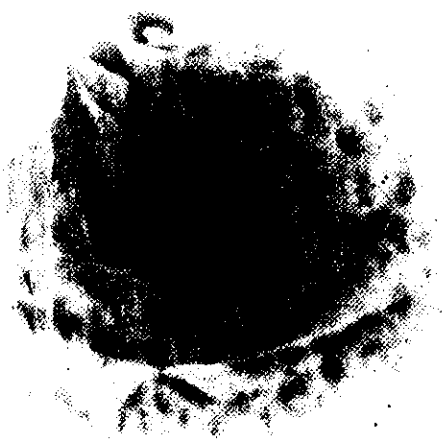
III- Results and Discussion



III- RESULTS AND DISCUSSION

A: Electrochemical Studies on Some Quinazoline Phenyl Hydrazone Derivatives.

3.1 Determination of Corrosion Rate by Non – Electrochemical Measurements:

Weight loss method was used in the present work to investigate the effect of quinazoline phenylhydrazone derivatives on the corrosion rate of copper in 0.1 M HCl. The obtained weight loss – time curves in presence and absence of different concentrations of quinazoline phenylhydrazone derivatives are shown in Figs. (3.1 – 3.11). They are characterized by a sharp rise in weight loss from the beginning and the curves for the additives containing system fall below that of the free acid. This indicates that the investigated compounds act as inhibitors for copper corrosion in HCl and the corrosion inhibition of copper depends on both the type and concentration of additives. Increase in bulk concentration and consequently increase of surface coverage by the additive increase their inhibition efficiency as indicated by the decrease in weight loss.

The percentage inhibition of copper dissolution was determined after different time intervals from the start of each concentration and for all studied compounds.

Tables (3.1a – 3.3a) showed that the percentage inhibition (In) of the three series which is defined as:

$$\% \text{ In} = [(\text{Wt. Loss}_{\text{pure}} - \text{Wt. Loss}_{\text{inh.}}) / \text{Wt. Loss}_{\text{pure}}] \text{ X100} \qquad (3.1)$$

increases with the increase of inhibitor concentration in the corrosive medium. This confirms the results exhibited in the weight loss – time curves. It is thus obvious that increase in the bulk concentration and

consequently increases of surface area coverage by the additives retards the dissolution of copper.

The order of the inhibition efficiency of the additives of the three series in 0.1M HCl solution Table (3.1a – 3.3a) after 60 minutes is:

First series: 2 > 3 > 1

Second series: a > b > c > d

Third series: I > II > III > IV

Synergistic Effect of Quinazoline Phenylhydrazone Derivatives and Iodide Ions on The Corrosion Inhibition of Copper in Hydrochloric Acid:

In this study: Concentration of KI are varied ($1X\ 10^{-6} - 1X10^{-3}M$) while the concentration of inhibitors remains constant ($1X10^{-4}M$).

Tables (3.1b – 3.3b) show the percentage inhibition of copper at various concentrations of KI and at constant concentration of the additives.

Figs. (3.12 – 3.23) represent the weight loss plots for copper in 0.1M hydrochloric acid for various concentrations of KI and at constant concentration of all additives used.

It can be seen from the Tables (3.1b – 3.3b) that the addition of KI inhibits the corrosion of Cu to a large extent and by increasing concentration of KI ($1X10^{-6} - 1X10^{-3}M$) the percentage inhibition increases compared to the percent inhibition when the inhibitor presents alone, in corrosion medium.

This can be interpreted according to Schmitt and Bedbur[166] which proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption the anion and cation are adsorbed at different sites on the electrods surfaces, and in cooperative adsorption,

the anion is chemisorbed on the surface and the cation is adsorbed on a layer of the anion, apart from the adsorption on the surface directly. These two are illustrated in Fig. (3.24)[167].

Effect of Temperature on The Corrosion Inhibition of Copper by Different Additives:

Weight loss of copper in 0.1M hydrochloric acid solution was studied in the temperature range (30 – 50°C) in the absence and presence of different additives.

The results obtained in Figs. (3.25 – 3.68) showing that as the temperature increases the weight loss – time curves in both blank and additives containing solution are shifted to higher value. However, in the presence of additives, the increase of corrosion rate as the temperature increases occur at lower rate than that in uninhibited solutions.

The increase of corrosion rate, as temperature increases, indicates that the protection efficiency of the additives decreases with the rise in temperature. This behaviour proves that the inhibition of copper dissolution occurs through physical adsorption of the additives on the metal surface.

Desorption is aided by increasing the reaction temperature, plots of log K (corrosion rate constant) against 1/T Figs. (3.69 – 3.81) for copper in 0.1M HCl in presence of different inhibitors ($1X10^{-4}$, $1X10^{-5}$, $1X10^{-6}$ and $1X10^{-7}$ M) concentrations, gave straight lines. The values of the slopes obtained at different temperatures permit the calculation of the Arrhenius activation energy (E_a), according to the following equation:

$$\text{Log } K = - E_a / 2.303\ RT + \text{constant.} \qquad (3.2)$$

The results are summarized and given in Tables (3.4 – 3.6) from which it can be seen that:

(1) The presence of inhibitors increases the activation energy of copper dissolution reaction.

(2) The degree of adsorption by these inhibitors on copper surface is to be in the order:-

First series:	2 > 3 > 1
Second series:	a > b > c > d
Third series:	I > II > III > IV

Tables (3.4 – 3.6) exhibit the values of energy, entropy and enthalpy of activation for the corrosion of copper in 0.1M hydrochloric acid solution in the absence and presence of $1X10^{-5}M$ of different inhibitors. The obtained values reveal that, the free energy of activation increases in presence of inhibitors and increasing of temperature. These results showing that in presence of first series, compound (2) which gives the maximum efficiency has the most negative values for the adsorption energy indicating that it's strongly adsorbed on the metal surface[168]. Also, it was found in the second series, compound (a) has the most negative values for the adsorption energy and also in third series, compound (I) has the most negative values of the adsorption energy. ΔS^* (the entropy of activation) in the presence of additives is larger than that in their absence, and has negative values meaning that a decrease in disordering takes place in going from reactants to the activated complex[169,170].

Table (3.1 a): Data from weight loss of copper in 0.1 M HCl for various concentrations of the first series compounds after 60 min. immersion, at 30°C.

Concentration of compounds, (M)	% Inhibition		
	Inhibitor (1)	Inhibitor (2)	Inhibitor (3)
1×10^{-7}	15.0	20.0	17.5
5×10^{-7}	17.5	25.0	20.0
1×10^{-6}	30.0	40.0	35.0
5×10^{-6}	37.0	45.0	40.0
1×10^{-5}	50.0	62.5	52.5
5×10^{-5}	60.0	67.5	62.5
1×10^{-4}	67.5	75.0	73.8

Table (3.1 b): Data from weight loss of copper in 0.1 M HCl + 1×10^{-4} M of the first series compounds for various KI concentrations after 60 min. immersion, at 30°C.

Concentration of KI (M)	% Inhibition		
	Inhibitor (1)	Inhibitor (2)	Inhibitor (3)
1×10^{-6}	70.0	82.5	77.5
1×10^{-5}	72.5	87.5	82.5
1×10^{-4}	75.0	88.8	87.5
1×10^{-3}	80.0	92.5	90.0

Table (3.2a): Data from weight loss of copper in 0.1 M HCl for various concentrations of the second series compounds after 60 min. immersion, at 30°C.

Concentration of compounds, (M)	% Inhibition			
	Inhibitor (a)	Inhibitor (b)	Inhibitor (c)	Inhibitor (d)
1×10^{-7}	37.5	32.5	22.5	20.0
5×10^{-7}	42.5	37.5	30.0	25.0
1×10^{-6}	50.0	42.5	32.5	30.0
5×10^{-6}	62.5	57.5	55.0	52.5
1×10^{-5}	70.0	65.0	62.5	57.5
5×10^{-5}	75.0	70.0	65.0	62.5
1×10^{-4}	80.0	77.5	70.0	67.5

Table (3.2b): Data from weight loss of copper in 0.1 M HCl +1 X 10^{-4} M of the second series compounds for various KI concentrations after 60 min. immersion, at 30°C.

Concentration of KI (M)	% Inhibition			
	Inhibitor (a)	Inhibitor (b)	Inhibitor (c)	Inhibitor (d)
1×10^{-6}	82.5	80.0	75.0	72.5
1×10^{-5}	85.0	82.5	77.5	77.5
1×10^{-4}	87.5	87.5	82.5	78.8
1×10^{-3}	92.5	90.0	85.0	80.0

Table (3.3a): Data from weight loss of copper in 0.1 M HCl for various concentrations of the third series compounds after 60 min. immersion, at 30°C.

Concentration of compounds, (M)	% Inhibition			
	Inhibitor (I)	Inhibitor (II)	Inhibitor (III)	Inhibitor (IV)
1×10^{-7}	30.0	27.5	22.5	17.5
5×10^{-7}	35.0	32.5	25.0	20.0
1×10^{-6}	45.0	40.0	30.0	22.5
5×10^{-6}	50.0	47.5	35.0	25.0
1×10^{-5}	58.0	55.0	40.0	37.5
5×10^{-5}	60.5	60.0	57.5	52.5
1×10^{-4}	67.5	65.0	62.5	55

Table (3.3b): Data from weight loss of copper in 0.1 M HCl +1 X 10^{-4} M of the third series compounds for various KI concentrations after 60 min. immersion, at 30°C.

Concentration of KI (M)	% Inhibition			
	Inhibitor (I)	Inhibitor (II)	Inhibitor (III)	Inhibitor (IV)
1×10^{-6}	73.0	70.0	68.8	69.0
1×10^{-5}	75.0	72.5	72.5	73..0
1×10^{-4}	80.0	77.5	75.0	75.0
1×10^{-3}	83.0	80.0	77.5	78.0

Table (3.4): Activation energy (E_a), free energy (ΔG^*), enthalpy (ΔH^*) and entropy of activation (ΔS^*) in 0.1M HCl in presence of $1X10^{-5}$ M of the first series inhibitors.

Temperature	30°C	35°C	40°C	45°C	50°C
0.1M HCl					
E_a in KJ mol^{-1}	22.98				
ΔH^* in KJ mol^{-1}	25.49	25.54	25.58	25.62	25.66
ΔG^* in KJ mol^{-1}	64.80	65.60	66.30	67.00	67.70
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	129.70	130.00	130.10	130.13	130.16
Inhibitor (1)					
E_a in KJ mol^{-1}	28.80				
ΔH^* in KJ mol^{-1}	31.30	31.36	31.40	31.44	31.48
ΔG^* in KJ mol^{-1}	66.56	67.30	68.00	68.76	69.50
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	116.40	116.70	116.93	117.40	117.70
Inhibitor (2)					
E_a in KJ mol^{-1}	36.60				
ΔH^* in KJ mol^{-1}	39.10	39.15	39.20	39.24	39.30
ΔG^* in KJ mol^{-1}	67.20	67.80	68.50	69.10	69.66
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	92.70	93.00	93.60	93.90	94.00
Inhibitor (3)					
E_a in KJ mol^{-1}	32.20				
ΔH^* in KJ mol^{-1}	34.71	34.76	34.80	34.84	34.90
ΔG^* in KJ mol^{-1}	66.82	67.49	68.20	68.79	69.60
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	106.00	106.30	106.70	106.80	107.43

Table (3.5): Activation energy (E_a), free energy (ΔG^*), enthalpy (ΔH^*) and entropy of activation (ΔS^*) in 0.1M HCl in presence of $1X10^{-5}$ M of the second series inhibitors.

Temperature	30°C	35°C	40°C	45°C	50°C
Inhibitor (a)					
E_a in KJ mol^{-1}	58.52				
ΔH^* in KJ mol^{-1}	61.00	61.08	61.10	61.20	61.20
ΔG^* in KJ mol^{-1}	67.00	67.72	67.86	68.47	69.49
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	19.80	21.57	21.59	22.90	25.67
Inhibitor (b)					
E_a in KJ mol^{-1}	55.80				
ΔH^* in KJ mol^{-1}	58.36	58.40	58.40	58.44	58.48
ΔG^* in KJ mol^{-1}	66.70	67.07	67.47	67.94	68.74
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	27.50	28.15	29.00	29.90	31.76
Inhibitor (c)					
E_a in KJ mol^{-1}	48.10				
ΔH^* in KJ mol^{-1}	50.60	50.74	50.70	50.74	50.78
ΔG^* in KJ mol^{-1}	66.10	66.95	67.30	67.80	68.47
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	51.15	52.63	53.00	53.65	54.80
Inhibitor (d)					
E_a in KJ mol^{-1}	45.80				
ΔH^* in KJ mol^{-1}	48.30	48.36	48.40	48.44	48.48
ΔG^* in KJ mol^{-1}	65.80	66.70	67.10	67.54	68.60
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	57.70	59.55	59.70	60.10	62.30

Table (3.6): Activation energy (E_a), free energy (ΔG^*), enthalpy (ΔH^*) and entropy of activation (ΔS^*) in 0.1M HCl in presence of $1X10^{-5}$ M of the third series inhibitors.

