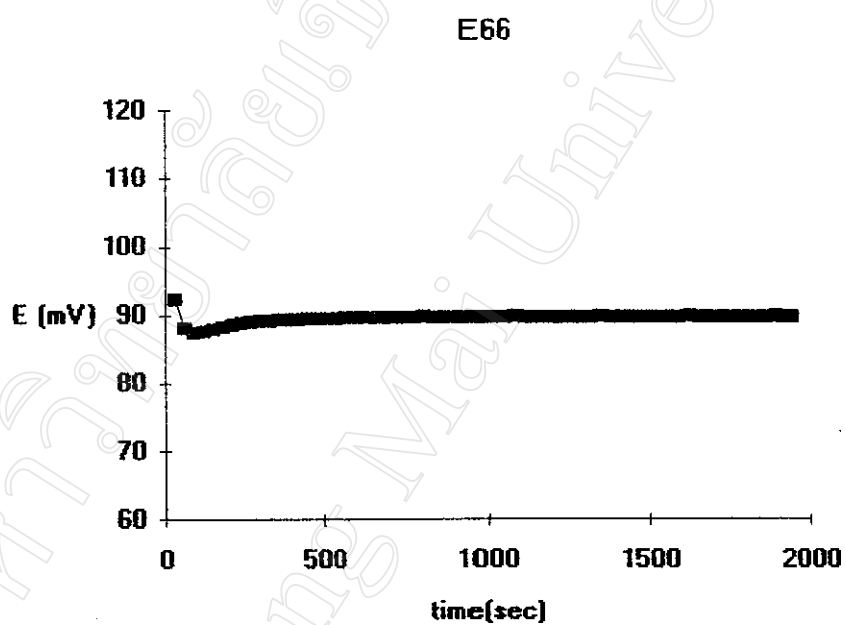


Figure 3.3 Response curve for estimation of response time of conditioned iodide CWISE (E66)

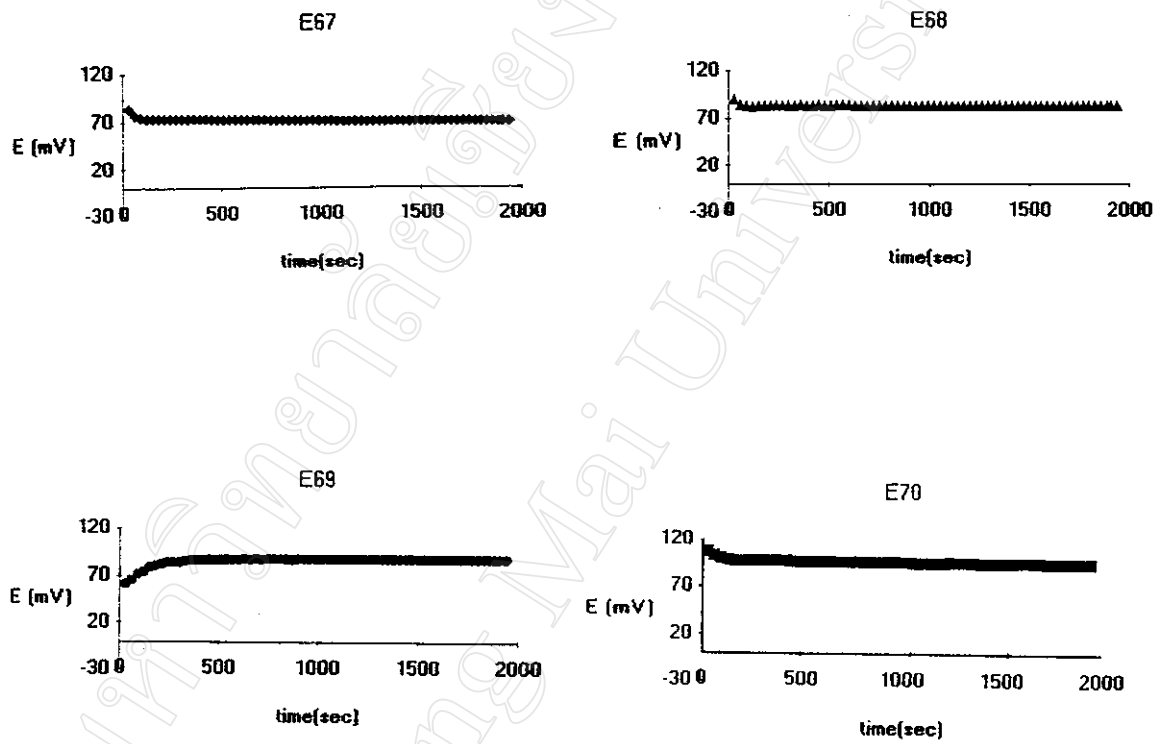


Figure 3.4 Response curve for estimation of response time of conditioned iodide CWISE (E67-70)

### 3.6 Effect of concentration on response time of iodide CWISE

Table 3.17 Potential of iodide CWISE (E66) in  $10^{-5}$  M iodide solution at  $25.0 \pm 0.5$  °C. The curve is shown in Fig. 3.5(i)

Time(sec)	E(mV)	Time(sec)	E(mV)	Time(sec)	E(mV)
0	123.6	420	126.6	840	124.8
30	123.5	450	126.4	870	124.8
60	123.5	480	126.8	900	124.7
90	123.9	510	127.5	930	124.5
120	124.1	540	127.2	960	124.5
150	124.6	570	127.6	990	124.4
180	125.0	600	126.9	1020	124.4
210	124.7	630	126.0	1050	124.3
240	124.7	660	125.8	1080	124.2
270	124.7	690	125.5	1110	124.2
300	125.0	720	125.4	1140	124.1
330	125.9	750	125.1	1170	124.1
360	125.9	780	125.0	1200	124.1
390	126.4	810	124.9		

Table 3.18 Potential of iodide CWISE (E66) in  $10^{-4}$  M iodide solution at  $25.0 \pm 0.5$  °C. The curve is shown in Fig. 3.5(ii)

Time(sec)	E(mV)	Time(sec)	E(mV)	Time(sec)	E(mV)
0	75.5	420	77.0	840	77.0
30	75.4	450	77.0	870	76.9
60	76.0	480	77.1	900	76.8
90	76.3	510	77.0	930	77.0
120	76.6	540	76.8	960	77.0
150	76.8	570	76.9	990	77.0
180	77.1	600	76.9	1020	76.9
210	77.0	630	76.9	1050	76.9
240	77.1	660	76.9	1080	76.9
270	77.2	690	76.9	1110	76.9
300	77.1	720	76.9	1140	76.8
330	77.1	750	76.9	1170	76.9
360	77.1	780	76.9	1200	77.0
390	77.1	810	76.9		

Table 3.19 Potential of iodide CWISE (E66) in  $10^{-3}$  M iodide solution at  $25.0 \pm 0.5$  °C. The curve is shown in Fig. 3.5(iii)

Time(sec)	E(mV)	Time(sec)	E(mV)	Time(sec)	E(mV)
0	89.0	420	74.5	840	73.7
30	79.4	450	74.4	870	73.8
60	76.8	480	74.3	900	73.8
90	76.3	510	74.2	930	73.7
120	75.9	540	74.1	960	73.8
150	75.6	570	74.0	990	73.8
180	75.4	600	74.0	1020	73.8
210	75.3	630	73.9	1050	73.8
240	75.1	660	73.9	1080	73.8
270	75.0	690	73.9	1110	73.8
300	74.9	720	73.8	1140	73.8
330	74.9	750	73.8	1170	73.7
360	74.7	780	73.7	1200	73.7
390	74.6	810	73.7		

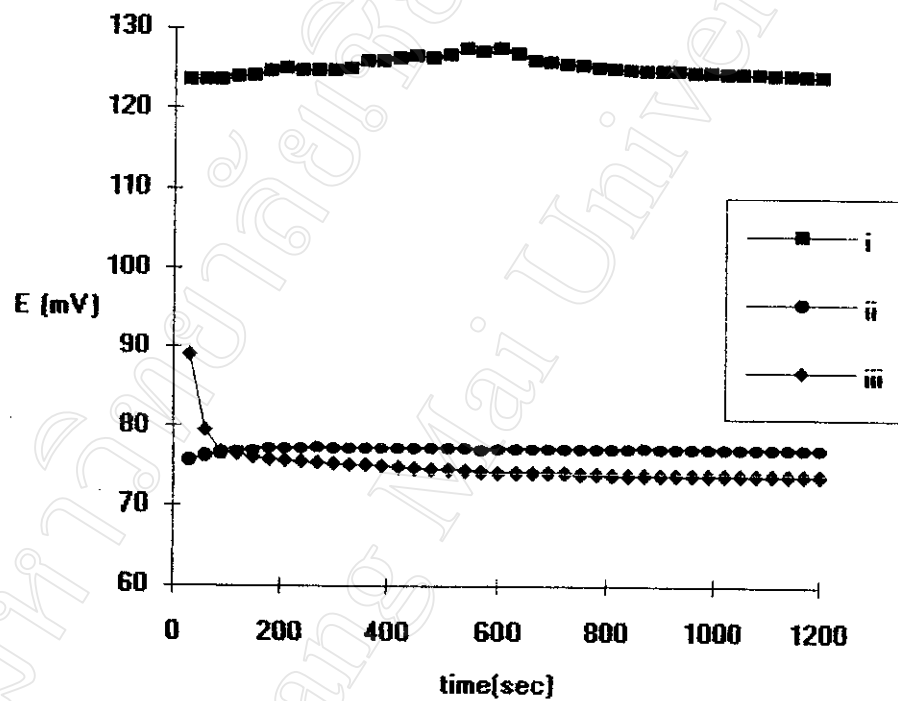


Figure 3.5 Response curve for estimation of response time of iodide CWISE (E66) in difference iodide concentrations

- (i)  $[I^-] = 10^{-5} \text{ M}$  ; response time = 13.30 min
- (ii)  $[I^-] = 10^{-4} \text{ M}$  ; response time = 2.50 min
- (iii)  $[I^-] = 10^{-3} \text{ M}$  ; response time = 1.50 min

### 3.7 Characteristics of iodide CWISE

#### 3.7.1 Response time of iodide CWISE and Orion iodide electrode

Table 3.20 Response time of iodide CWISE for the ratio AgI:epoxy resin of 3:1 w/w (E71-E75) and that of Orion iodide electrode in  $1 \times 10^{-3}$  M at  $25.0 \pm 0.5$  °C

Electrode number	Response time (min)
E71	1.00
E72	1.00
E73	1.00
E74	2.00
E75	1.50
Orion iodide electrode	0.50