Temperature	30°C	35°C	40°C	45°C	50°C
Inhibitor (I)					
E_a in KJ mol^{-1}	43.89				
ΔH^* in KJ mol^{-1}	46.40	46.45	46.49	46.50	46.57
ΔG^* in KJ mol^{-1}	66.70	67.49	68.20	68.60	69.20
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	67.00	68.30	69.40	69.50	70.10
Inhibitor (II)					
E_a in KJ mol^{-1}	38.46				
ΔH^* in KJ mol^{-1}	40.97	41.00	41.06	41.10	41.14
ΔG^* in KJ mol^{-1}	66.59	67.30	67.90	68.40	69.10
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	84.54	85.40	85.75	85.90	86.90
Inhibitor (III)					
E_a in KJ mol^{-1}	33.44				
ΔH^* in KJ mol^{-1}	35.95	36.00	36.04	36.08	36.10
ΔG^* in KJ mol^{-1}	66.10	66.70	67.60	68.30	69.00
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	99.50	99.70	100.80	101.30	101.90
Inhibitor (IV)					
E_a in KJ mol^{-1}	30.93				
ΔH^* in KJ mol^{-1}	33.44	33.49	33.53	33.57	33.61
ΔG^* in KJ mol^{-1}	65.92	66.54	67.50	68.20	68.90
$-\Delta S^*$ in $JK^{-1}mol^{-1}$	107.20	107.30	108.50	108.80	109.30

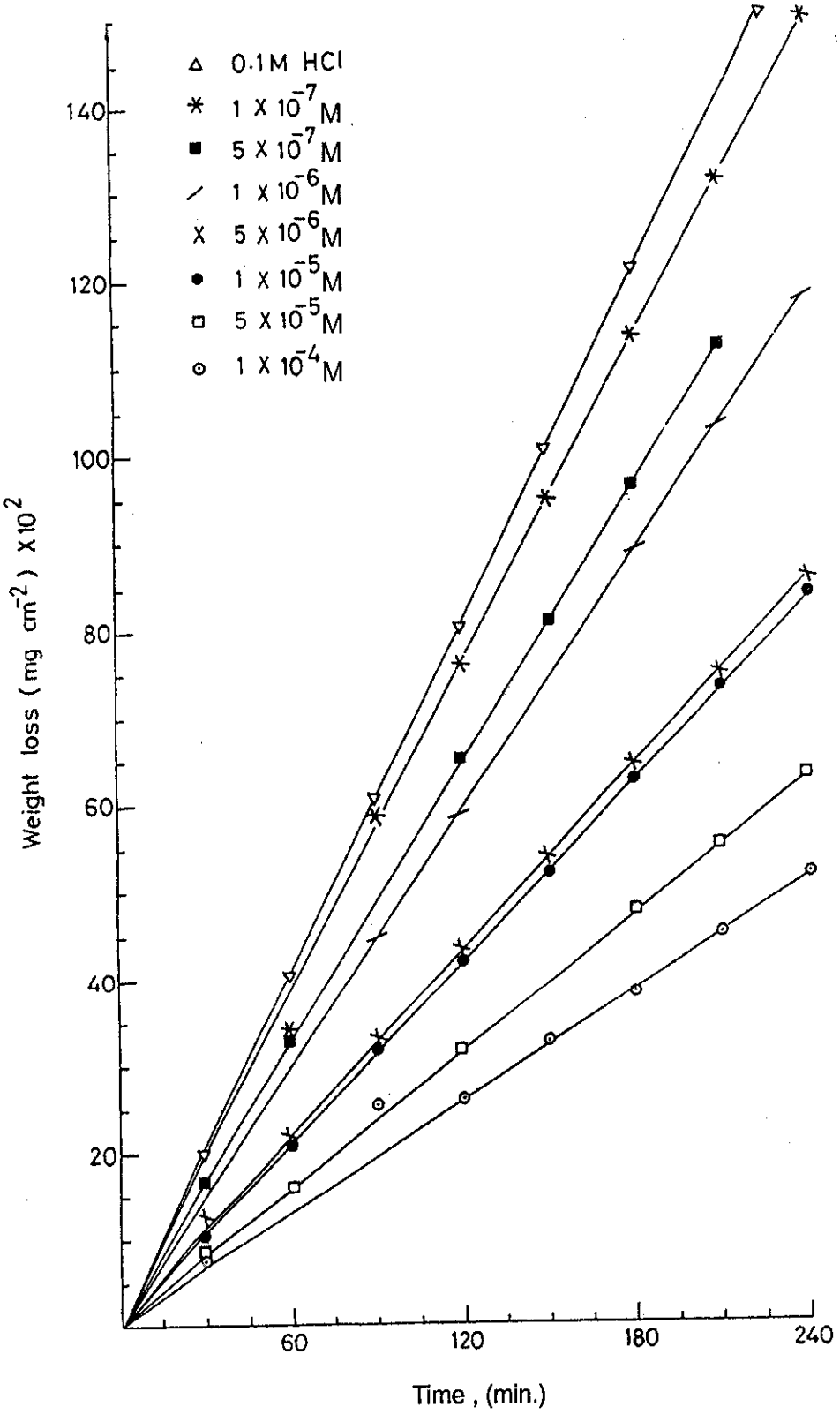


Fig. (3.1): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (1) at 30°C.

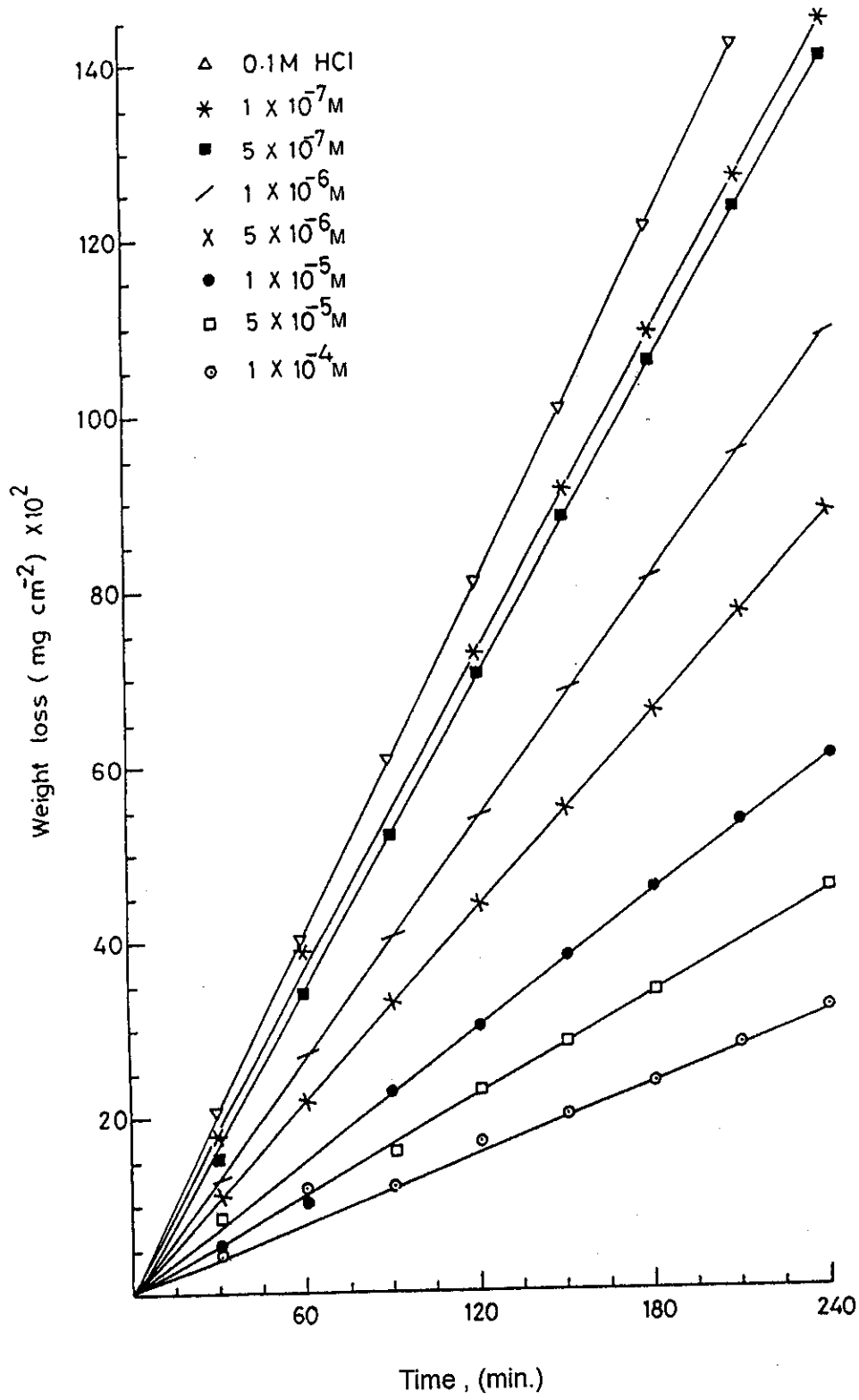


Fig. (3.2): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (2) at 30°C.

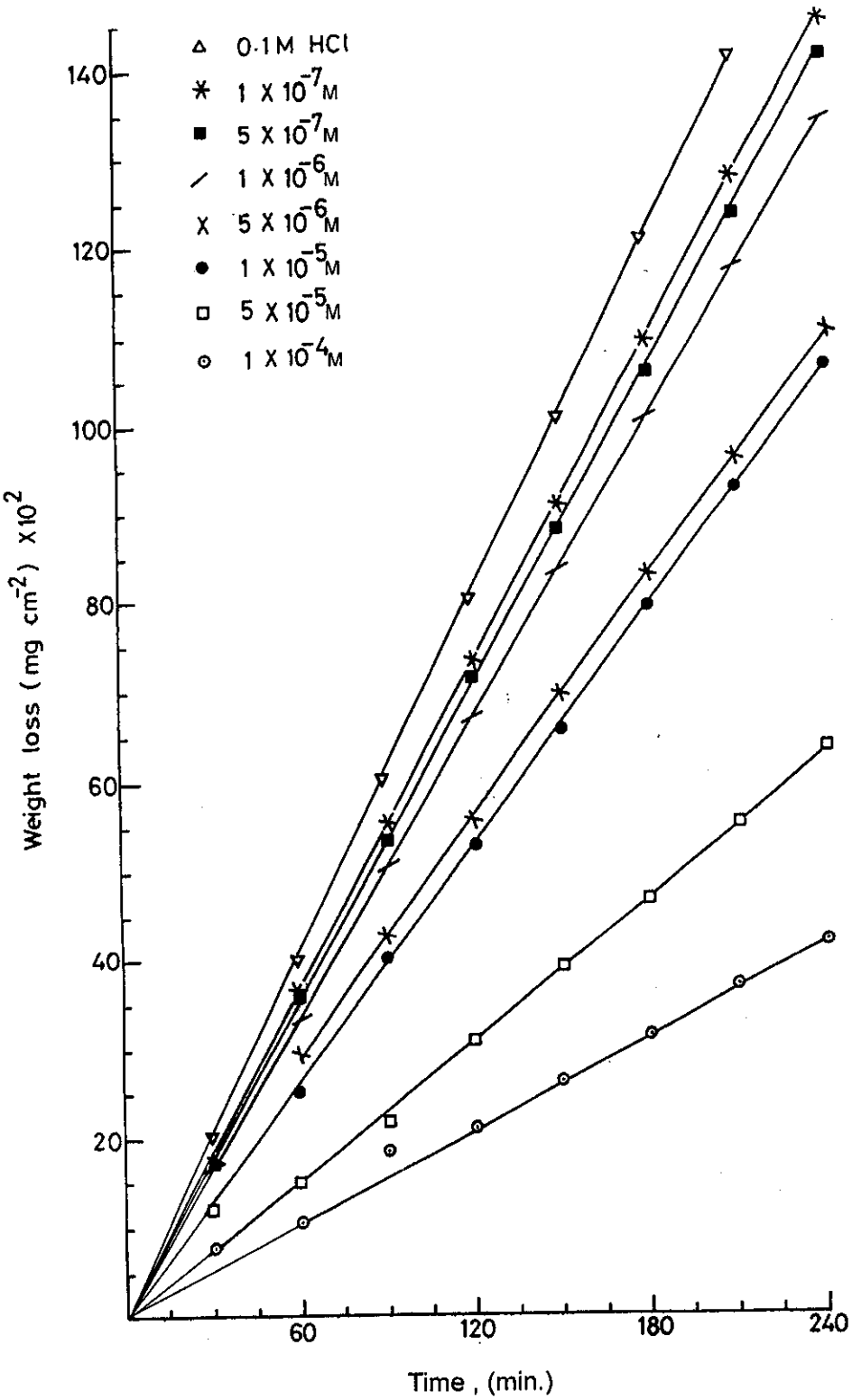


Fig. (3.3): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (3) at 30°C.

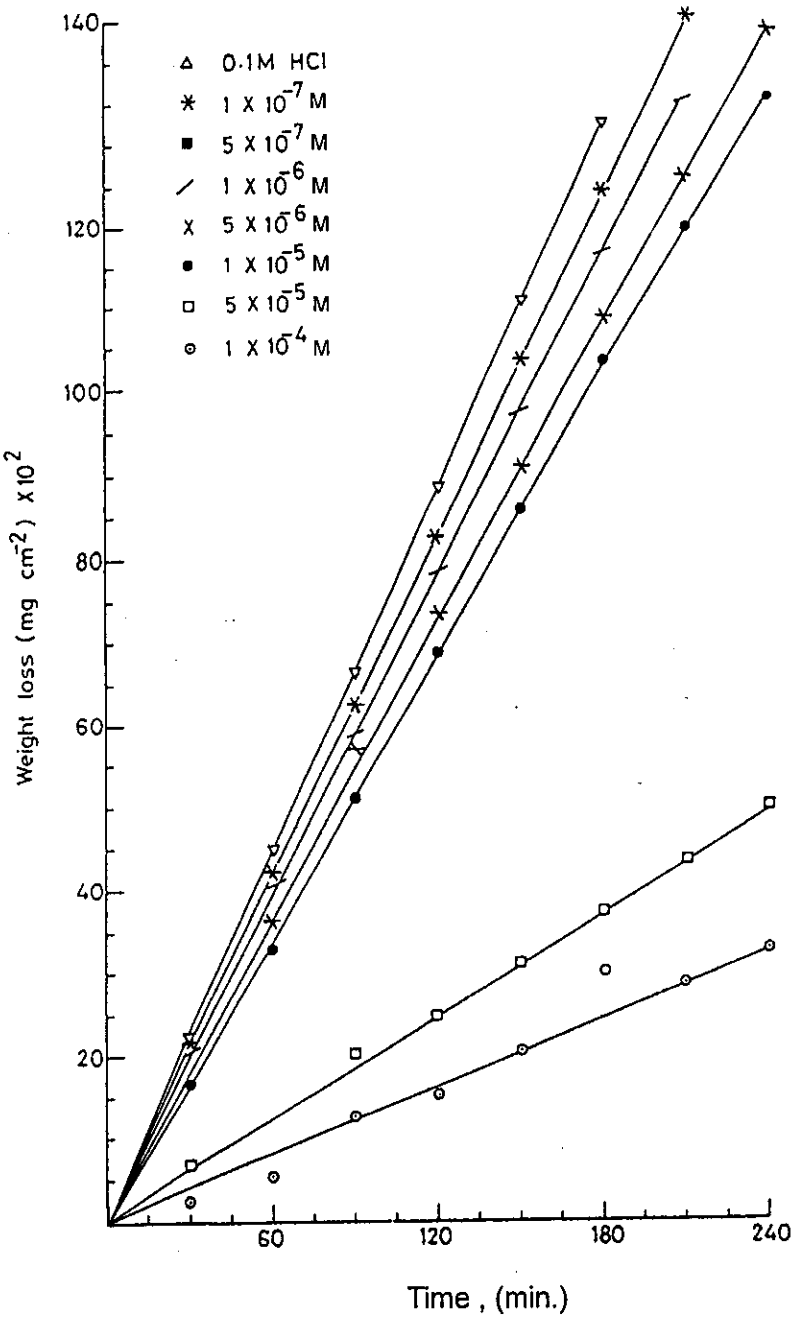


Fig. (3.4): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (a) at 30°C.