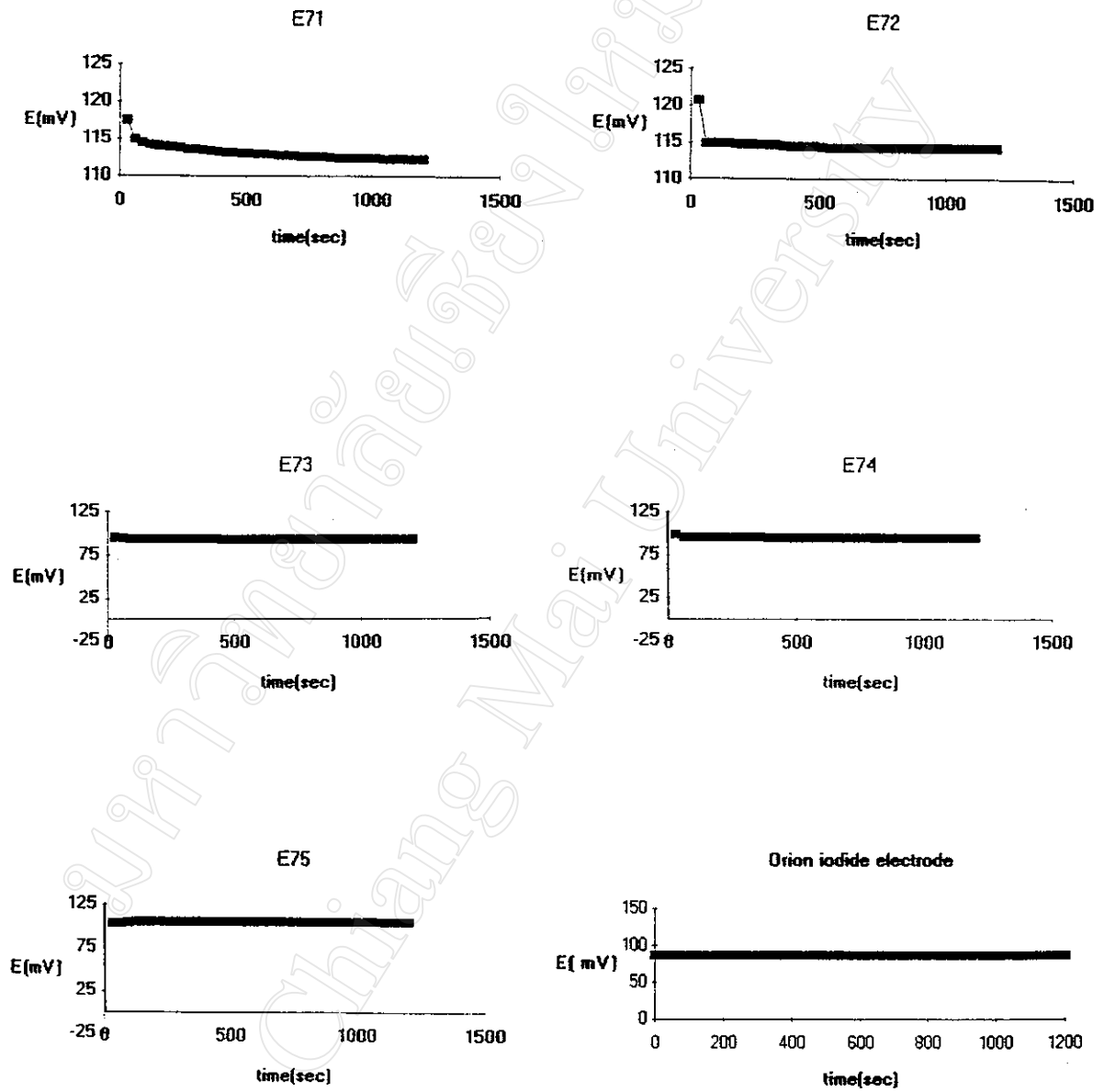


Figure 3.6 Response curve for estimation of response time of iodide CWISE and Orion iodide electrode

### 3.7.2 Detection limit of iodide CWISE and Orion iodide electrode

Table 3.21 Potentials of iodide CWISE (E71-E75) in the ratio of 3:1 (AgI:epoxy resin) w/w and that of Orion iodide electrode in iodide solution  $10^{-10}$  –  $10^0$  M at  $25.0 \pm 0.5$  °C. The curves are shown in Fig. 3.7-3.9

concentration of iodide solution (M)	Potential* (mV)					
	E71	E72	E73	E74	E75	Orion
$10^{-10}$	115.0	156.3	186.6	194.9	107.6	199.8
$10^{-9}$	196.1	171.1	175.0	182.6	192.6	196.6
$10^{-8}$	181.6	180.4	164.0	172.9	189.2	186.2
$10^{-7}$	164.6	166.2	142.8	159.1	174.5	174.1
$10^{-6}$	146.9	133.2	106.3	137.2	157.4	150.8
$10^{-5}$	123.0	89.9	96.6	118.6	130.3	132.5
$10^{-4}$	74.4	34.0	55.3	73.9	76.6	84.6
$10^{-3}$	22.2	-25.7	-1.3	21.4	17.0	28.0
$10^{-2}$	-29.9	-90.5	-58.0	-32.2	-47.1	-28.8
$10^{-1}$	-91.6	-148.5	-120.6	-86.9	-107.8	-89.3
$10^0$	-151.6	-191.0	-153.6	-150.9	-149.8	-149.3

\* = mean value from duplicate measurement

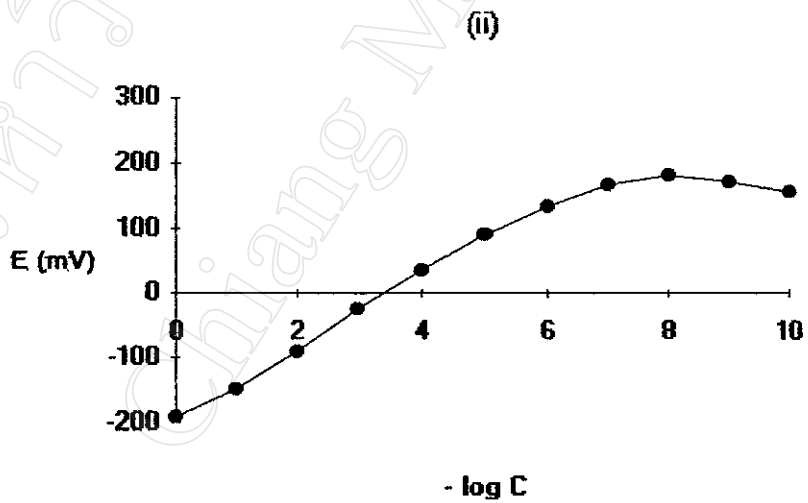
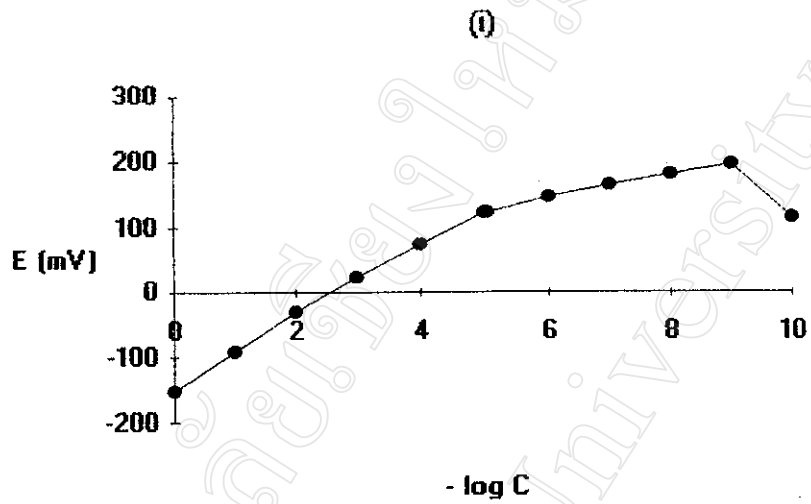


Figure 3.7 Response curve for estimation of detection limit of iodide CWISE

(i) E71

(ii) E72

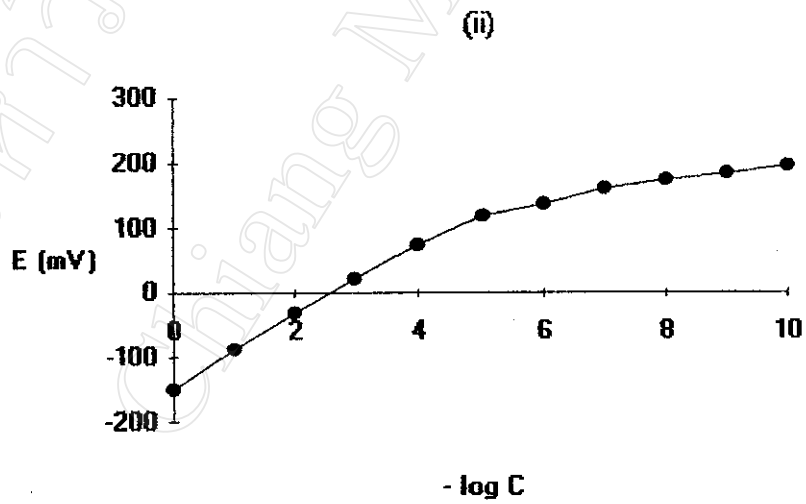
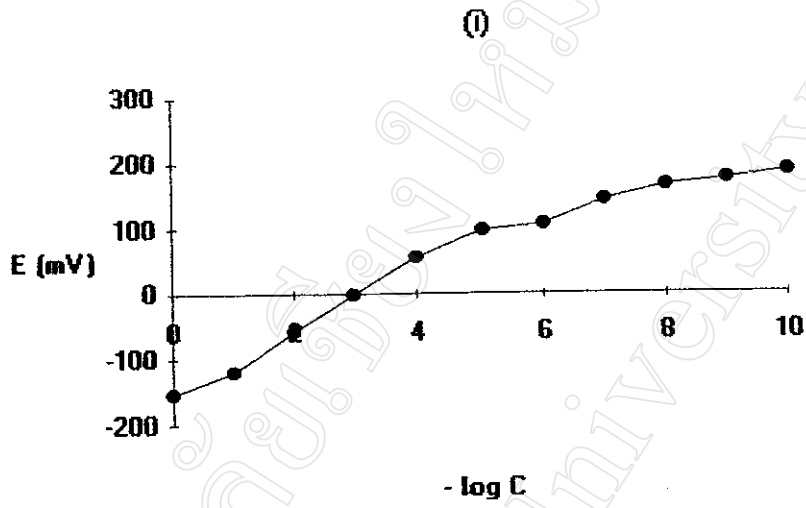


Figure 3.8 Response curve for estimation of detection limit of iodide CWISE

(i) E73

(ii) E74

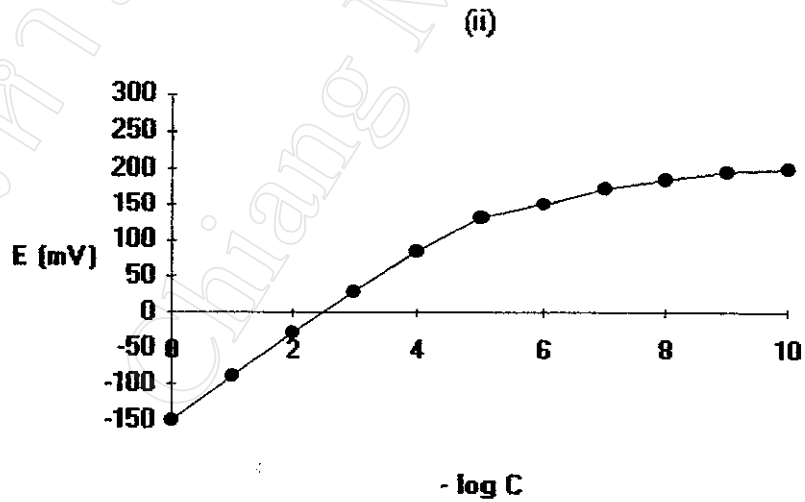
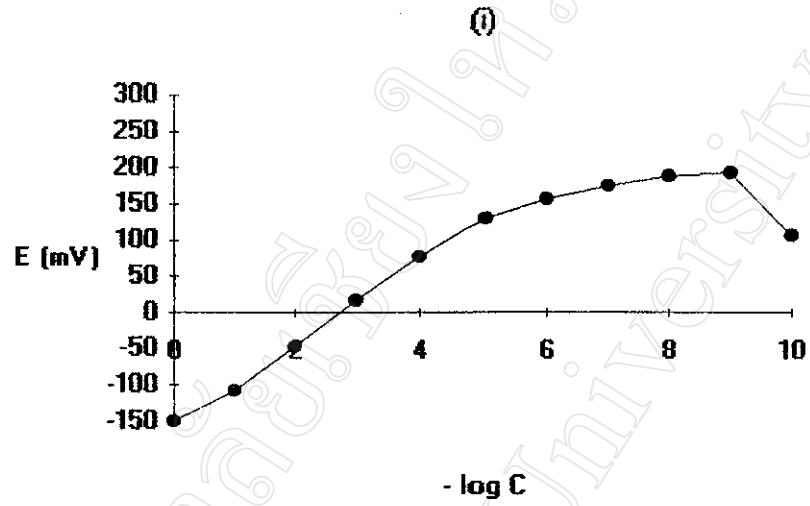


Figure 3.9 Response curve for estimation of detection limit of  
(i) iodide CWISE (E75)      (ii) Orion iodide electrode

Table 3.22 Detection limit of iodide CWISE (E71-E75) in the ratio of 3:1 (AgI:epoxy resin)w/w and Orion iodide electrode in iodide solution  $10^{-10}$ - $10^0$  M at  $25.0 \pm 0.5$  °C.