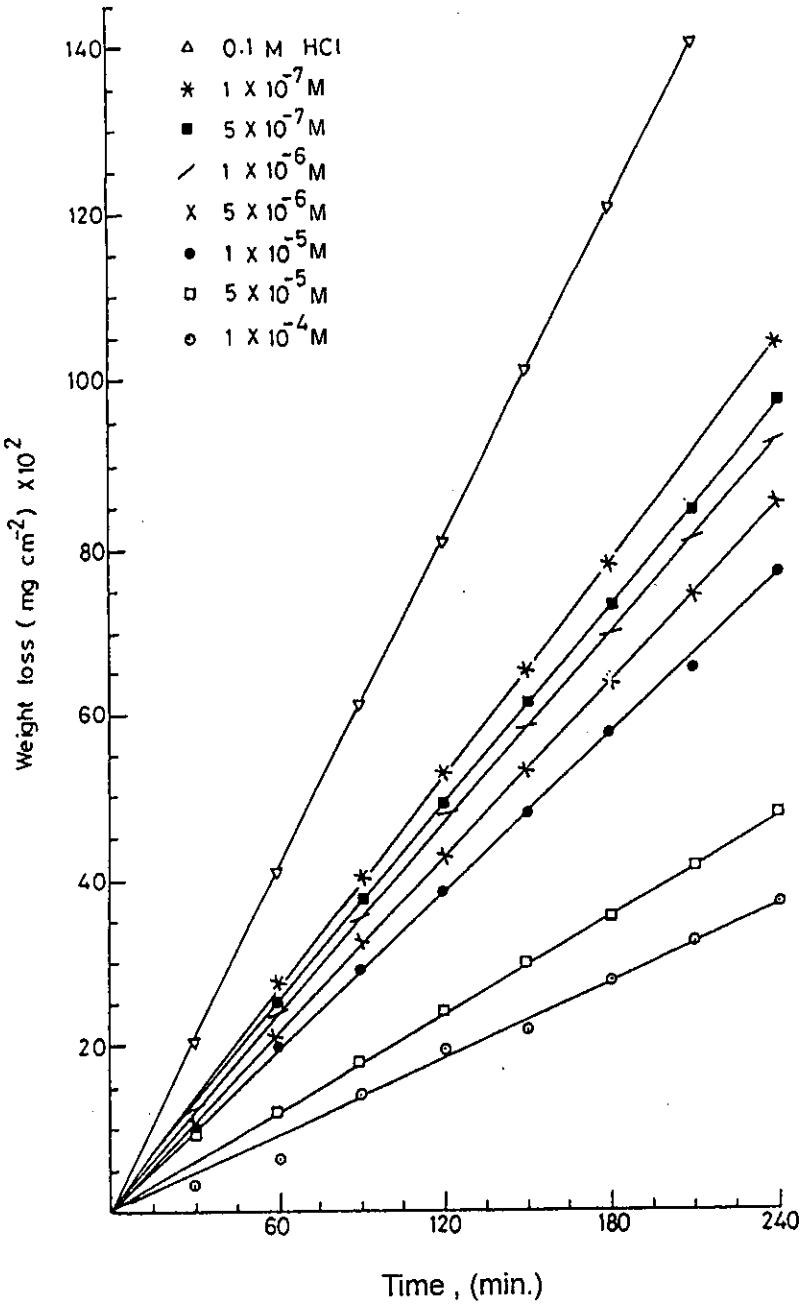


Fig. (3.5): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (b) at 30°C.

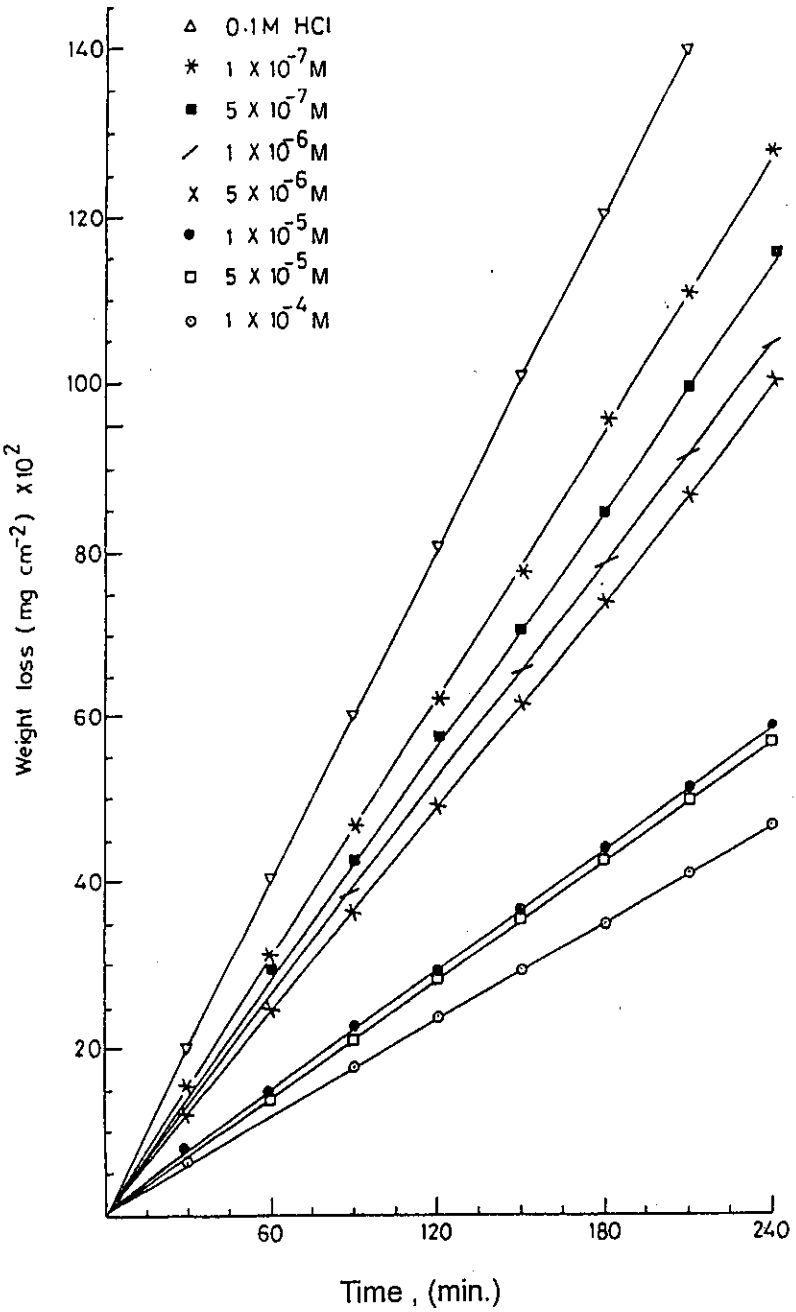


Fig. (3.6): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (c) at 30°C.

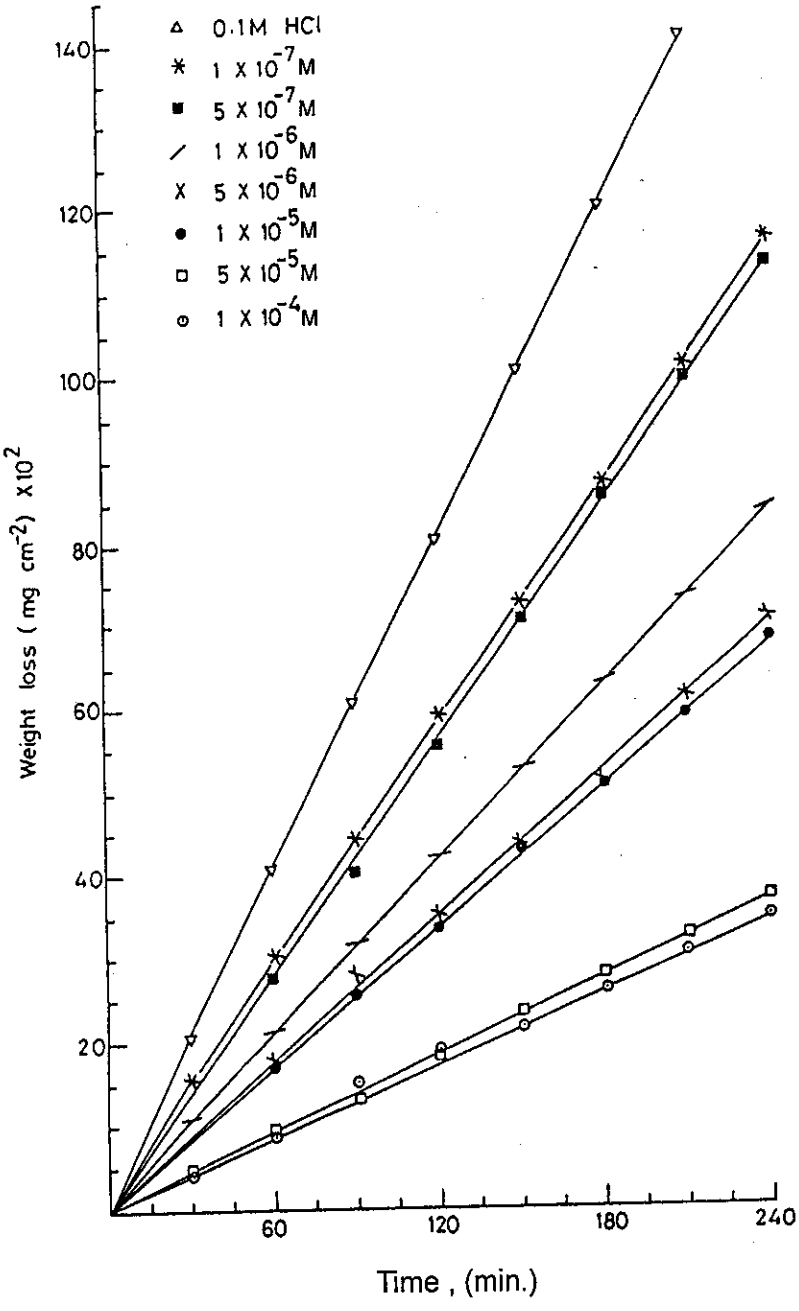


Fig. (3.7): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (d) at 30°C.

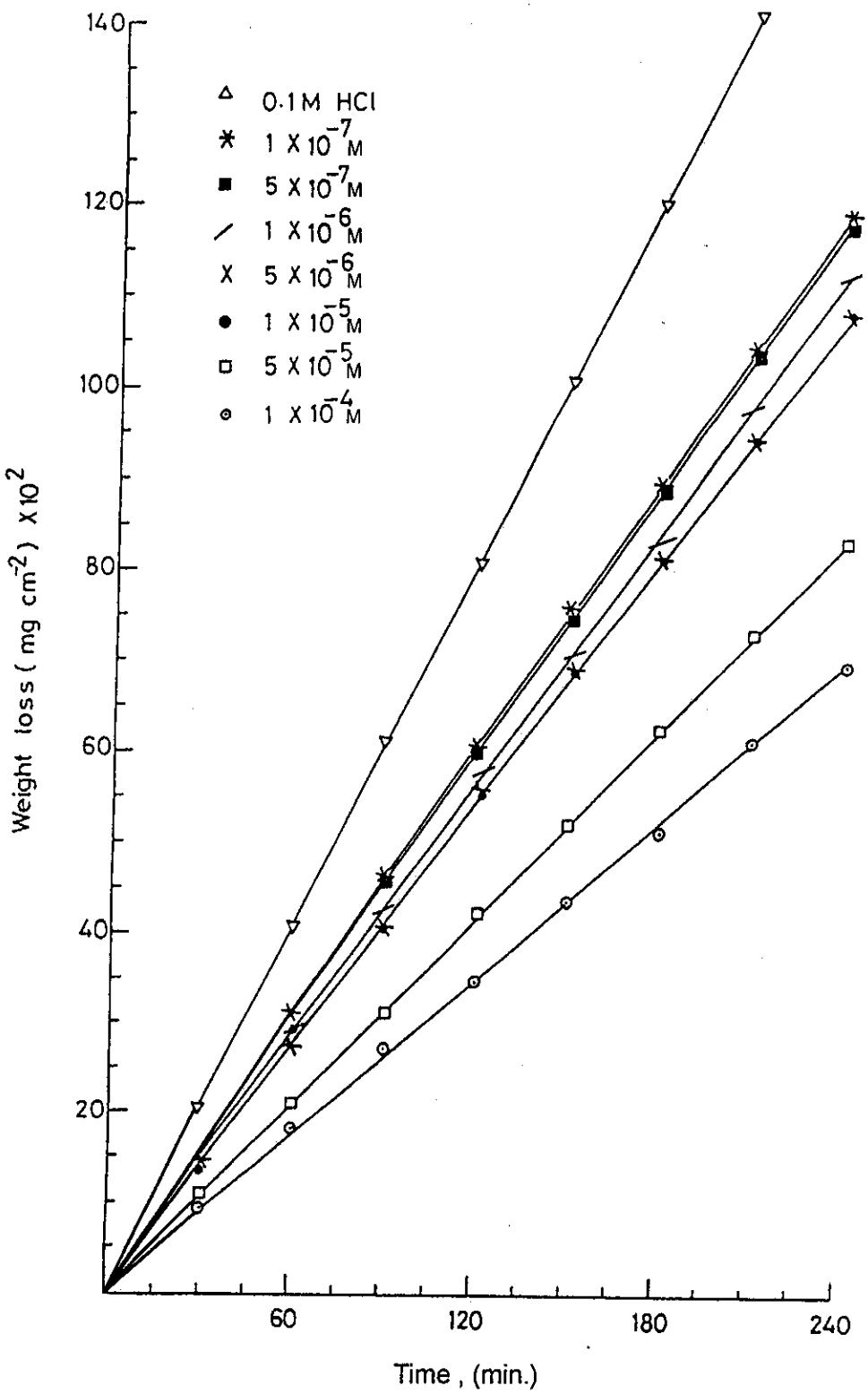


Fig. (3.8): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (I) at 30°C.

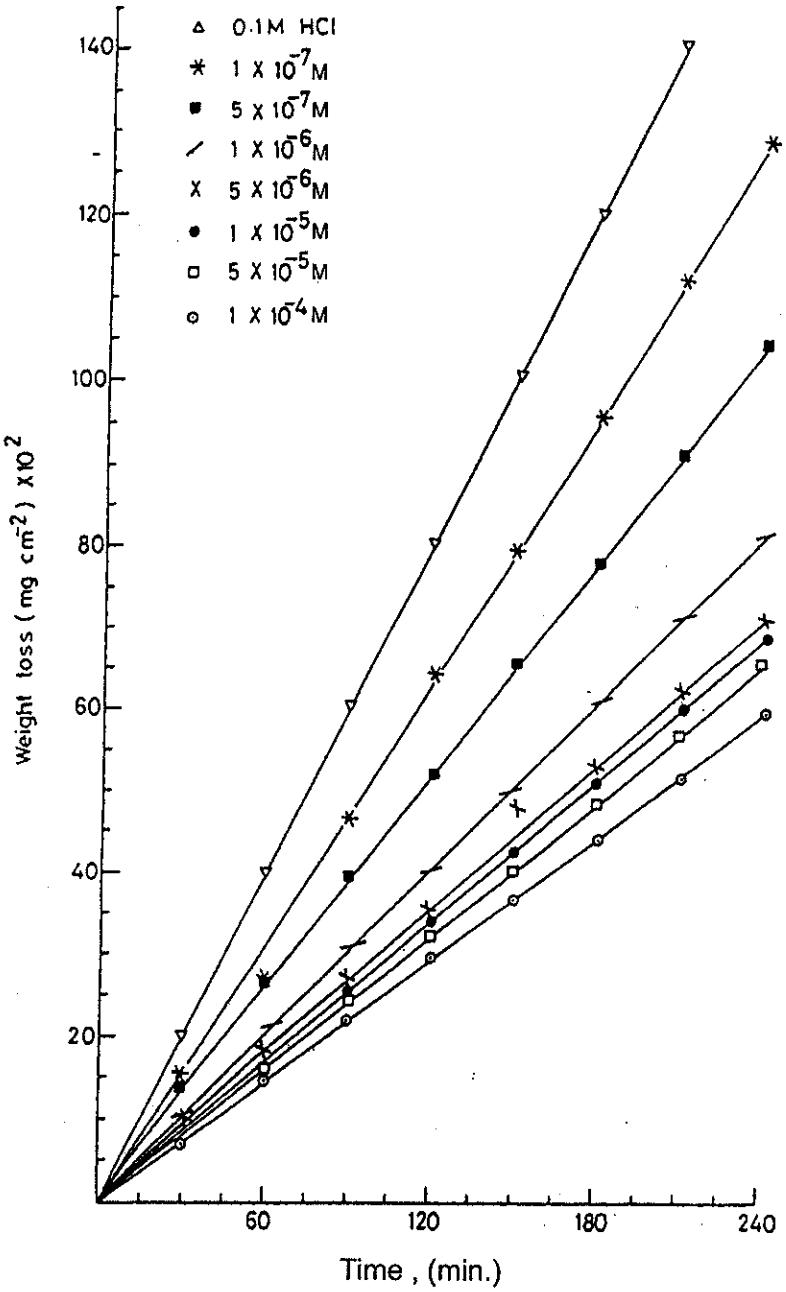


Fig. (3.9): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (II) at 30°C.