Electrode number	Detection limit ( $\times 10^{-5}$ ) (M)
E71	1.0
E72	0.3
E73	0.9
E74	1.0
E75	0.9
Orion iodide electrode	0.5

### 3.7.3 Sensitivity of electrodes

Electrode slope is a change of potentials which is obtained at tenfold concentration difference. Electrode slope is the best method to investigate the sensitivity of electrodes. In generally, it is in the range of 54-60 mV/decade.

### 3.7.3.1 Electrode slope of iodide CWISE

Table 3.23 Electrode slope of iodide CWISE for the ratio of AgI:epoxy resin 3:1 w/w (E71) at  $25.0 \pm 0.5$  °C.

Time(min)	Potential(mV)		Slope(mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
30	154.6	98.1	56.5
60	152.3	96.7	55.6
90	152.0	96.0	56.0
120	151.0	96.7	54.3
150	150.9	96.3	54.6
180	150.9	97.1	53.8
210	150.5	96.5	54.0
240	150.8	96.7	54.1
		$\bar{X}$	54.9
		(S.D.) <sub>n</sub>	0.96
		%R.S.D.	1.75

Table 3.24 Electrode slope of iodide CWISE for the ratio of AgI:epoxy resin 3:1 w/w (E72) at  $25.0 \pm 0.5$  °C.

Time(min)	Potential(mV)		Slope(mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
30	142.0	83.2	58.8
60	139.6	83.9	55.7
90	139.8	84.0	55.8
120	138.8	85.4	53.4
150	137.8	85.3	52.5
180	133.7	85.7	52.0
210	138.0	85.0	53.0
240	137.9	84.8	53.1
		$\bar{X}$	54.3
		(S.D.) <sub>n</sub>	2.14
		%R.S.D.	3.94

Table 3.25 Electrode slope of iodide CWISE for the ratio of AgI:epoxy resin 3:1 w/w (E73) at  $25.0 \pm 0.5$  °C.

Time(min)	Potential(mV)		Slope(mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
30	140.5	82.0	58.5
60	139.6	81.8	57.8
90	139.4	81.8	57.6
120	138.0	82.2	55.8
150	137.8	81.9	55.9
180	138.0	81.8	56.2
210	137.3	82.1	55.2
240	137.8	82.0	55.8
		$\bar{X}$	56.6
		(S.D.) <sub>n</sub>	1.11
		%R.S.D.	1.96

Table 3.26 Electrode slope of iodide CWISE for the ratio of AgI:epoxy resin 3:1 w/w (E74) at  $25.0 \pm 0.5$  °C.

Time(min)	Potential(mV)		Slope(mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
30	149.3	94.2	55.1
60	146.5	91.8	54.7
90	145.0	89.4	55.6
120	145.7	90.2	55.5
150	145.8	92.0	53.8
180	144.8	89.6	55.2
210	145.0	89.7	55.3
240	145.1	89.7	55.4
		$\bar{X}$	55.1
		(S.D.) <sub>n</sub>	0.54
		%R.S.D.	0.98

Table 3.27 Electrode slope of iodide CWISE for the ratio of AgI:epoxy resin 3:1 w/w (E75) at  $25.0 \pm 0.5$  °C.

Time(min)	Potential(mV)		Slope(mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
30	155.4	97.0	58.3
60	151.2	93.2	58.0
90	147.8	93.0	54.8
120	145.9	93.9	52.0
150	146.9	92.9	54.0
180	147.0	94.2	52.8
210	146.0	93.0	53.0
240	146.8	93.5	53.3
		$\bar{X}$	54.5
		(S.D.) <sub>n</sub>	2.23
		%R.S.D.	4.09

### 3.7.3.2 Electrode slope of Orion iodide electrode

Table 3.28 Electrode slope of Orion iodide electrode at  $25.0 \pm 0.5$  °C.

Time(min)	Potential(mV)		Slope(mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
30	101.1	45.7	55.4
60	100.4	45.3	55.1
90	100.0	45.8	54.7
120	101.4	46.1	55.3
150	100.1	45.2	54.9
180	100.8	45.1	55.7
210	101.9	46.0	55.9
240	101.0	46.2	54.8
		$\bar{x}$	55.2
		(S.D.) <sub>n</sub>	0.40
		%R.S.D.	0.72

### 3.7.4 Calibration curve of iodide CWISE and Orion iodide electrode

Table 3.29 Potential measurements with iodide CWISE and Orion iodide electrode for preparation of calibration curve at  $25.0 \pm 0.5$  °C. The curves are shown in Fig. 3.10-3.12

added volume of iodide (ml)	total added volume of iodide (ml)	final concentration of iodide ; $c_{I^-}$ (M)	$-\log c_{I^-}$	potential* (mV)					
				E71	E72	E73	E74	E75	Orion
0.30	0.30	$2.10 \times 10^{-5}$	4.68	91.8	78.4	76.1	94.3	80.8	95.1
0.20	0.50	$3.50 \times 10^{-5}$	4.46	80.1	66.5	64.4	82.9	69.1	82.0
0.20	0.70	$4.89 \times 10^{-5}$	4.30	71.5	58.5	56.1	74.6	60.9	74.0
0.30	1.00	$6.97 \times 10^{-5}$	4.16	63.0	49.2	47.0	65.2	51.4	65.2
2.00	3.00	$2.06 \times 10^{-4}$	3.69	36.0	22.2	19.4	38.0	24.6	39.8
2.00	5.00	$3.37 \times 10^{-4}$	3.47	23.6	9.2	6.9	24.8	12.0	25.0
2.00	7.00	$4.46 \times 10^{-4}$	3.33	15.3	1.2	-2.7	14.2	3.2	19.0
3.00	10.00	$6.46 \times 10^{-4}$	3.19	7.0	-7.5	-10.8	6.8	-5.2	12.3
20.00	30.00	$1.66 \times 10^{-3}$	2.78	-17.3	-31.4	-34.5	-16.8	-29.4	-9.9
20.00	50.00	$2.43 \times 10^{-3}$	2.61	-26.7	-41.9	-44.3	-26.9	-39.5	-20.1
20.00	70.00	$3.03 \times 10^{-3}$	2.52	-32.5	-47.0	-49.2	-32.2	-45.2	-25.2
30.00	100.00	$3.72 \times 10^{-3}$	2.43	-37.7	-51.9	-54.1	-37.2	-50.0	-30.2

\* = mean value from duplicate measurement

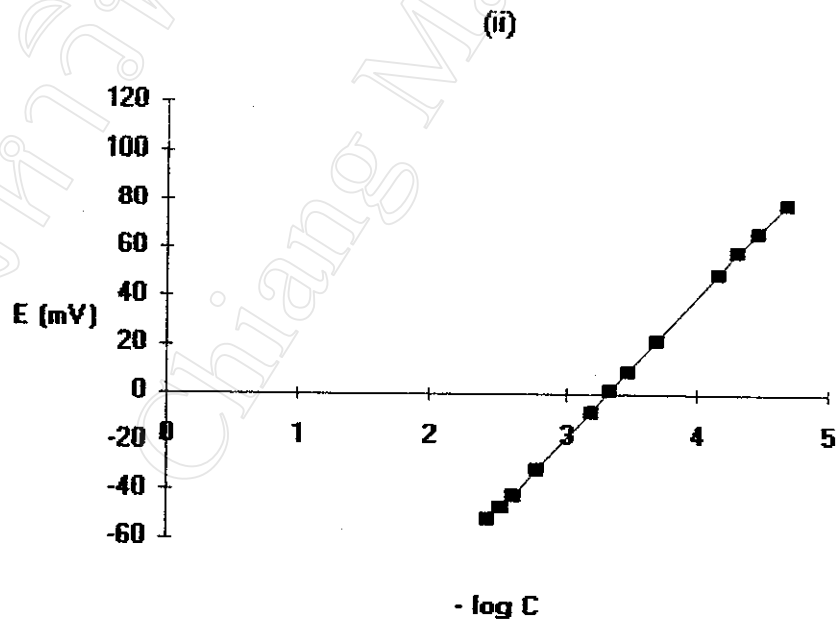
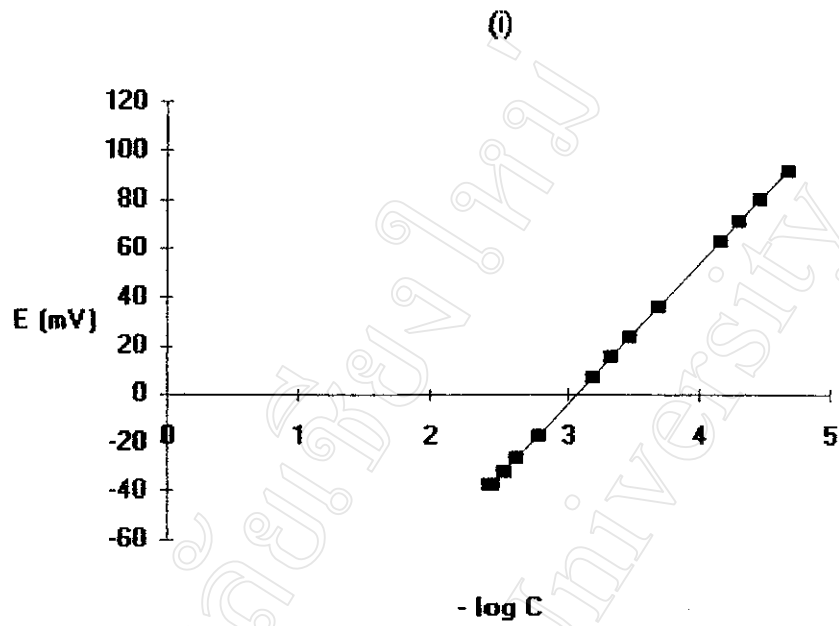