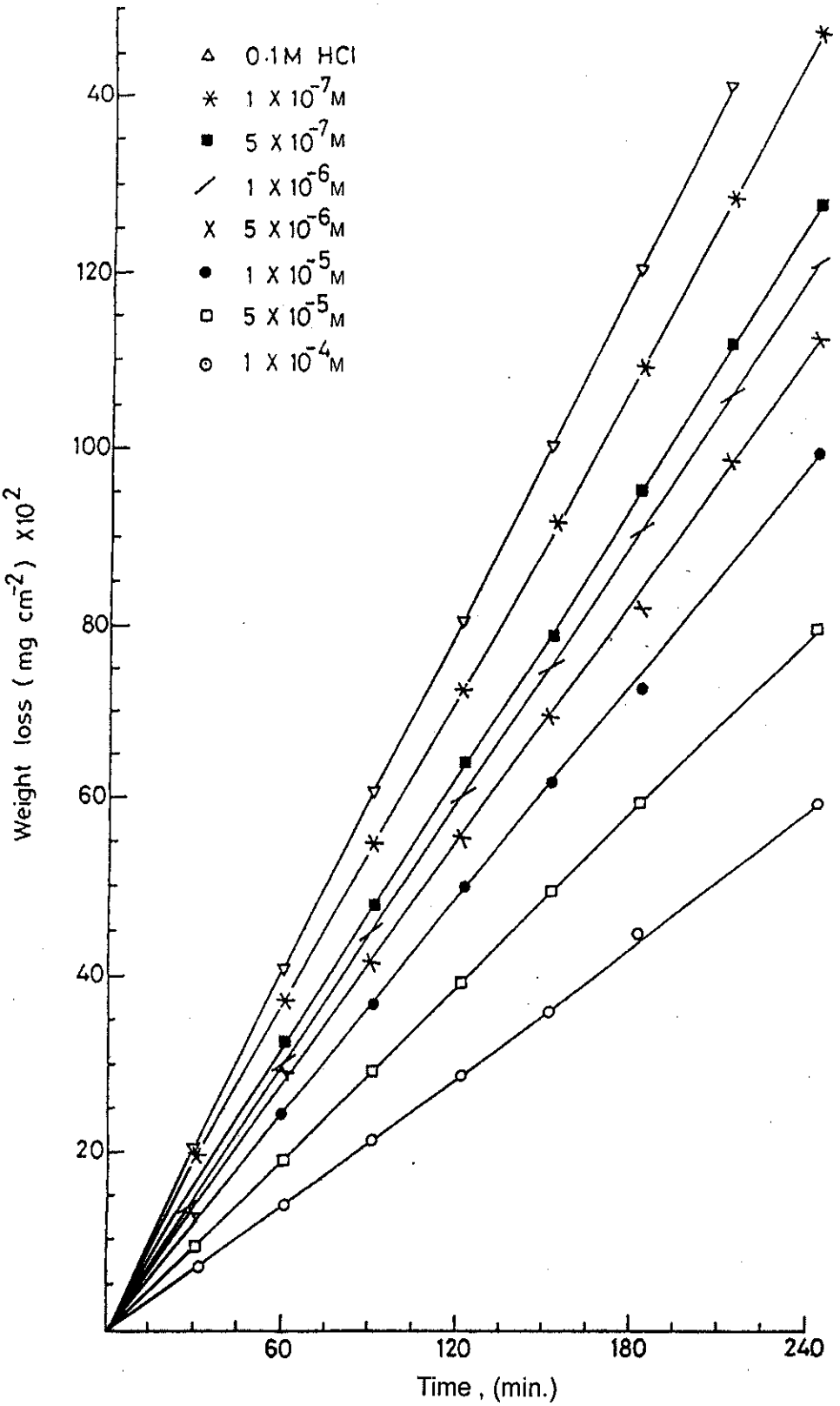


Fig. (3.10): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (III) at 30°C.

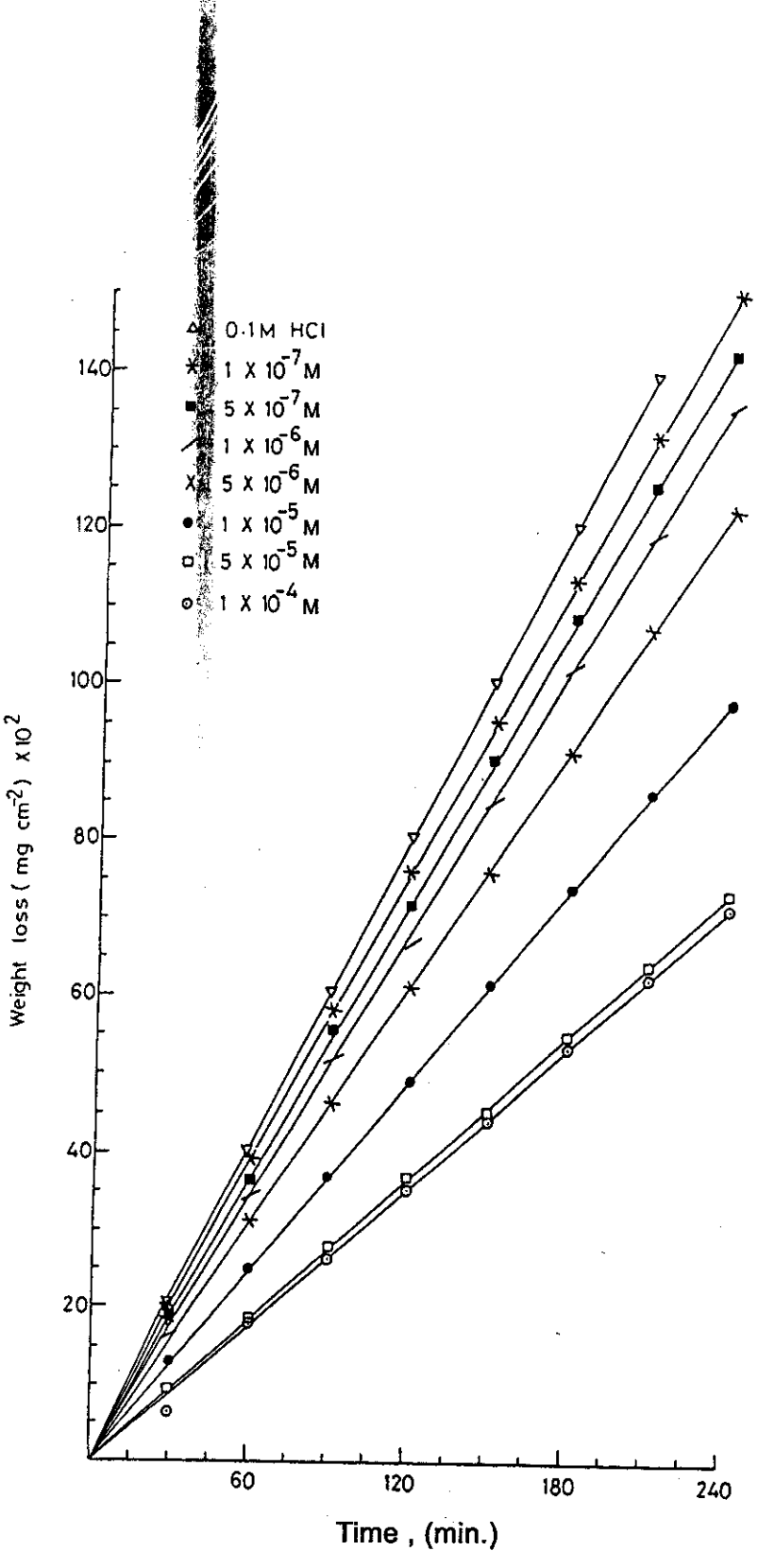


Fig. (3.11): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of compound (IV) at 30°C.

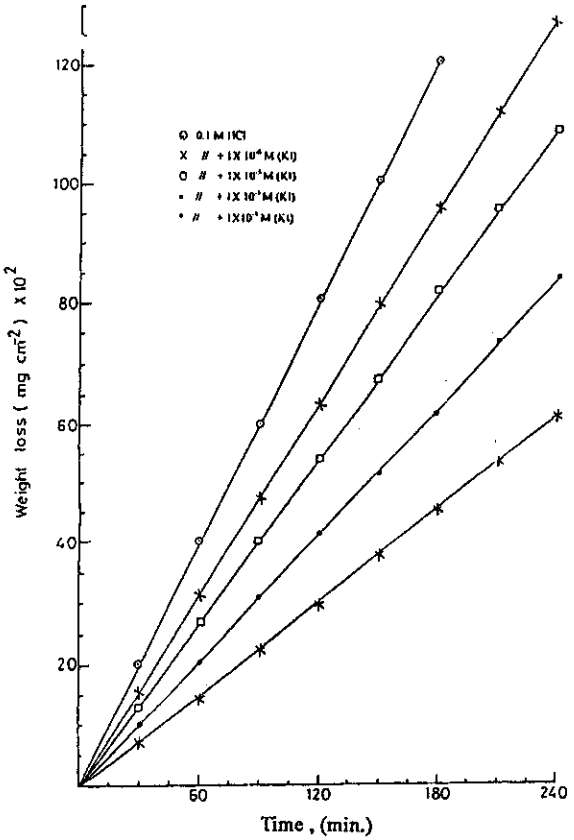


Fig. (3.12): weight loss – time curves for copper in 0.1 M HCl in presence and absence of different concentrations of KI at 30°C

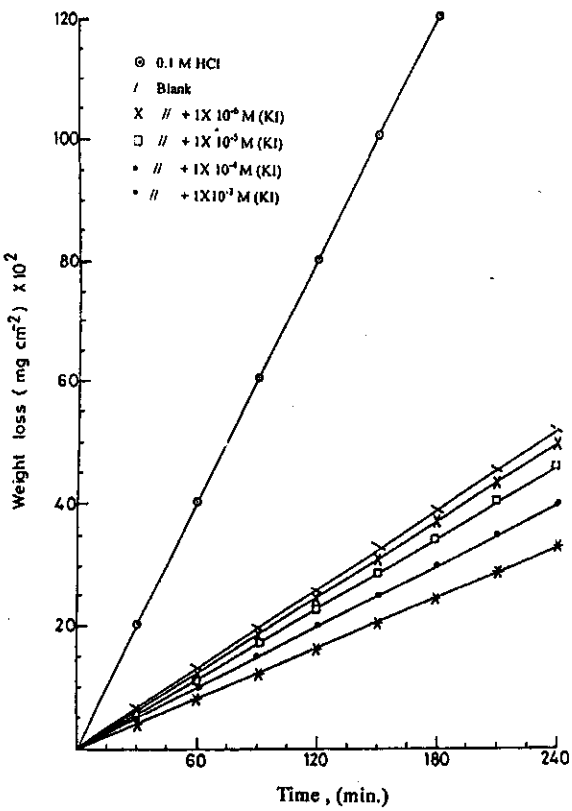


Fig. (3.13): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (1) (blank) in presence and absence of different concentrations of KI at 30°C.

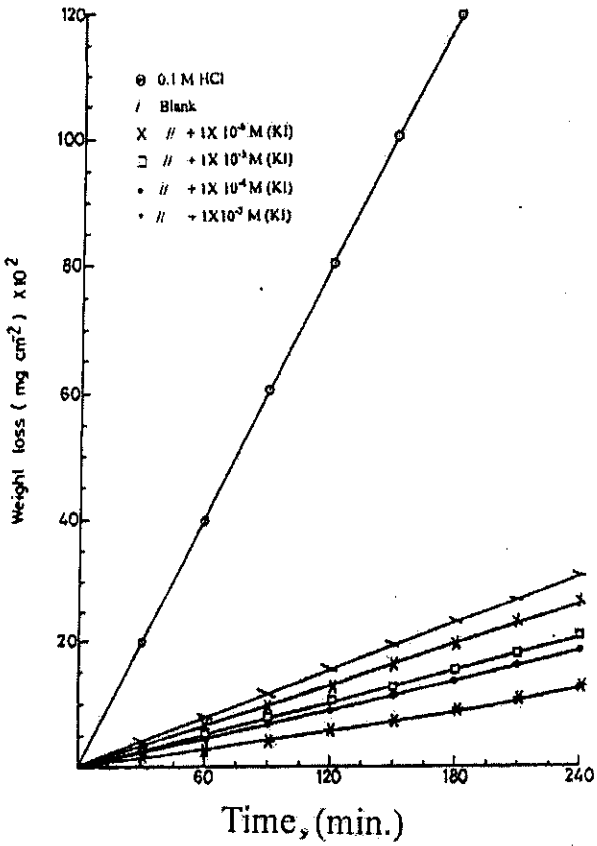


Fig. (3.14): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (2) (blank) in presence and absence of different concentrations of KI at 30°C.

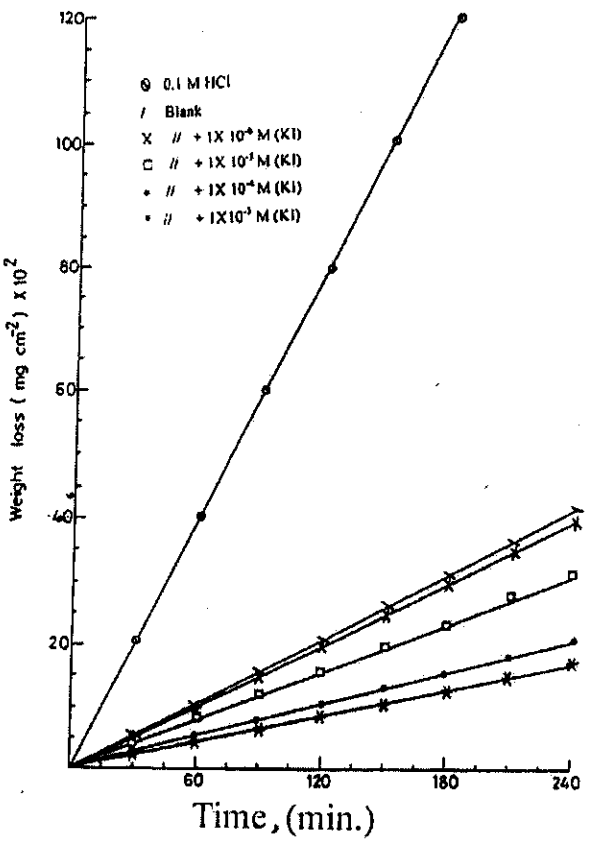


Fig. (3.15): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (3) (blank) in presence and absence of different concentrations of KI at 30°C.

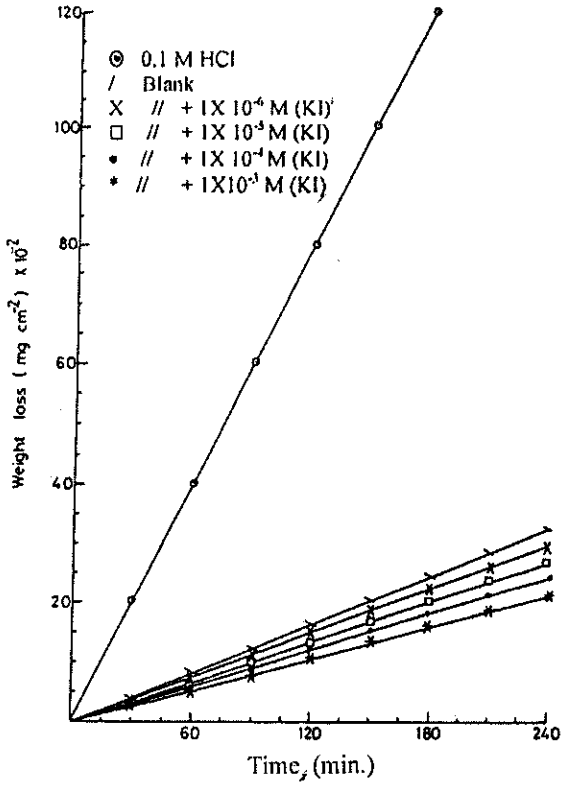


Fig. (3.16): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (a) (blank) in presence and absence of different concentrations of KI at 30°C.

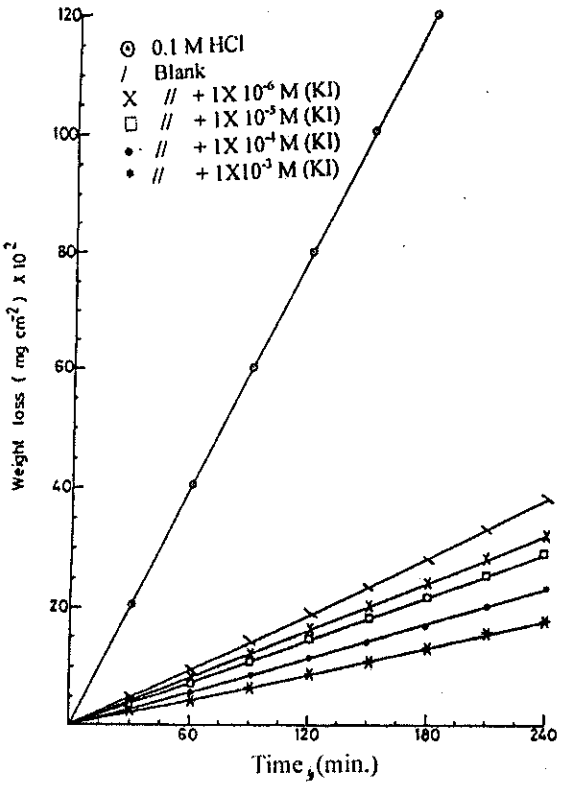


Fig. (3.17): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (b) (blank) in presence and absence of different concentrations of KI at 30°C.

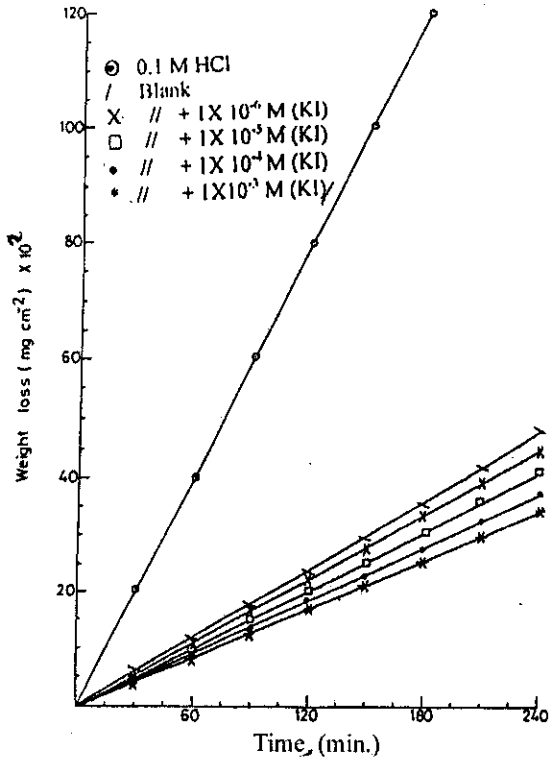


Fig. (3.18): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (c) (blank) in presence and absence of different concentrations of KI at 30°C.

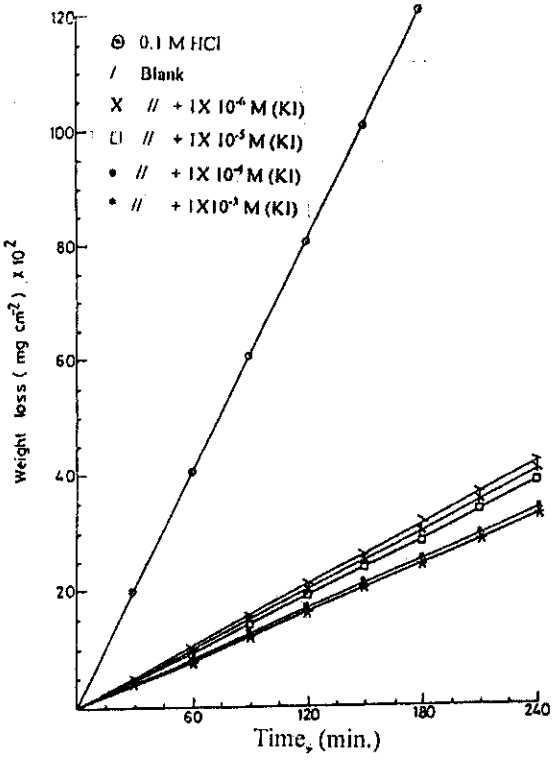


Fig. (3.19): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (d) (blank) in presence and absence of different concentrations of KI at 30°C.

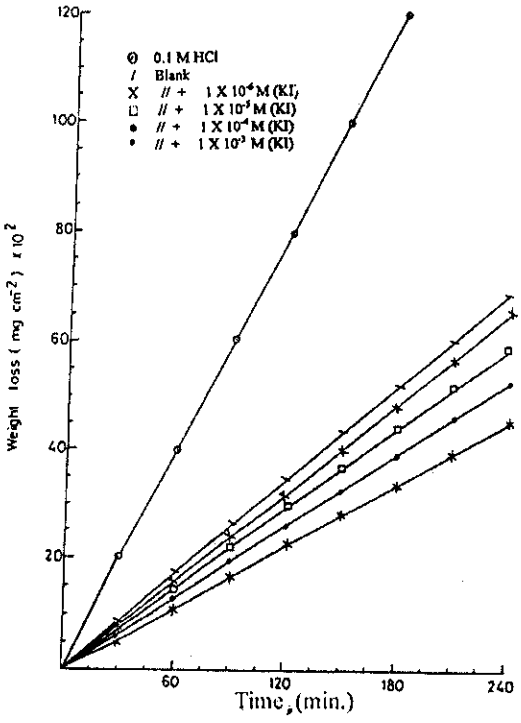


Fig. (3.20): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (I) (blank) in presence and absence of different concentrations of KI at 30°C.

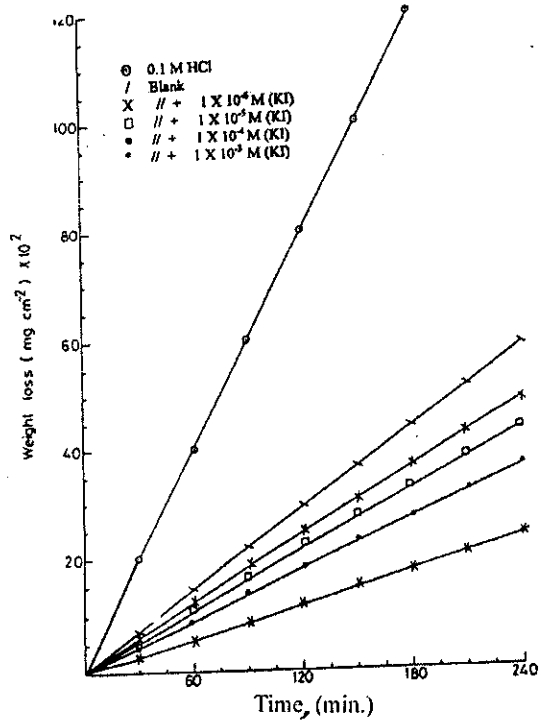


Fig. (3.21): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (II) (blank) in presence and absence of different concentrations of KI at 30°C.

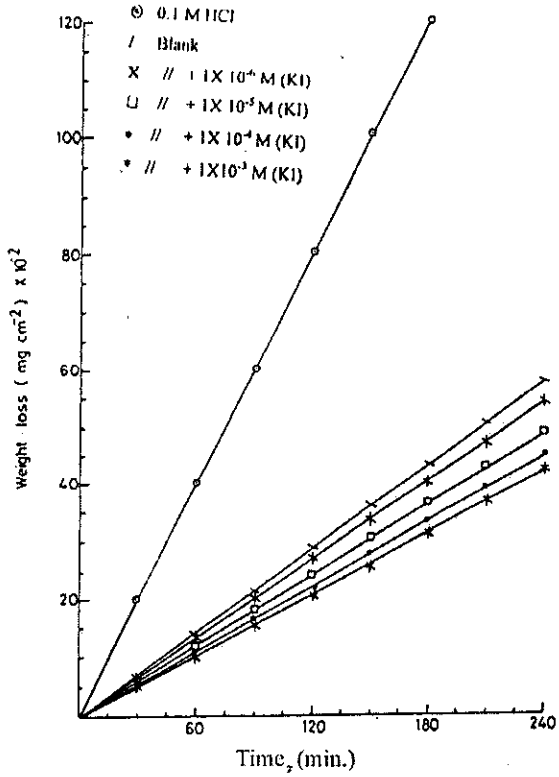


Fig. (3.22): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (III) (blank) in presence and absence of different concentrations of KI at 30°C.

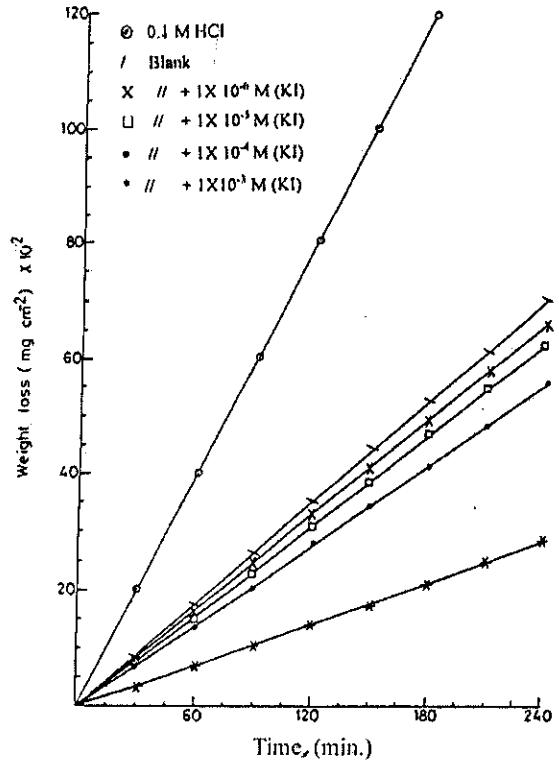
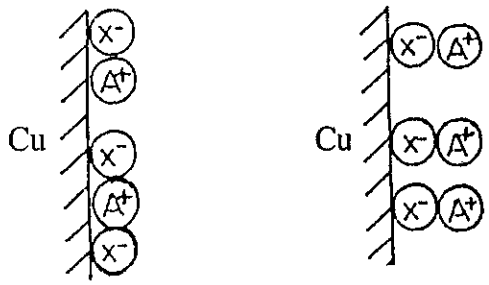


Fig. (3.23): weight loss – time curves for copper in 0.1 M HCl + 1X 10^{-4} M compound (IV) (blank) in presence and absence of different concentrations of KI at 30°C.



A. Competitive adsorption B. Cooperative adsorption

Fig. (3.24): Schematic diagrams of competitive and cooperative adsorption of anion and cation.

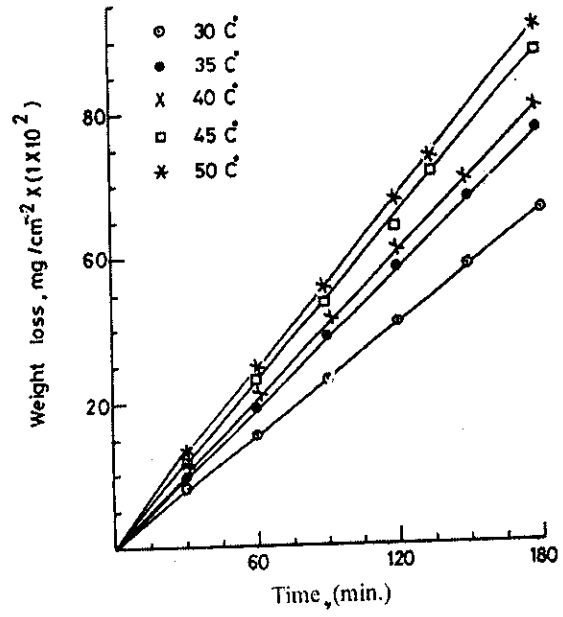


Fig. (3.25): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (1) at different temperatures.

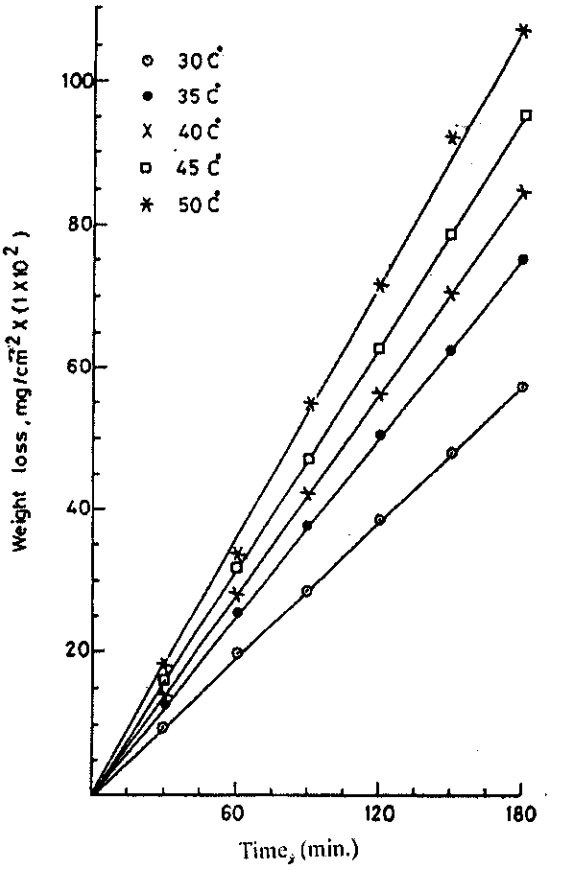


Fig. (3.26): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (1) at different temperatures.