Figure 3.10 Calibration curve of iodide CWISE

(i) E71 ;  $r = 0.986$ , slope = 55.5 mV

(ii) E72 ;  $r = 0.999$ , slope = 58.5 mV

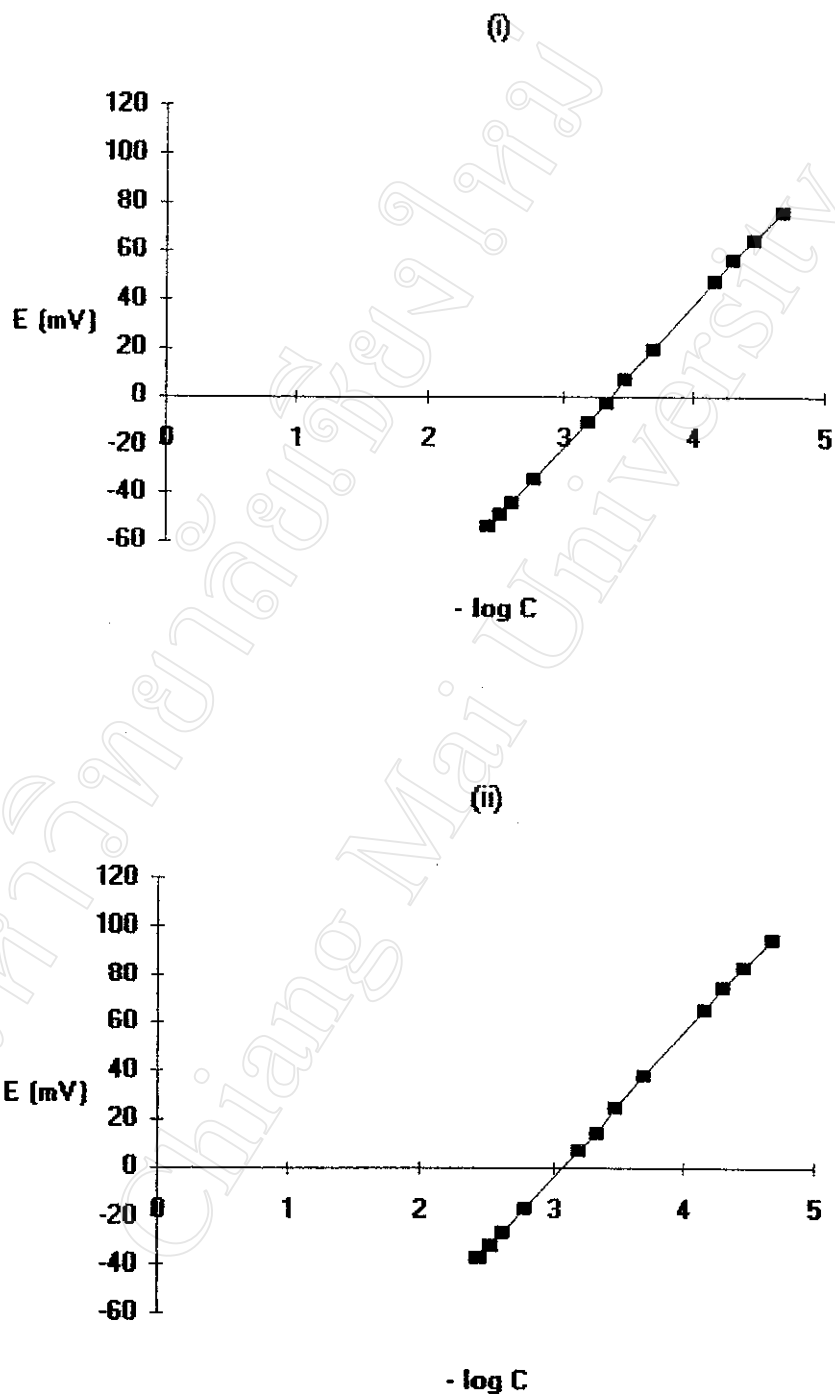


Figure 3.11 Calibration curve of iodide CWISE

(i) E73 ;  $r = 0.999$ , slope = 58.6 mV

(ii) E74 ;  $r = 0.999$ , slope = 59.2 mV

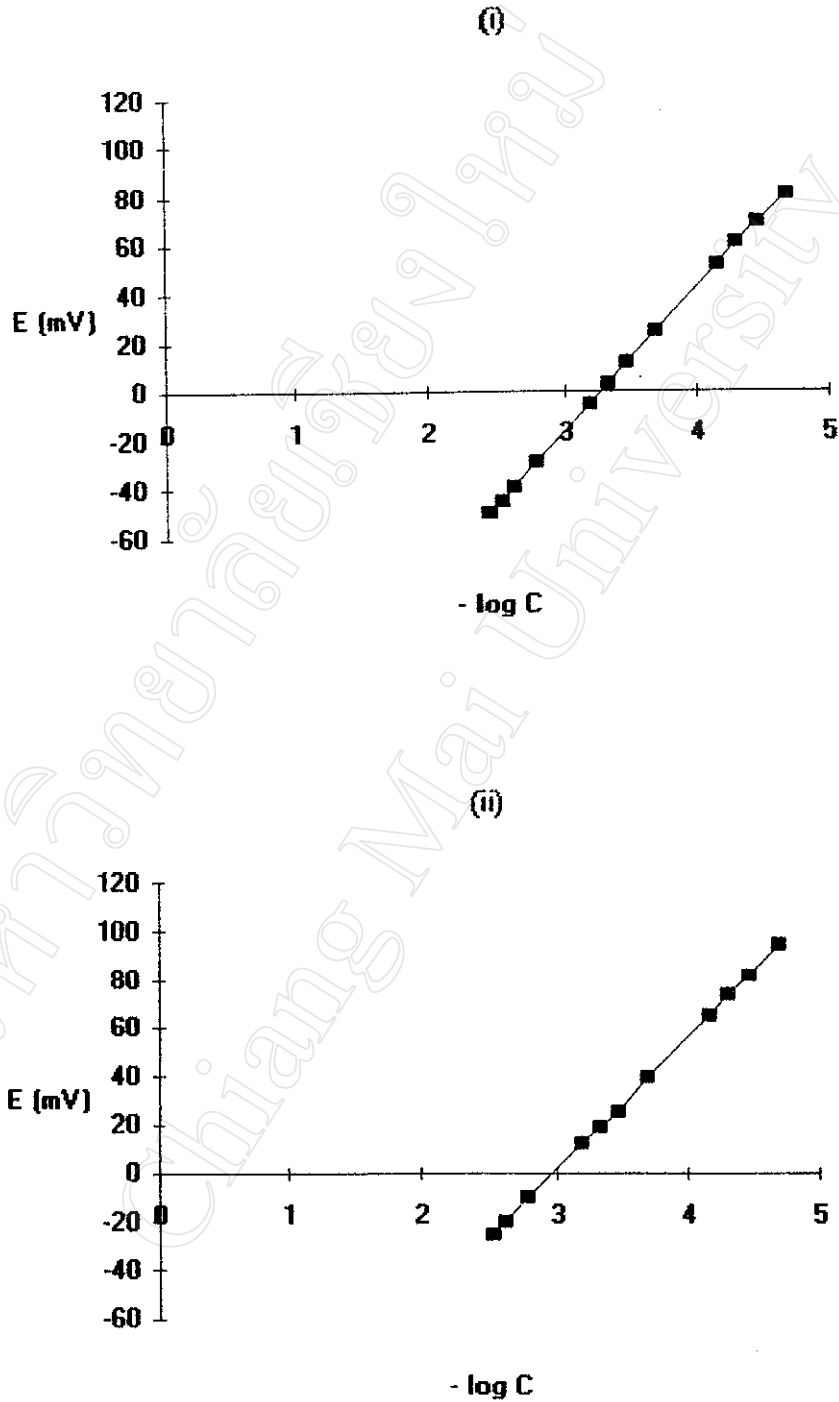


Figure 3.12 Calibration curve of

(i) iodide CWISE (E75) ;  $r = 0.999$ , slope = 58.7 mV

(ii) Orion iodide electrode;  $r = 0.999$ , slope = 55.4 mV

### 3.7.5 Selectivity coefficient of iodide CWISE

#### 3.7.5.1 Selectivity coefficient of iodide CWISE and Orion iodide electrode with bromide as interfering ion

Table 3.30 Potential of iodide CWISE and Orion iodide electrode for the estimation of  $K_{I,Br}^{pot}$  at  $25.0 \pm 0.5^\circ\text{C}$  The curves are shown in Fig 3.13-3.15

added volume of iodide (ml)	total added volume of iodide (ml)	final concentration of iodide ; $C_I$ (M)	$-\log C_I$	potential* (mV)					
				E71	E72	E73	E74	E75	Orion
0.03	0.03	$2.68 \times 10^{-6}$	5.57	135.4	124.9	125.2	134.5	127.4	162.3
0.03	0.06	$5.35 \times 10^{-6}$	5.27	127.3	115.7	115.5	125.3	118.6	147.8
0.02	0.08	$7.14 \times 10^{-6}$	5.14	121.6	110.0	109.1	119.2	112.5	138.8
0.22	0.30	$2.67 \times 10^{-5}$	4.57	94.3	81.5	80.9	91.0	84.6	108.1
0.30	0.60	$5.33 \times 10^{-5}$	4.27	77.8	65.1	64.0	74.1	67.4	90.9
0.30	0.90	$7.97 \times 10^{-5}$	4.09	68.6	55.2	54.4	64.2	57.4	79.6
2.10	3.00	$2.61 \times 10^{-4}$	3.58	38.9	25.0	24.0	34.4	27.8	50.3
3.00	6.00	$5.08 \times 10^{-4}$	3.29	22.1	7.8	6.7	17.4	11.0	32.8
3.00	9.00	$7.44 \times 10^{-4}$	3.13	12.6	-1.54	-3.1	7.8	1.5	22.8
11.00	20.00	$1.52 \times 10^{-3}$	2.82	-5.3	-19.6	-21.4	-10.2	-16.6	4.0
20.00	40.00	$2.63 \times 10^{-3}$	2.58	-19.5	-34.2	-35.4	-24.2	-30.5	-10.8
20.00	60.00	$3.49 \times 10^{-3}$	2.46	-26.9	-42.0	-43.1	-31.9	-38.3	-18.8

\* = mean value from duplicate measurement

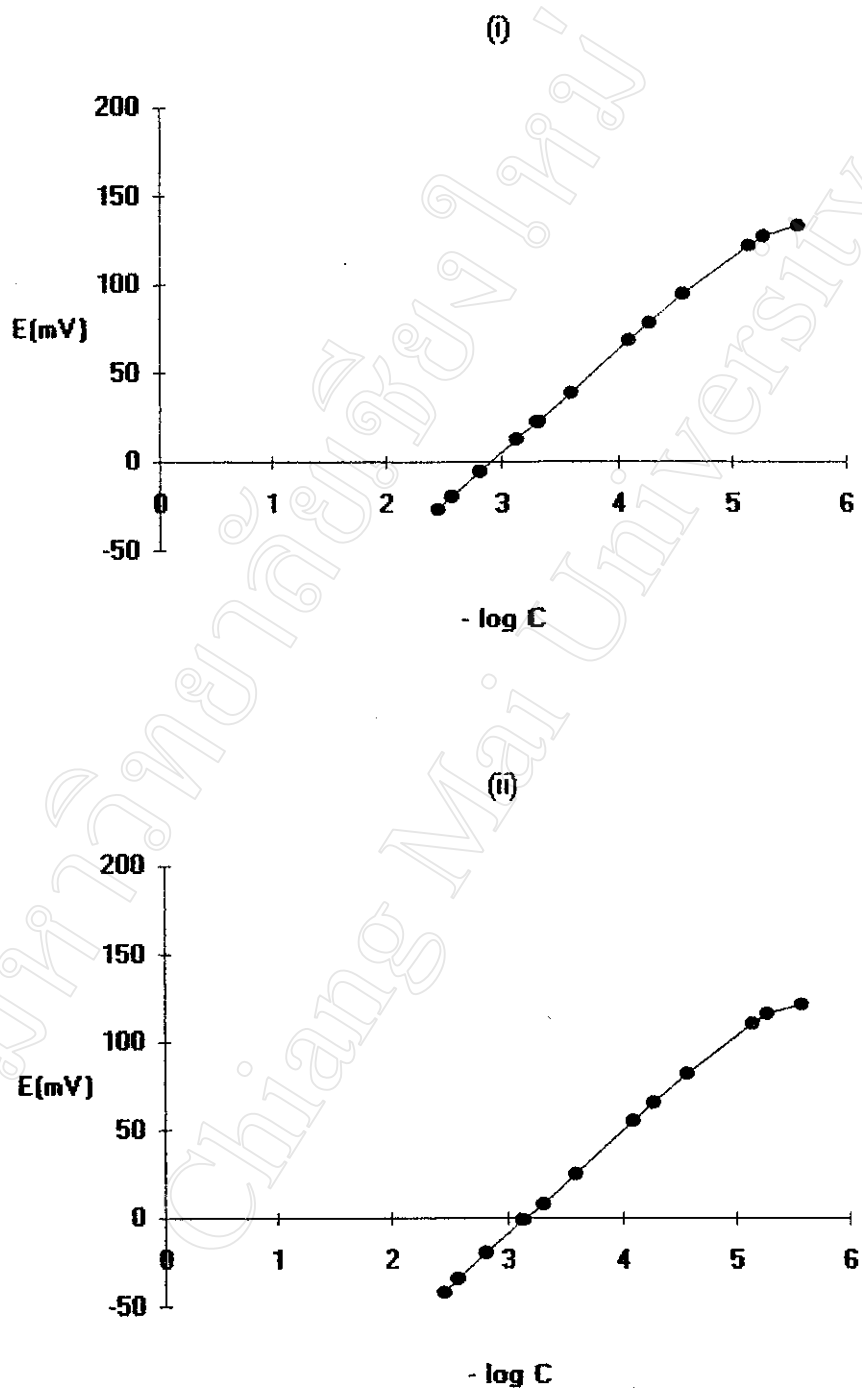


Figure 3.13 Response curve for estimation of selectivity coefficient of iodide CWISE with  $10^{-2}$  M bromide as interfering ion

(i) E71

(ii) E72

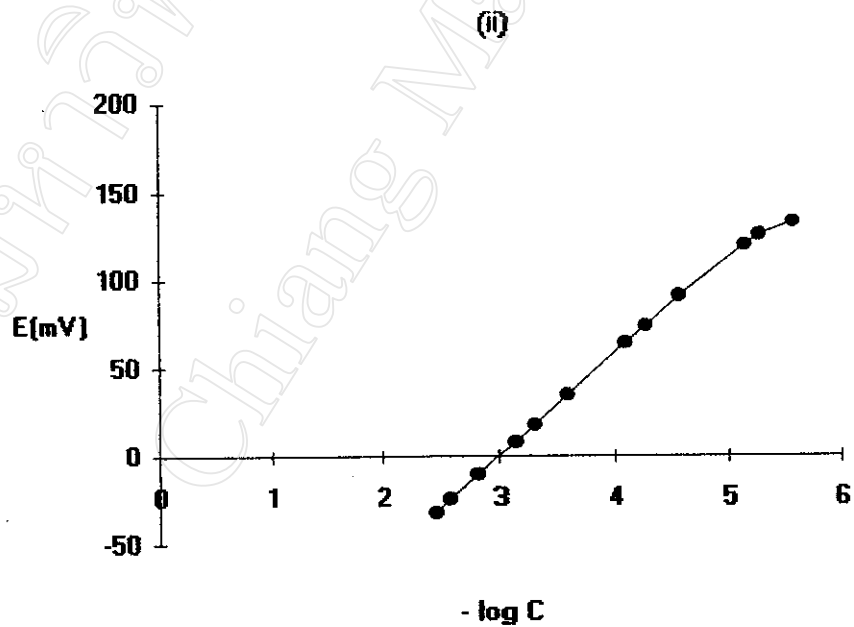
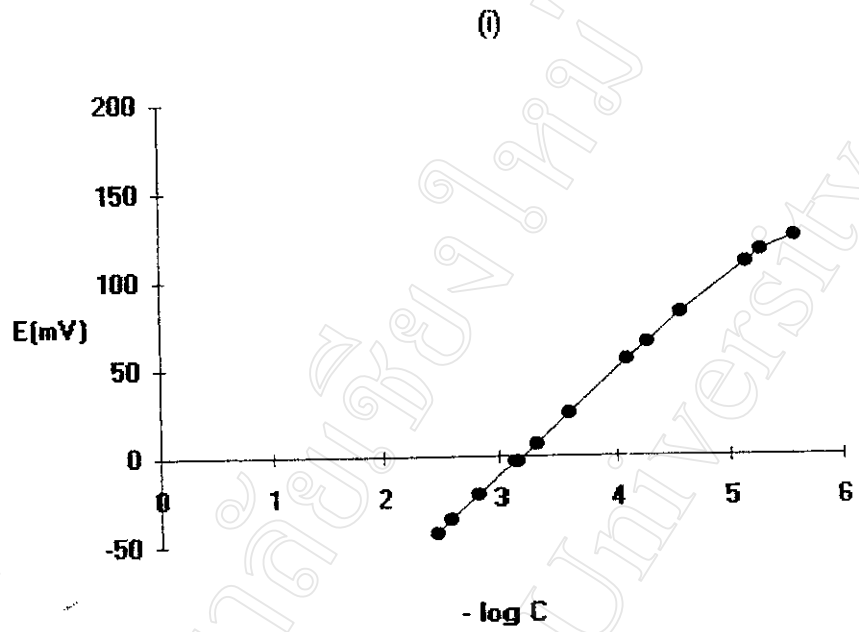


Figure 3.14 Response curve for estimation of selectivity coefficient of iodide CWISE with  $10^{-2}$  M bromide as interfering ion

(i) E73

(ii) E74

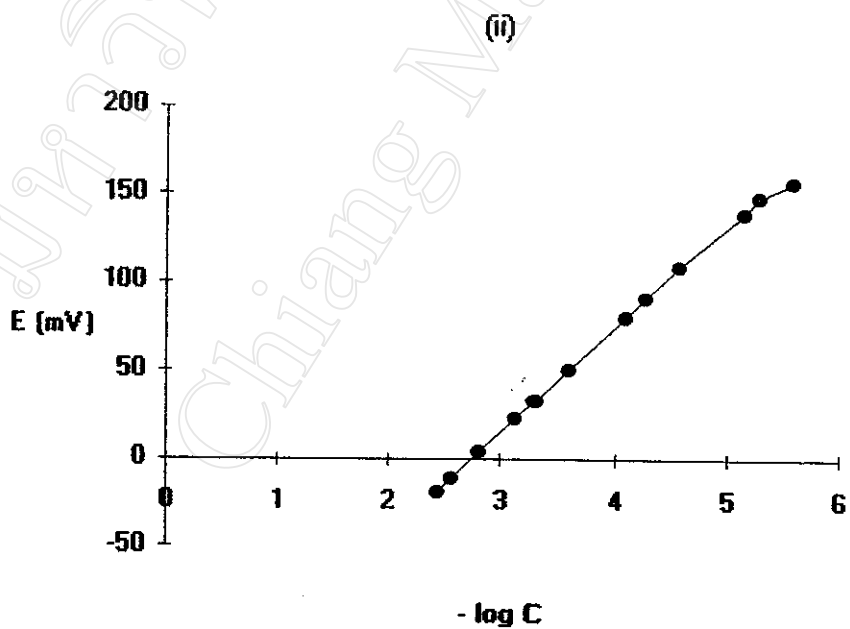
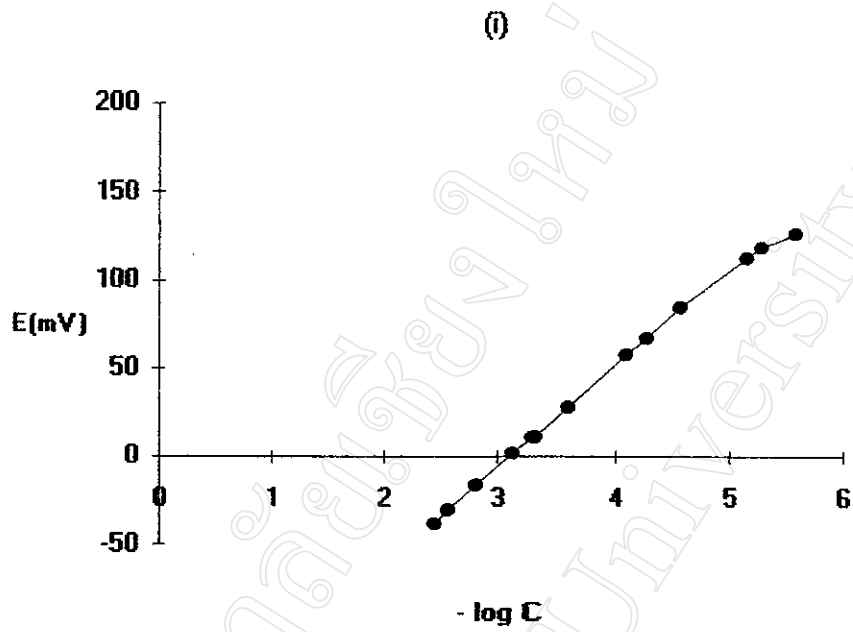


Figure 3.15 Response curve for estimation of selectivity coefficient of (i) iodide CWISE (E75) and (ii) Orion iodide electrode, with  $10^{-2}$  M bromide as interfering ion

### 3.7.5.2 Selectivity coefficient of iodide CWISE and Orion iodide electrode with fluoride as interfering ion

Table 3.31 Potential of iodide CWISE and Orion iodide electrode for the estimation of  $K_{IF}^{pot}$  at  $25.0 \pm 0.5^\circ\text{C}$  The curves are shown in Fig 3.16-3.18

added volume of iodide (ml)	total added volume of iodide (ml)	final concentration of iodide ; $c_{I^-}$ (M)	$-\log c_{I^-}$	potential* (mV)					
				E71	E72	E73	E74	E75	Orion
0.03	0.03	$2.68 \times 10^{-6}$	5.57	101.3	103.9	101.9	107.5	101.9	146.8
0.03	0.06	$5.35 \times 10^{-6}$	5.27	100.1	100.2	98.3	105.6	99.0	132.2
0.02	0.08	$7.14 \times 10^{-6}$	5.14	97.7	97.3	95.6	103.0	96.1	122.3
0.22	0.30	$2.67 \times 10^{-5}$	4.57	77.4	74.4	72.4	81.0	74.0	110.5
0.30	0.60	$5.33 \times 10^{-5}$	4.27	64.5	59.5	58.1	66.9	59.9	84.7
0.30	0.90	$7.97 \times 10^{-5}$	4.09	56.7	50.0	48.9	58.4	51.5	74.3
2.10	3.00	$2.61 \times 10^{-4}$	3.58	30.9	21.8	20.6	30.9	23.6	46.2
3.00	6.00	$5.08 \times 10^{-4}$	3.29	16.9	6.4	5.2	16.0	8.3	29.6
3.00	9.00	$7.44 \times 10^{-4}$	3.13	8.8	-3.1	-4.2	7.1	-0.5	20.0
11.00	20.00	$1.52 \times 10^{-3}$	2.82	-6.9	-20.4	-21.0	-9.3	-17.4	1.8
20.00	40.00	$2.63 \times 10^{-3}$	2.58	-19.3	-33.7	-34.5	-22.2	-31.1	-12.6
20.00	60.00	$3.49 \times 10^{-3}$	2.46	-25.6	-40.0	-41.5	-28.9	-37.2	-20.2