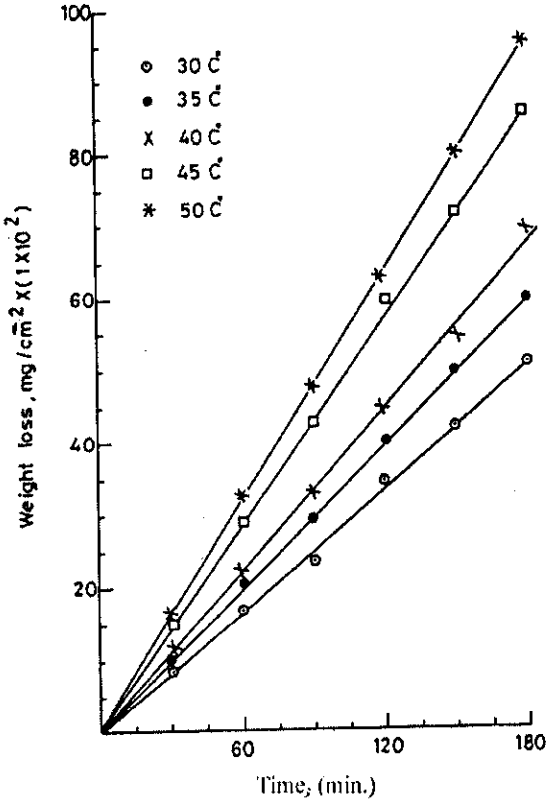


Fig. (3.27): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (1) at different temperatures.

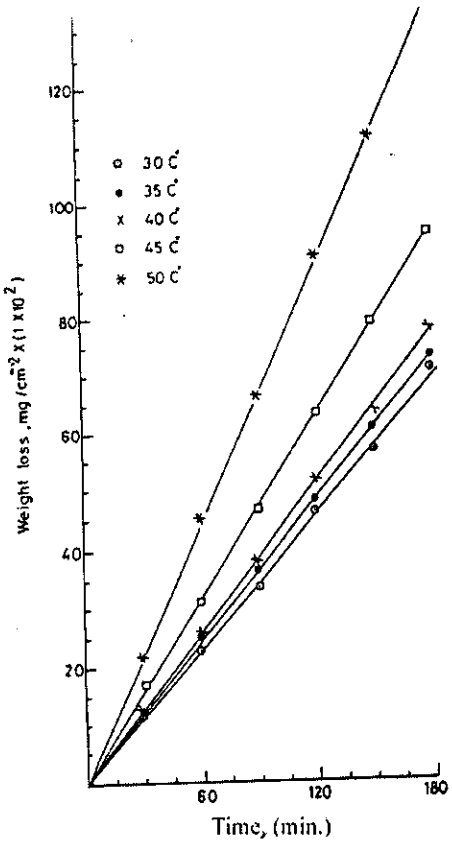


Fig. (3.28): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (1) at different temperatures.

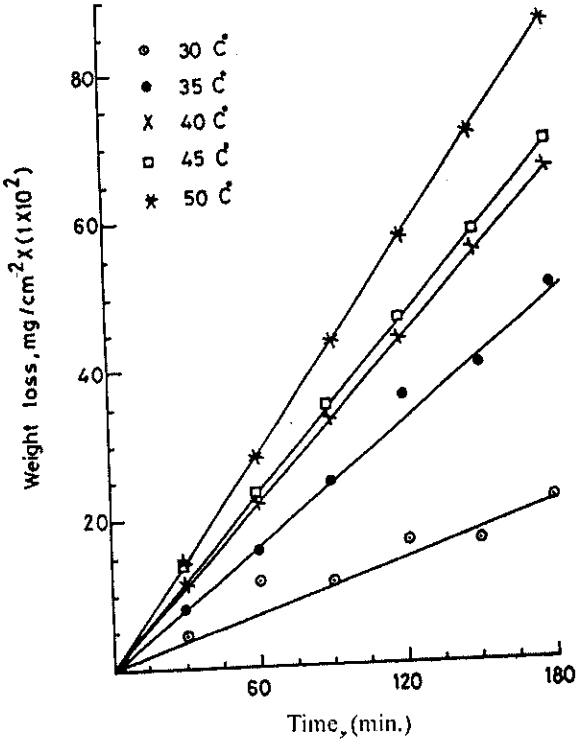


Fig. (3.29): weight loss – time curves for copper in 0.1 M HCl in presence of 1X10^{-4}M compound (2) at different temperatures.

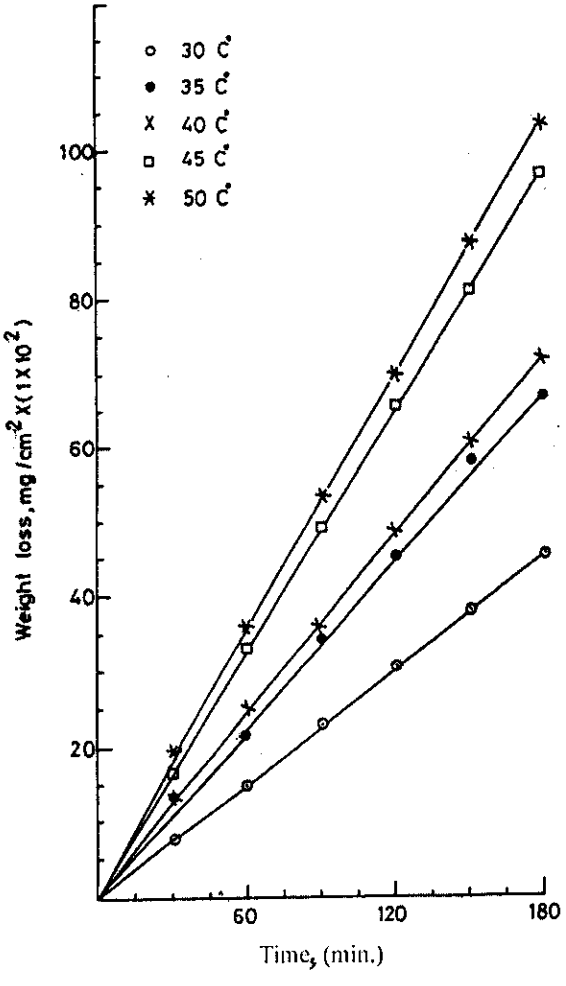


Fig. (3.30): weight loss – time curves for copper in 0.1 M HCl in presence of 1X10^{-5}M compound (2) at different temperatures.

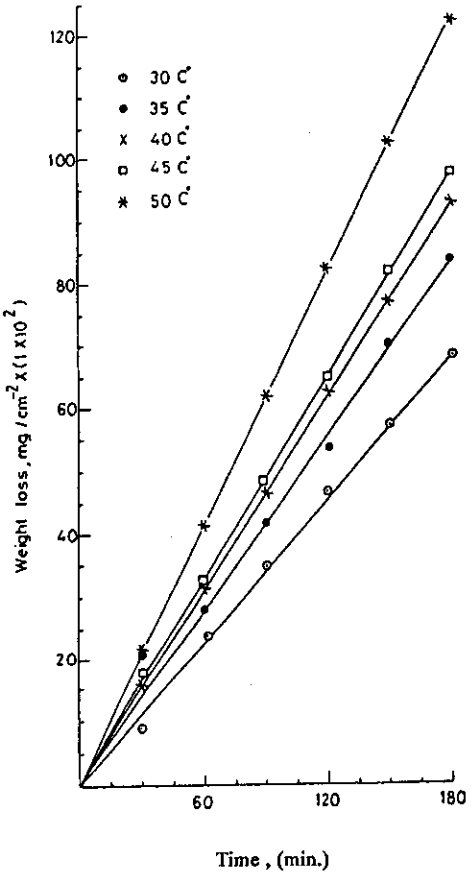


Fig. (3.31): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (2) at different temperatures.

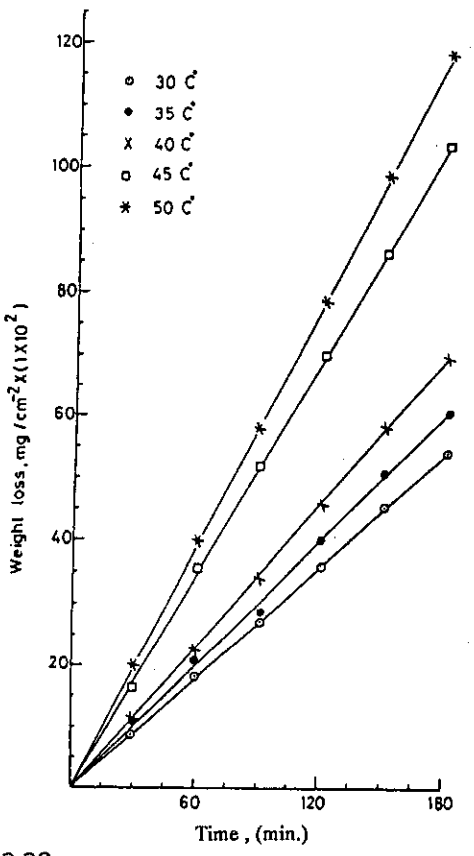


Fig. (3.32): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (2) at different temperatures.

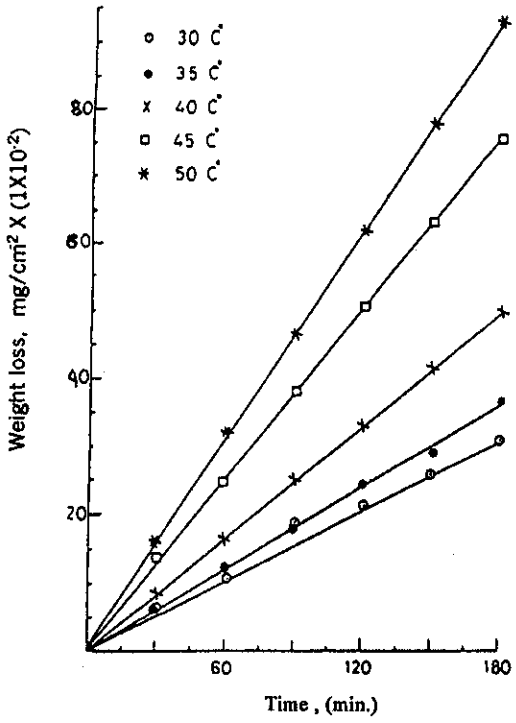


Fig. (3.33): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (3) at different temperatures.

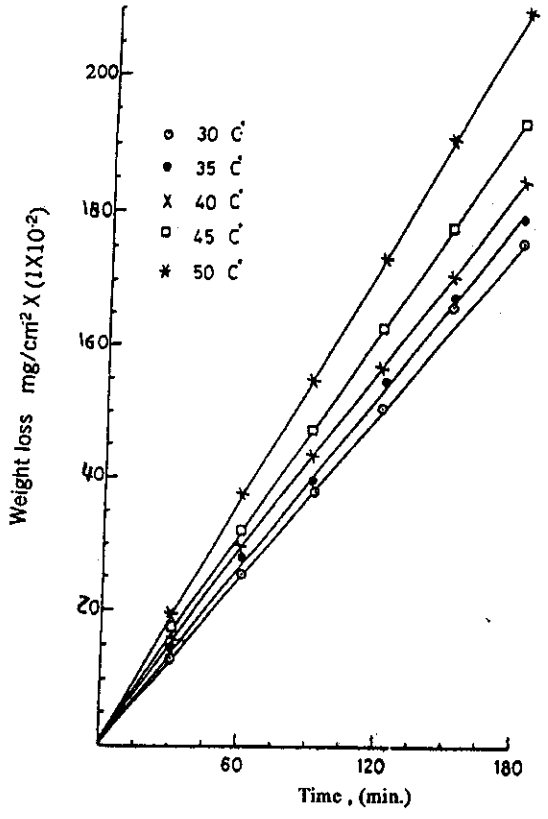


Fig. (3.34): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (3) at different temperatures.

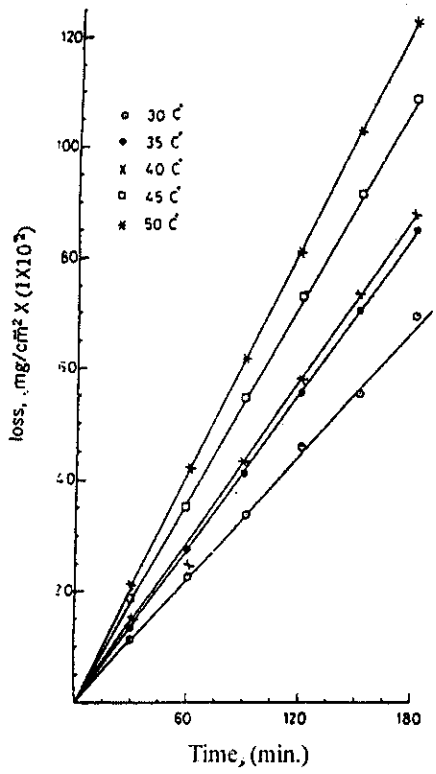


Fig. (3.35): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (3) at different temperatures.

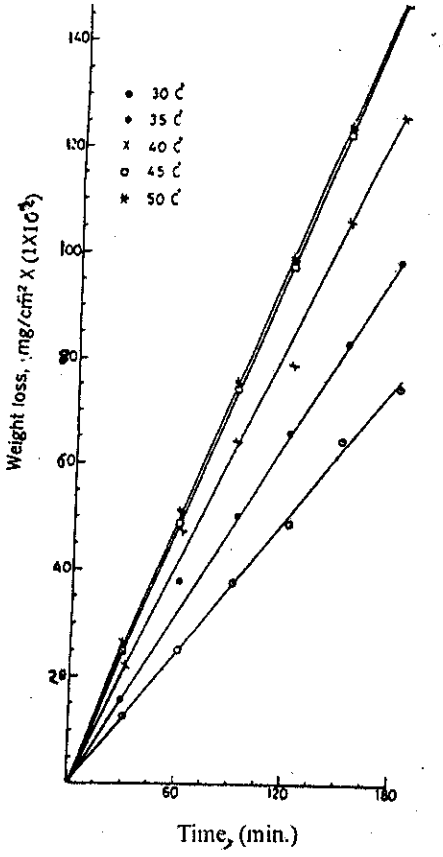


Fig. (3.36): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (3) at different temperatures.