\* = mean value from duplicate measurement

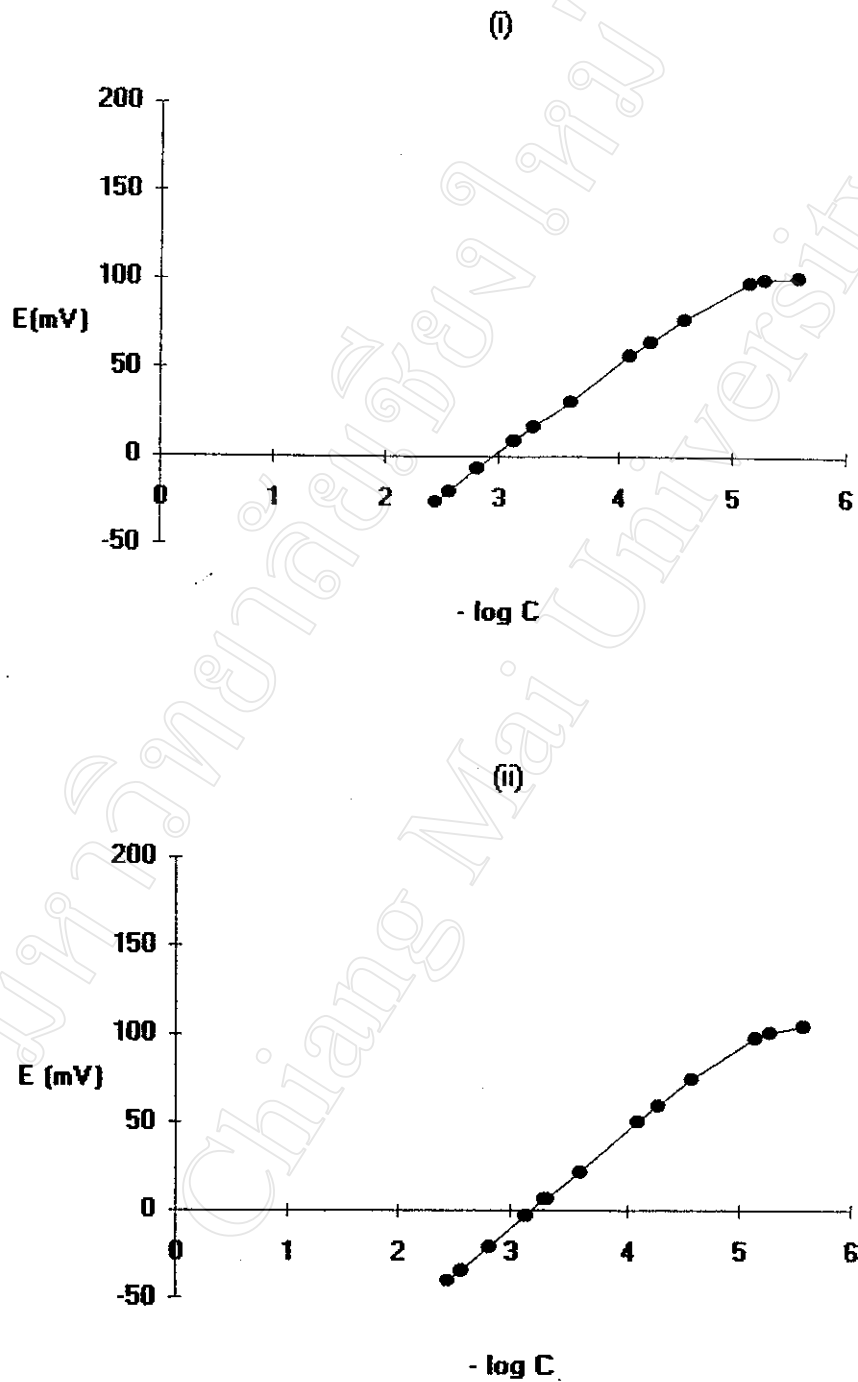


Figure 3.16 Response curve for estimation of selectivity coefficient of iodide CWISE with  $10^{-2}$  M fluoride as interfering ion

(i) E71      (ii) E72

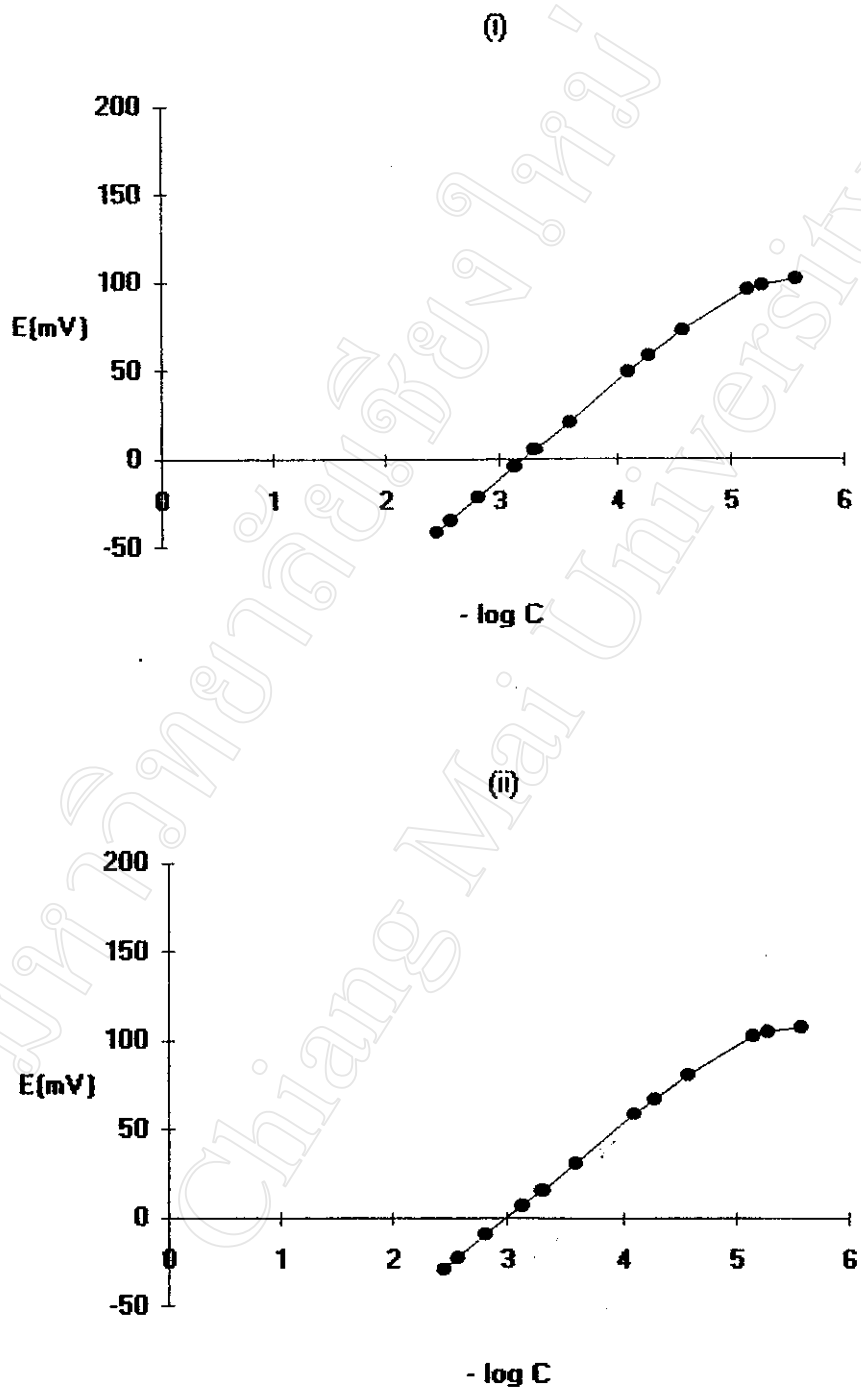


Figure 3.17 Response curve for estimation of selectivity coefficient of iodide CWISE with  $10^{-2}$  M fluoride as interfering ion

(i) E73

(ii) E74

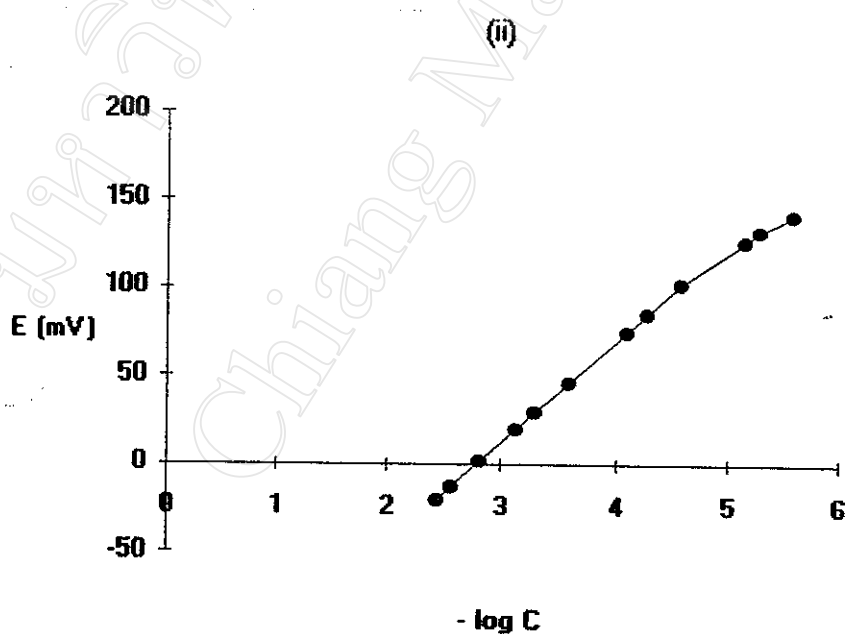
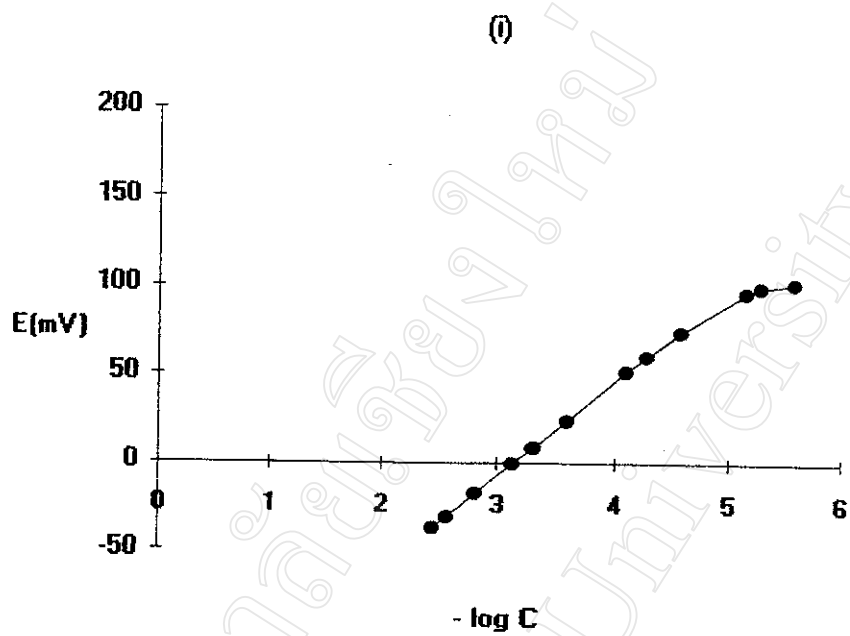


Figure 3.18 Response curve for estimation of selectivity coefficient of (i) iodide CWISE (E75) and (ii) Orion iodide electrode, with  $10^{-2}$  M fluoride as interfering ion

### 3.7.5.3 Selectivity coefficient of iodide CWISE and Orion iodide electrode with chloride as interfering ion

Table 3.32 Potential of iodide CWISE and Orion iodide electrode for the estimation of  $K_{I,Cl}^{pot}$  at  $25.0 \pm 0.5^\circ C$  The curves are shown in Fig 3.19-3.21

added volume of iodide (ml)	total added volume of iodide (ml)	final concentration of iodide ; $c_{I^-}$ (M)	$-\log c_{I^-}$	potential* (mV)					
				E71	E72	E73	E74	E75	Orion
0.03	0.03	$2.68 \times 10^{-6}$	5.57	124.0	123.6	122.7	131.5	121.5	122.4
0.03	0.06	$5.35 \times 10^{-6}$	5.27	114.9	112.7	112.0	120.7	111.2	116.2
0.02	0.08	$7.14 \times 10^{-6}$	5.14	110.0	107.3	106.5	115.2	105.8	111.8
0.22	0.30	$2.67 \times 10^{-5}$	4.57	82.8	77.5	76.6	86.9	77.1	91.6
0.30	0.60	$5.33 \times 10^{-5}$	4.27	68.6	61.9	60.7	70.4	62.0	80.6
0.30	0.90	$7.97 \times 10^{-5}$	4.09	59.3	52.5	51.0	60.7	53.1	72.9
2.10	3.00	$2.61 \times 10^{-4}$	3.58	30.2	21.3	20.1	30.1	22.2	46.9
3.00	6.00	$5.08 \times 10^{-4}$	3.29	15.6	5.3	4.2	14.4	6.9	30.7
3.00	9.00	$7.44 \times 10^{-4}$	3.13	6.9	-4.0	5.0	5.3	-2.3	21.2
11.00	20.00	$1.52 \times 10^{-3}$	2.82	-8.9	-20.8	-21.9	-11.4	-18.8	3.0
20.00	40.00	$2.63 \times 10^{-3}$	2.58	-21.3	-34.1	-35.1	-24.1	-31.4	-11.5
20.00	60.00	$3.49 \times 10^{-3}$	2.46	-27.8	-41.4	-42.2	-31.2	-37.9	-20.0