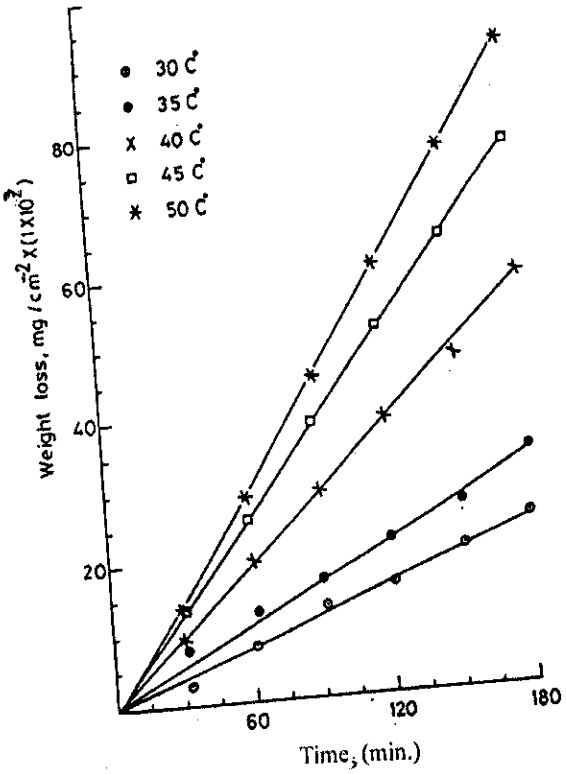


Fig. (3.37): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (a) at different temperatures.

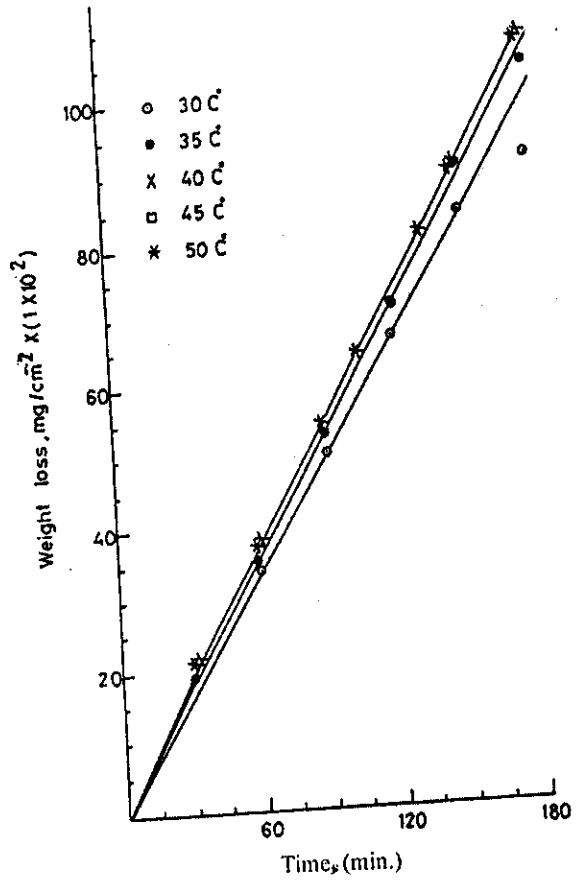


Fig. (3.38): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (a) at different temperatures.

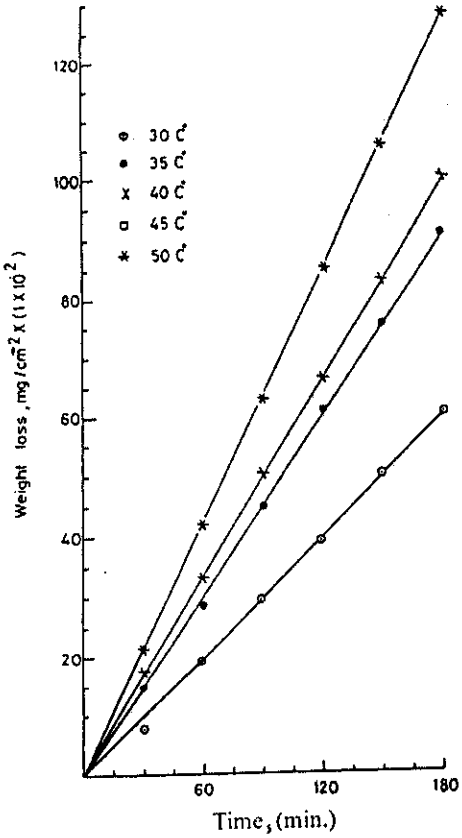


Fig. (3.39): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (a) at different temperatures.

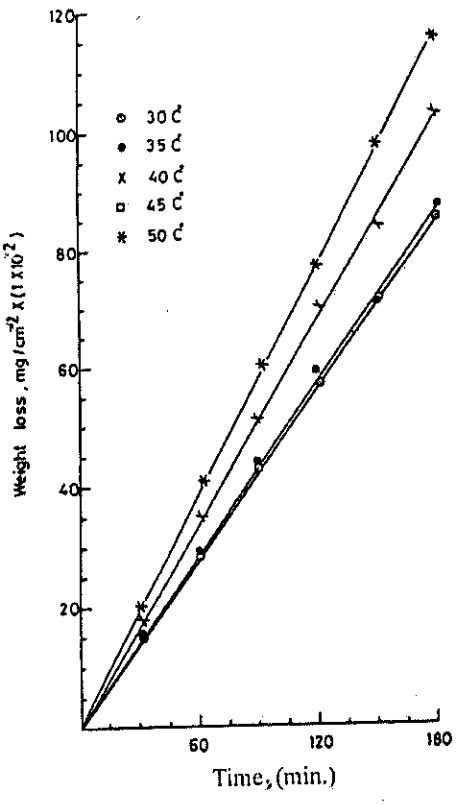


Fig. (3.40): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (a) at different temperatures.

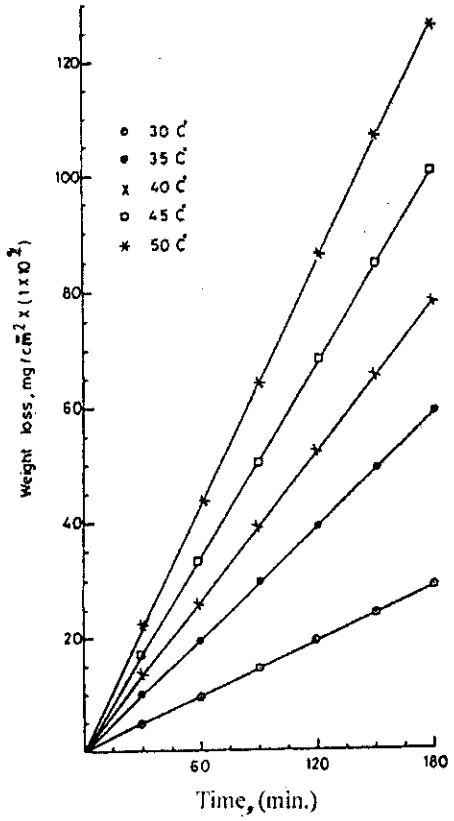


Fig. (3.41): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (b) at different temperatures

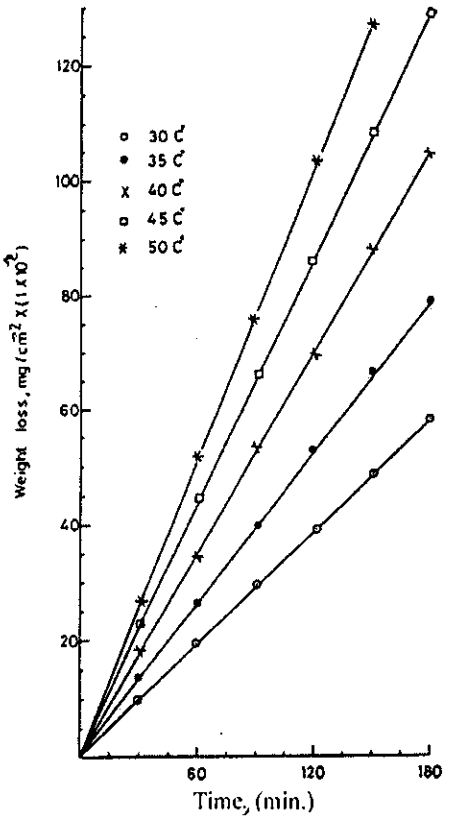


Fig. (3.42): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (b) at different temperatures.

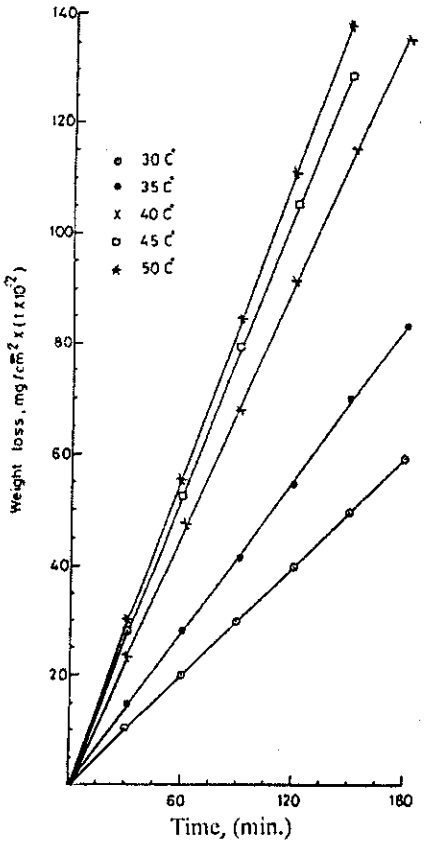


Fig. (3.43): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (b) at different temperatures.

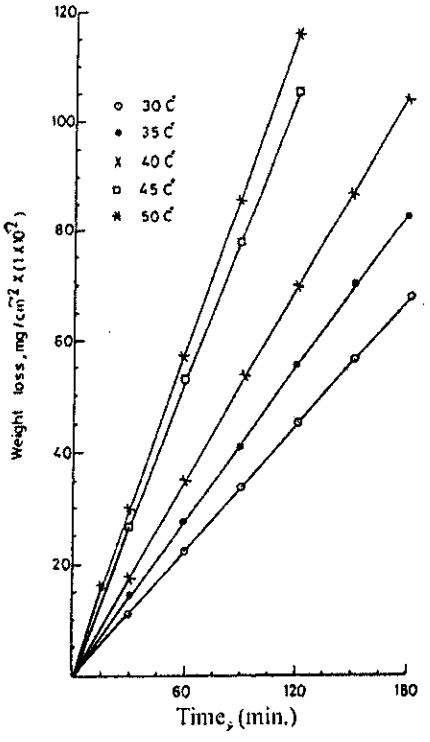


Fig. (3.44): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (b) at different temperatures.

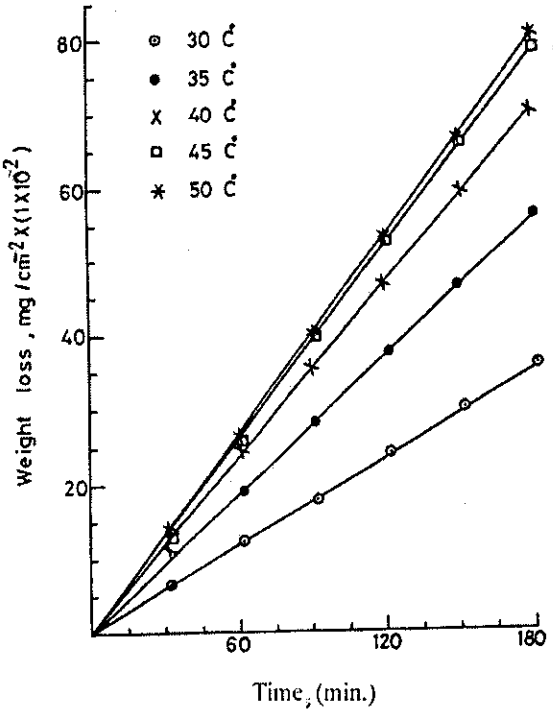


Fig. (3.45): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (c) at different temperatures.

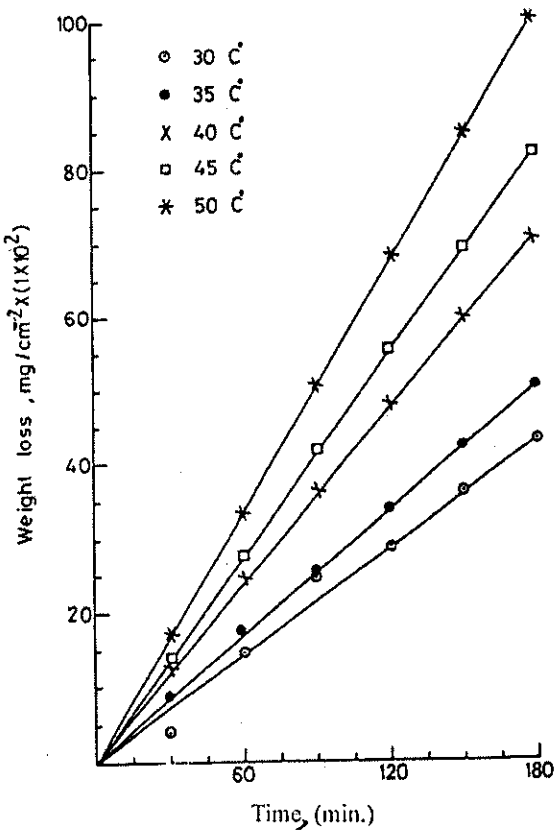


Fig. (3.46): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (c) at different temperatures.

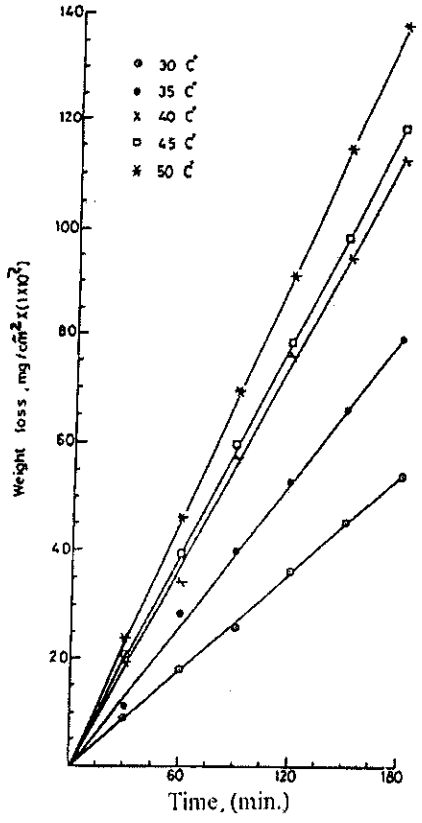


Fig. (3.47): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (c) at different temperatures.