\* = mean value from duplicate measurement

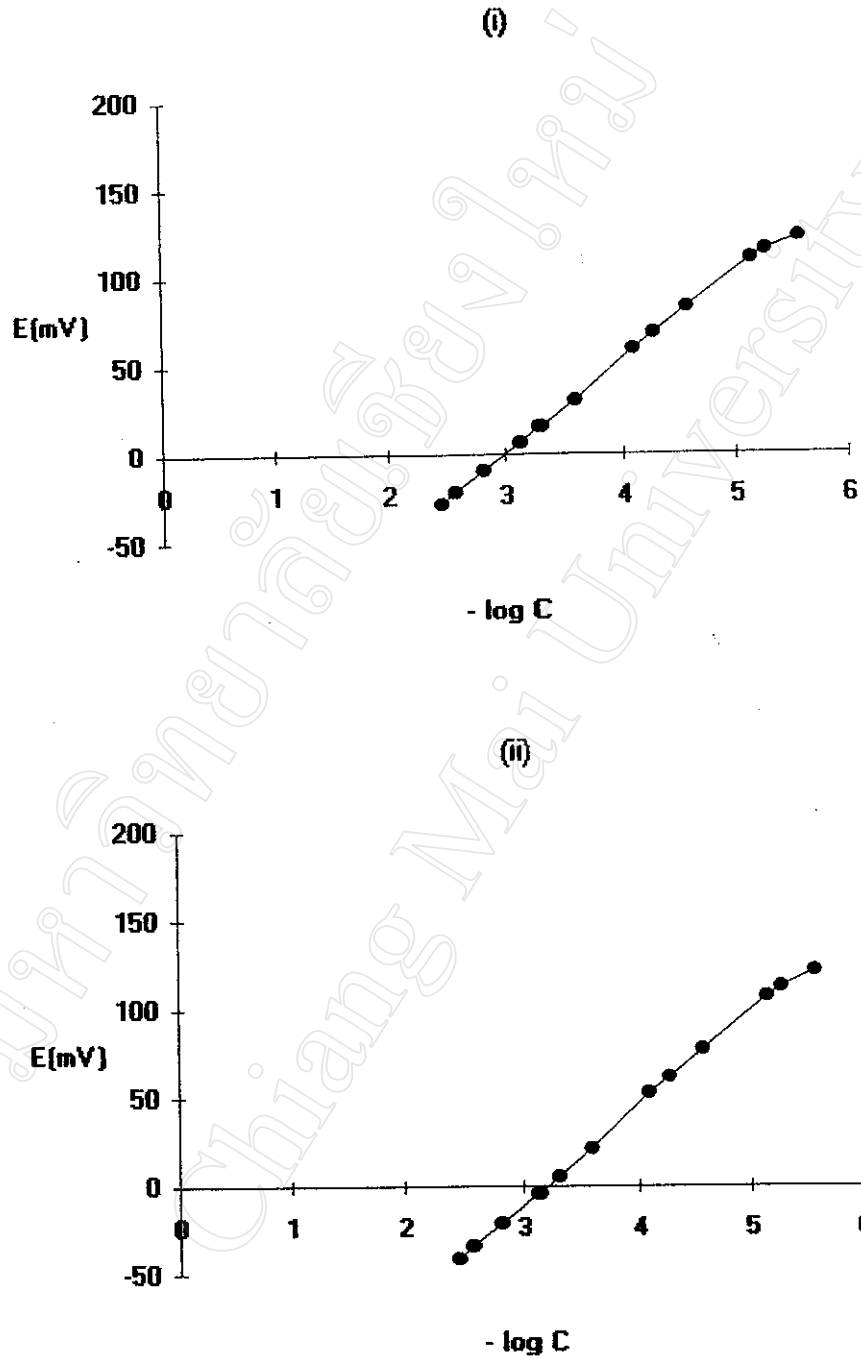


Figure 3.19 Response curve for estimation of selectivity coefficient of iodide CWISE with  $10^{-2}$  M chloride as interfering ion

(i) E71

(ii) E72

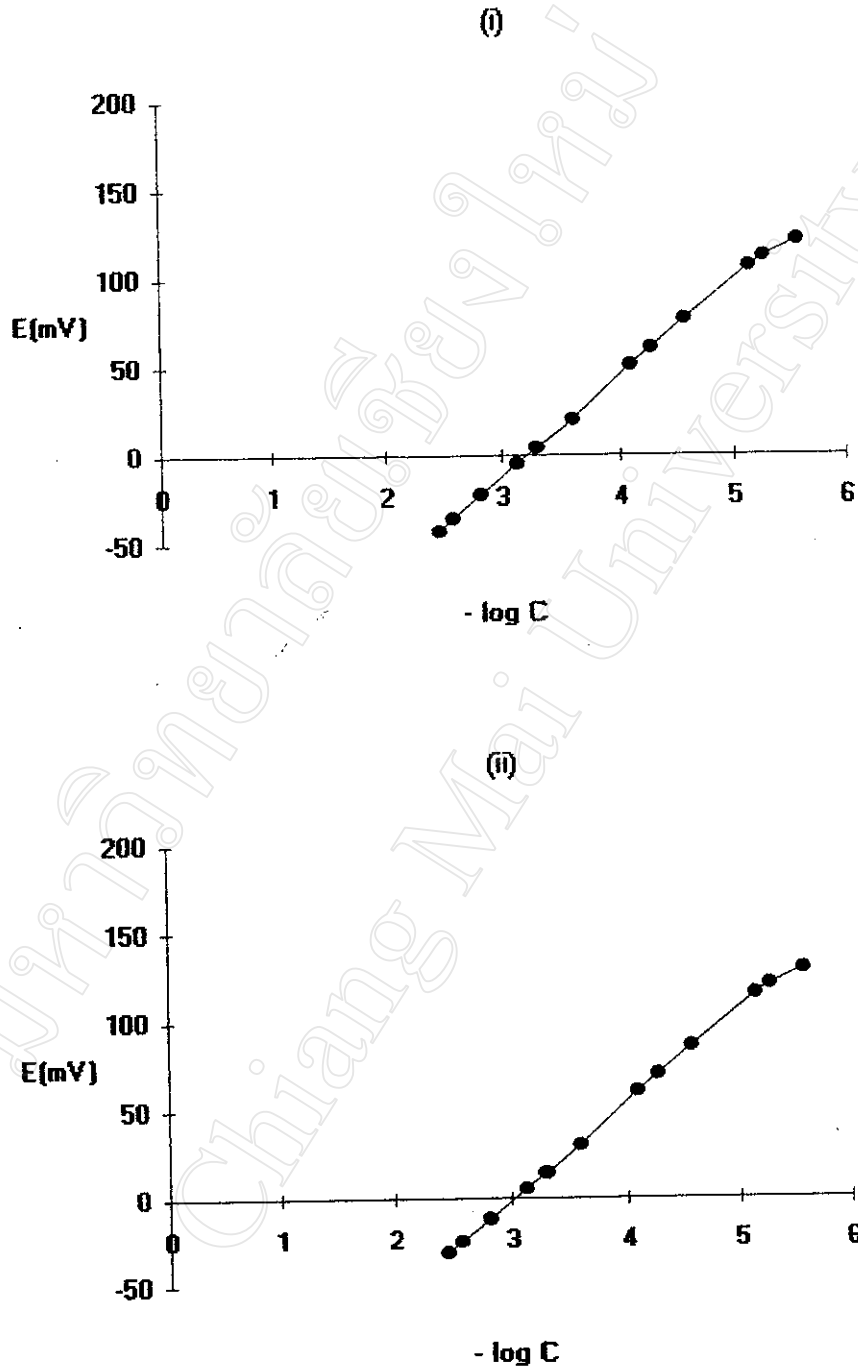


Figure 3.20 Response curve for estimation of selectivity coefficient of iodide CWISE with  $10^{-2}$  M chloride as interfering ion

(i) E73

(ii) E74

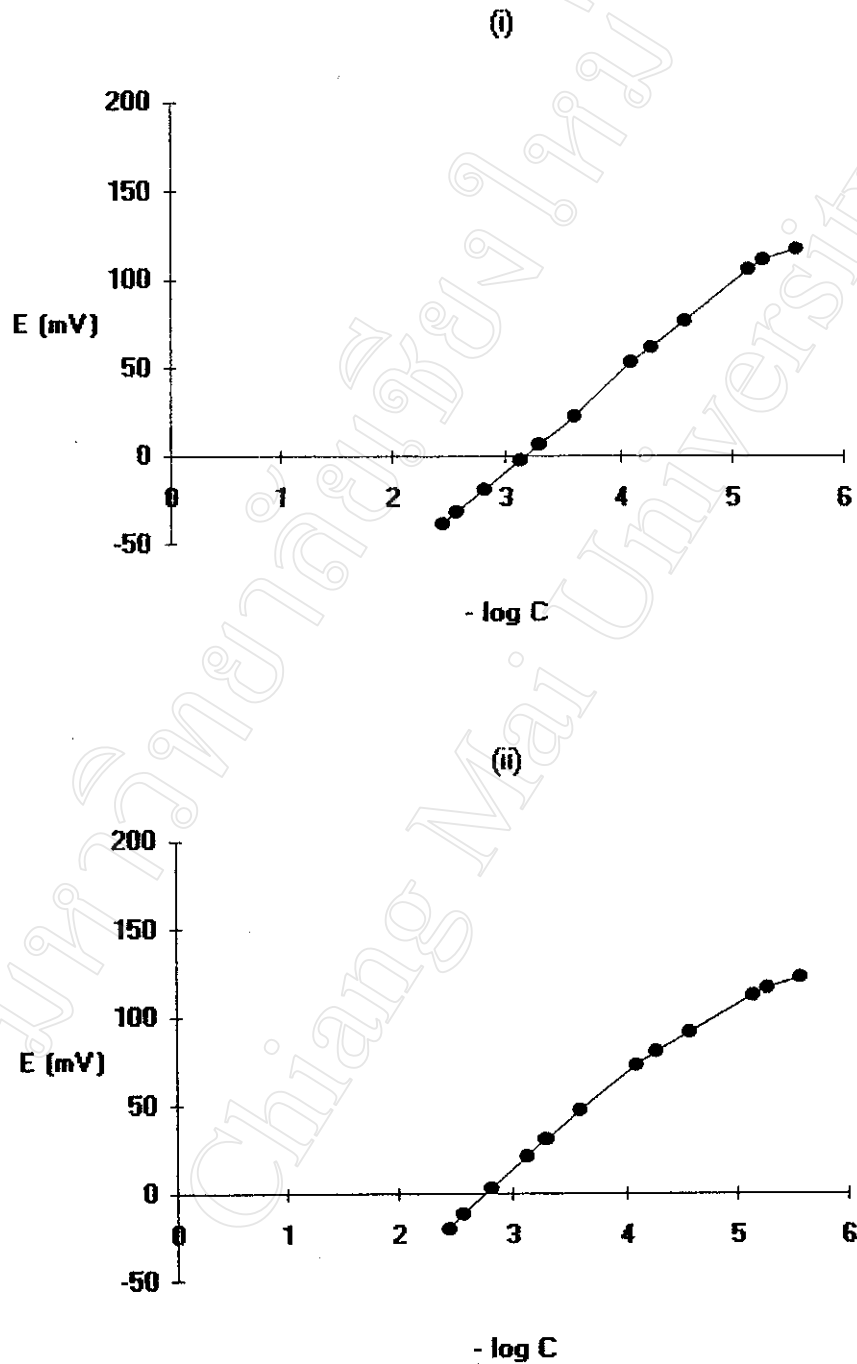


Figure 3.21 Response curve for estimation of selectivity coefficient of (i) iodide CWISE (E75) and (ii) Orion iodide electrode, with  $10^{-2}$  M chloride as interfering ion

Table 3.33 Potentiometric selectivity coefficient  $K_{A,B}^{pot}$  of iodide CWISE and Orion iodide electrode at  $25.0 \pm 0.5$  °C

Interferent ions	$K_{A,B}^{pot}$ *					Orion iodide electrode ( $\times 10^{-4}$ )
	Iodide CWISE ( $\times 10^{-4}$ )					
	E71	E72	E73	E74	E75	
Br <sup>-</sup>	2.51	1.85	1.78	2.00	2.51	1.26
Cl <sup>-</sup>	1.78	1.41	1.12	1.41	1.00	2.34
F <sup>-</sup>	3.55	3.98	3.39	3.98	3.72	1.41

\* A = primary ion = iodide ion

B = interfering ion with concentration of  $10^{-2}$  M

### 3.8 Comparison of characteristics of electrode sets

Table 3.34 Characteristics of the first electrode set (E76-E80)

Characteristics of electrode	Electrode number				
	E76	E77	E78	E79	E80
membrane thickness of electrode (g of coating solution)	0.0208	0.0234	0.0282	0.0228	0.0231
response time (min)	3.75	5.00	8.75	6.25	4.50
electrode slope (mV/decade)	60.3	62.7	60.7	63.1	58.5
detection limit ( $\times 10^{-5}$ M)	1.58	1.58	2.00	1.58	2.00
calibration curve					
-linear range (decade)	2	2	2	2	2
-correlation coefficient	0.997	0.999	0.998	0.999	0.999

Table 3.35 Characteristics of the second electrode set (E81-E85)

Characteristics of electrode	Electrode number				
	E81	E82	E83	E84	E85
membrane thickness of electrode (g of coating solution)	0.0200	0.0195	0.0200	0.0235	0.0154
response time (min)	5.00	10.00	7.50	10.00	5.00
electrode slope (mV/decade)	46.1	30.8	38.8	34.4	12.9
detection limit ( $\times 10^{-5}$ M)	1.58	1.00	0.794	1.00	1.00
calibration curve					
-linear range (decade)	2	2	2	2	2
-correlation coefficient	0.998	0.999	0.999	0.999	0.999

Table 3.36 Characteristics of the third electrode set (E86-E90)

Characteristics of electrode	Electrode number				
	E86	E87	E88	E89	E90
membrane thickness of electrode (g of coating solution)	0.0271	0.0279	0.0265	0.0285	0.0282
response time (min)	3.50	6.25	4.25	7.25	5.00
electrode slope (mV/decade)	57.9	58.5	58.6	59.2	58.7
detection limit ( $\times 10^{-5}$ M)	1.00	1.00	1.00	1.58	2.00
calibration curve					
-linear range (decade)	2	2	2	2	2
-correlation coefficient	0.997	0.998	0.999	0.999	0.998

### 3.9 Lifetime of iodide CWISE for the slope to fall to 50 mV/decade of concentration

Table 3.37 Electrode slope of iodide CWISE which is measured every week at  $25.0 \pm 0.5$  °C

Time (week)	Electrode slope (mV/decade)				
	E71	E72	E73	E74	E75
1	56.3	56.6	57.7	40.0	56.7
2	67.1	51.7	51.1	51.0	61.9
3	64.1	54.9	56.4	49.0	56.3
4	59.7	58.3	56.6	54.3	56.6
5	60.4	43.9	45.7	54.3	49.3
6	46.6	24.7	35.7	55.4	47.9
7	32.4	28.6	23.4	28.1	26.1
8	28.8	19.4	27.4	23.9	29.8
9	19.3	10.9	18.7	19.4	19.7

Table 3.38 Lifetime of iodide CWISE which is indicated by electrode slope to fall to 50 mV/decade of concentration at  $25.0 \pm 0.5$  °C

Electrode number	Life time (weeks)
E71	5
E72	4
E73	4
E74	5
E75	4

### 3.10 Percent yield of iodide CWISE preparation to find acceptable iodide CWISE with the slope in the range of 54-60 mV/decade of concentration

Table 3.39 Electrode slope of iodide CWISE (E91-E170 in the ratio of 3:1 (AgI : epoxy resin ) w/w at  $25.0 \pm 0.5$  °C

Electrode number	Electrode slope (mV/decade)	Electrode number	Electrode slope (mV/decade)	Electrode number	Electrode slope (mV/decade)
E91	54.0*	E118	50.4	E145	41.5
E92	54.5*	E119	87.4	E146	40.7
E93	68.9	E120	75.0	E147	47.3
E94	52.8	E121	55.1*	E148	42.5
E95	61.9	E122	64.3	E149	41.6
E96	28.2	E123	50.2	E150	41.0
E97	68.8	E124	70.4	E151	56.3*
E98	56.2*	E125	49.0	E152	56.6*
E99	66.6	E126	60.2*	E153	57.7*
E100	59.1*	E127	59.2*	E154	40.0
E101	43.4	E128	87.9	E155	56.7*
E102	20.5	E129	59.9*	E156	43.4
E103	52.4	E130	59.5*	E157	58.0*
E104	33.7	E131	86.6	E158	58.7*
E105	30.1	E132	36.5	E159	60.8*
E106	74.8	E133	96.5	E160	63.5
E107	104.8	E134	46.5	E161	59.7*
E108	81.4	E135	51.3	E162	54.9*
E109	83.0	E136	45.4	E163	56.6*
E110	64.3	E137	57.7*	E164	54.3*
E111	40.0	E138	60.3*	E165	56.6*
E112	43.6	E139	89.5	E166	55.1*
E113	42.9	E140	57.3*	E167	54.5*
E114	33.8	E141	42.6	E168	56.0*
E115	108.5	E142	42.0	E169	57.7*
E116	62.7	E143	43.5	E170	56.5*
E117	48.7	E144	45.0		

From table 3.39 , it could be shown that

Number of Nernstian-slope electrode = 29

Total electrode = 80

\* = Nernstian-slope electrode which its slope is in the range of 54-60 mV/decade.

Percent yield of iodide CWISE preparation was obtained by equation below;

$$\% \text{yield} = \frac{\text{Nernstian-slope electrode}}{\text{total electrode}} \times 100$$

so that

$$\% \text{yield} = \frac{29}{80} \times 100 = 36.25$$

### **3.11 Preparation of iodide CWISE with silver iodide in Poly(vinyl chloride)**

#### **3.11.1 Electrode potential measurement**

The iodide electrode was conditioned and potential was measured everyday during two weeks. The potential of all of electrode was unmeasurable (out of scale).

### 3.12 Preparation of iodide CWISE with AgI/Ag<sub>2</sub>S in Poly(vinyl chloride)

#### 3.12.1 Electrode potential measurement

Table 3.40 Potential of electrode (E171-E176)

Conditioned day	Potential of electrode (mV)					
	E171 <sup>1</sup>	E172 <sup>2</sup>	E173 <sup>3</sup>	E174 <sup>4</sup>	E175 <sup>5</sup>	E176 <sup>6</sup>
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	57.1	68.0	50.2	30.1	78.6	88.9
5	57.2	71.8	61.8	52.3	88.3	100.0
6	60.9	109.4	89.5	50.1	100.1	120.8
7	71.2	100.2	99.1	50.8	101.3	121.1
8	80.9	108.9	108.7	48.9	110.0	99.7
9	80.9	110.0	102.1	88.3	131.4	123.8
10	91.5	120.8	115.8	100.1	150.6	141.5

1 = 3 % w/v AgI/Ag<sub>2</sub>S in PVC solution\*

2 = 5 % w/v AgI/Ag<sub>2</sub>S in PVC solution\*

3 = 7 % w/v AgI/Ag<sub>2</sub>S in PVC solution\*

4 = 10 % w/v AgI/Ag<sub>2</sub>S in PVC solution\*

5 = 15 % w/v AgI/Ag<sub>2</sub>S in PVC solution\*

6 = 20 % w/v AgI/Ag<sub>2</sub>S in PVC solution\*

\* = 5%w/v PVC in cyclohexanone

### 3.12.2 Response time

Table 3.41 Response time of iodide CWISE in various ratios of AgI/Ag<sub>2</sub>S in PVC solution\* in iodide solution 10<sup>-3</sup> M at 25.0 ± 0.5 °C

AgI/Ag <sub>2</sub> S in PVC solution* (%w/v)	Response time (min)
3 (E171)	>60
5 (E172)	>60
7 (E173)	>60
10 (E174)	>60
15 (E175)	>60
20 (E176)	>60

\* = 5% w/v PVC in cyclohexanone

### 3.12.3 Determination of the optimum ratio of AgI/Ag<sub>2</sub>S in PVC

Table 3.42 Electrode slope of iodide CWISE in various ratios of AgI/Ag<sub>2</sub>S in PVC solution<sup>a</sup>

Electrode number	Potential (mV)		slope (mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
<b>E171</b> 3% w/v AgI/Ag <sub>2</sub> S in PVC solution	61.7-74.4 (68.1) <sup>b</sup>	92.4-105.3(98.8) <sup>b</sup>	30.8
<b>E172</b> 5% w/v AgI/Ag <sub>2</sub> S in PVC solution	23.7-34.4 (29.0) <sup>b</sup>	39.5-53.7(46.61) <sup>b</sup>	17.6
<b>E173</b> 7% w/v AgI/Ag <sub>2</sub> S in PVC solution	66.4-86.1 (76.2) <sup>b</sup>	51.3-88.4(69.8) <sup>b</sup>	6.4
<b>E174</b> 10% w/v AgI/Ag <sub>2</sub> S in PVC solution	78.8-96.8 (87.8) <sup>b</sup>	23.5-38.4 (30.9) <sup>b</sup>	56.9
<b>E175</b> 15% w/v AgI/Ag <sub>2</sub> S in PVC solution	46.9-60.6 (53.7) <sup>b</sup>	34.9-56.4 (45.6) <sup>b</sup>	8.1
<b>E176</b> 20% w/v AgI/Ag <sub>2</sub> S in PVC solution	29.8-47.4 (38.6) <sup>b</sup>	(-4.2)-(-37.8) (-16.8) <sup>b</sup>	55.4

a = 5 % w/v PVC in cyclohexanone

b = mean value

### 3.13 Preparation of iodide CWISE with AgI/Ag<sub>2</sub>S in plasticized PVC

#### 3.13.1 Effect of DOP added on response time of iodide CWISE

Table 3.43 Response time of iodide CWISE in the ratio of 10%w/v AgI/Ag<sub>2</sub>S in plasticized PVC solution at 25.0 ± 0.5 °C

DOP added* (% w/v)	Response time (min)
7 (E177)	> 60
25 (E178)	> 60
50 (E179)	> 60
90 (E180)	> 60

\* = into PVC solution

#### 3.13.2 Effect of DOP added on electrode slope of iodide CWISE

Table 3.44 Electrode slope of iodide CWISE in the ratio of 10 % w/v AgI/Ag<sub>2</sub>S in plasticized PVC solution

Electrode number	Potential (mV)		Slope (mV/decade)
	1 ml of 1000 ppm iodide added	10 ml of 1000 ppm iodide added	
<b>E177</b> 7% w/v DOP added <sup>a</sup>	108.114.0 (111.0) <sup>b</sup>	119.0-125.3(122.2) <sup>b</sup>	11.2
<b>E178</b> 25% w/v DOP added <sup>a</sup>	107.0-104.0 (105.5) <sup>b</sup>	100.0-107.2 (103.6) <sup>b</sup>	1.9
<b>E179</b> 50% w/v DOP added <sup>a</sup>	129.8-134.0 (131.9) <sup>b</sup>	85.1-81.2 (83.2) <sup>b</sup>	48.1
<b>E180</b> 90% w/v DOP added <sup>a</sup>	66.4-80.1 (73.3) <sup>b</sup>	125.2-130.3 (127.8) <sup>b</sup>	54.5

a = into PVC solution

b = mean value