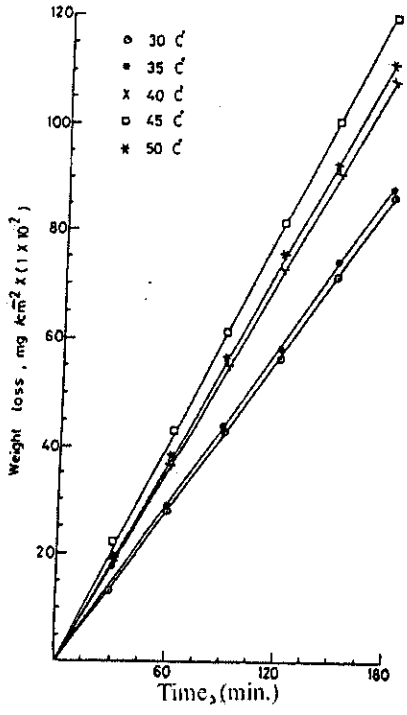


Fig. (3.48): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (c) at different temperatures.

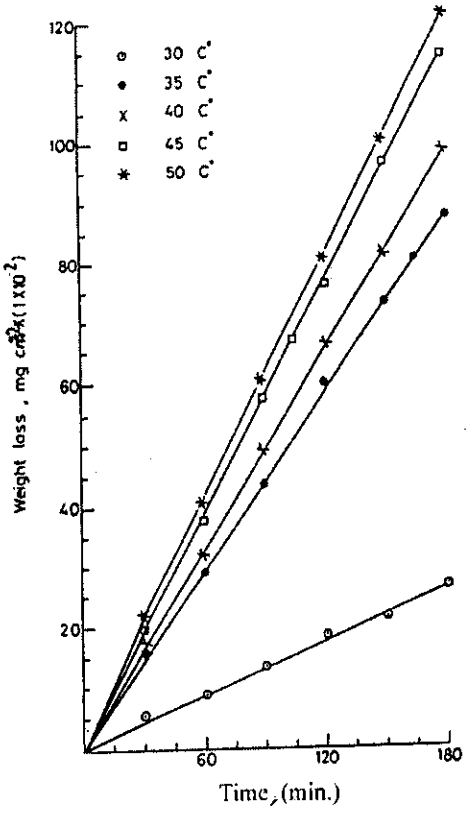


Fig. (3.49): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (d) at different temperatures.

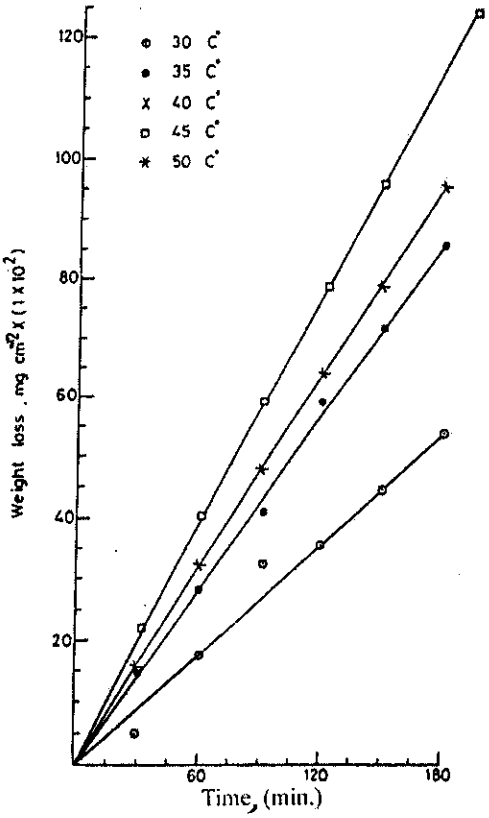


Fig. (3.50): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (d) at different temperatures.

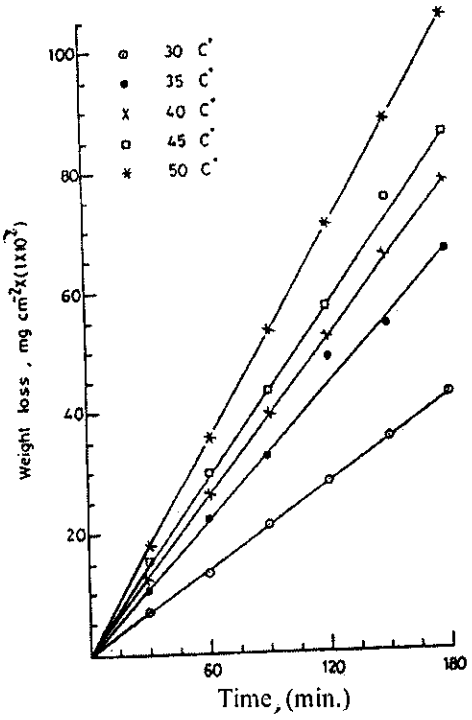


Fig. (3.51): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (d) at different temperatures.

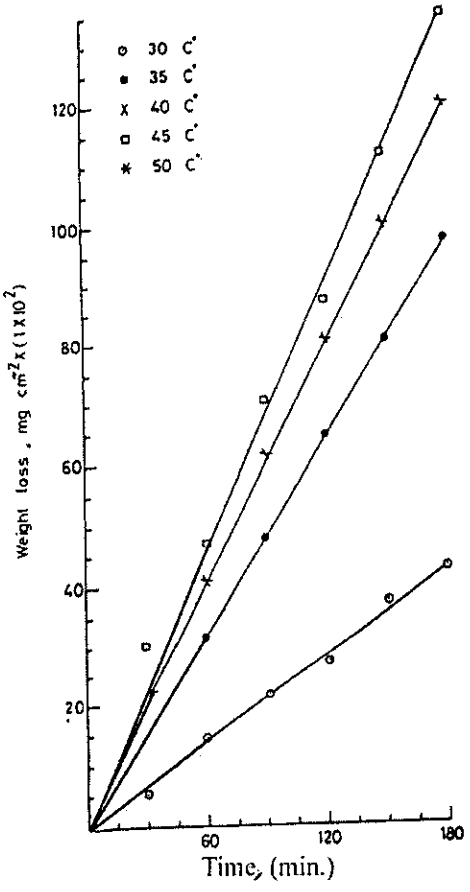


Fig. (3.52): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (d) at different temperatures.

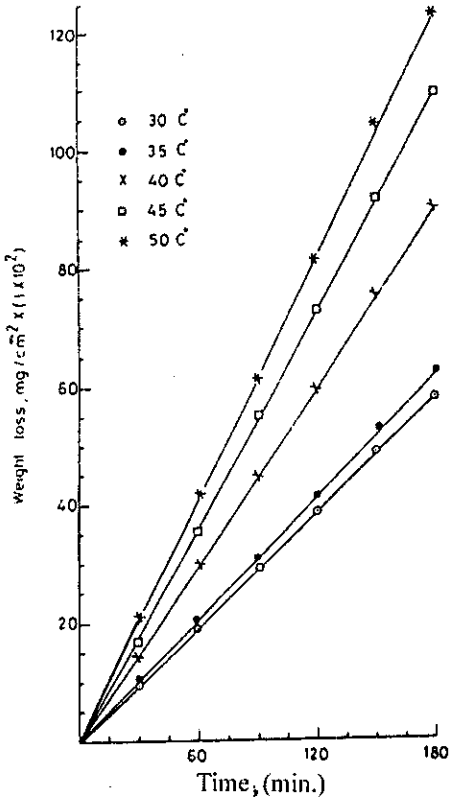


Fig. (3.53): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (I) at different temperatures.

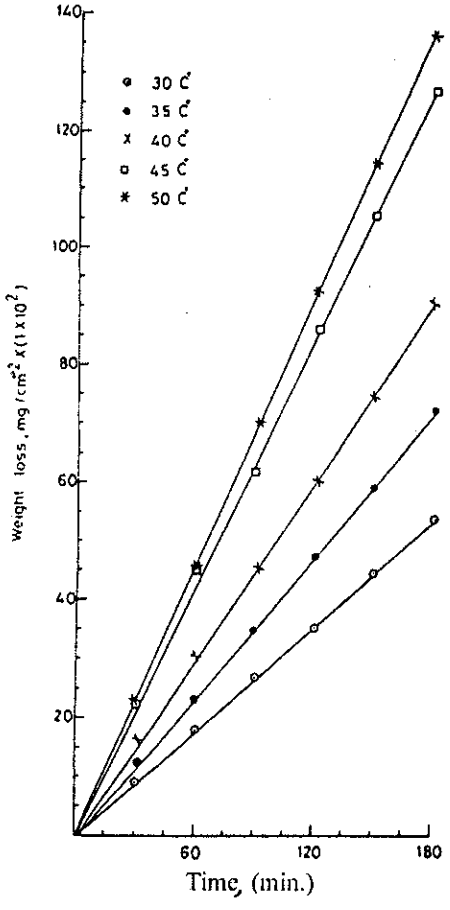


Fig. (3.54): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (I) at different temperatures.

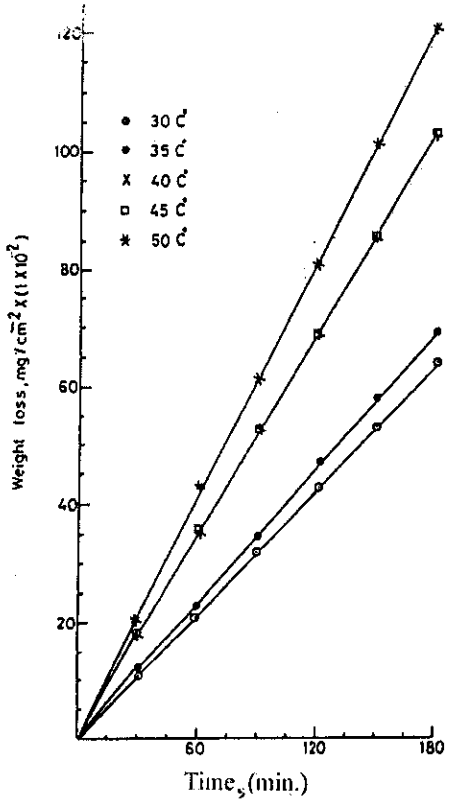


Fig. (3.55): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (I) at different temperatures.

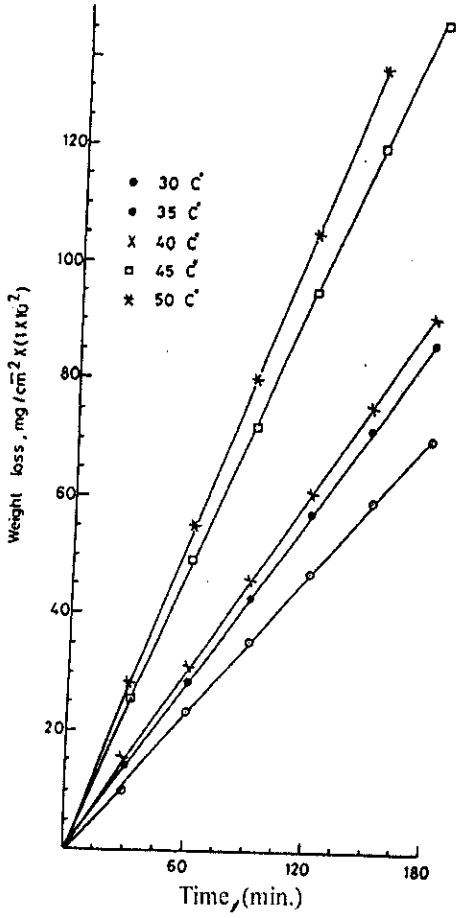


Fig. (3.56): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (I) at different temperatures.

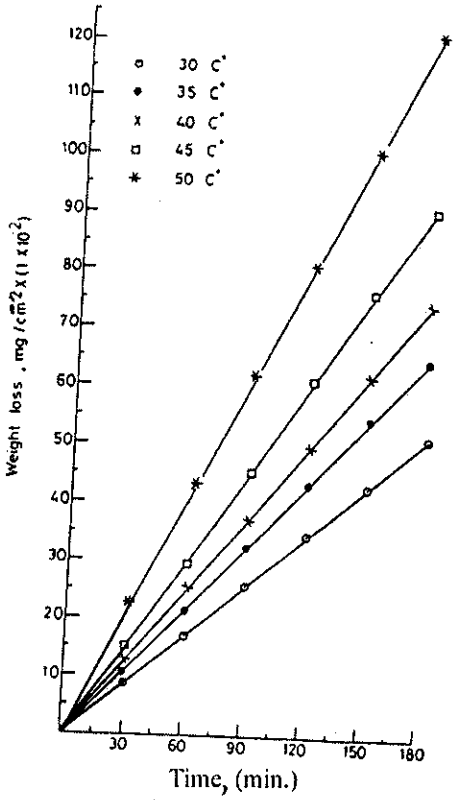


Fig. (3.57): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (II) at different temperatures.

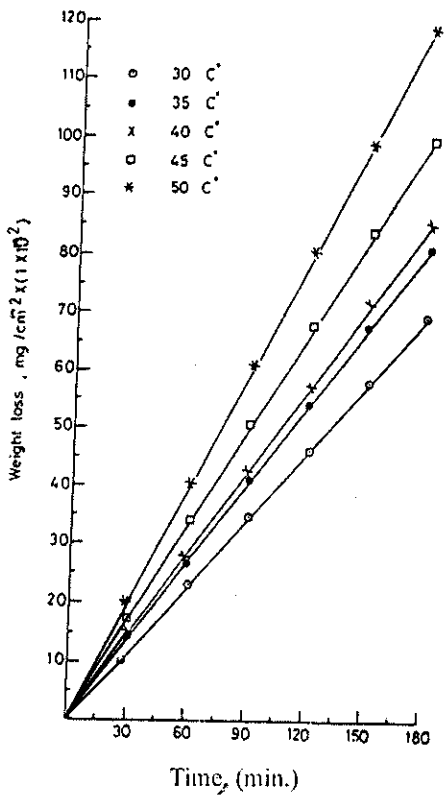


Fig. (3.58): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (II) at different temperatures.

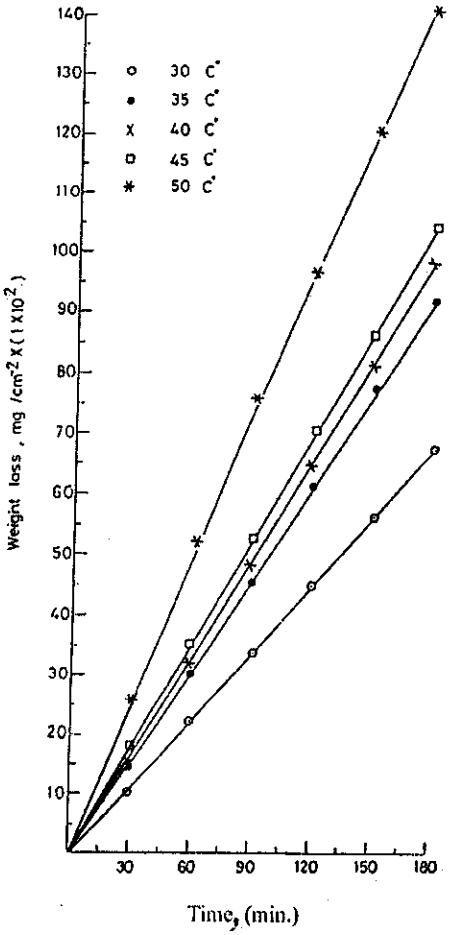


Fig. (3.59): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}M$ compound (II) at different temperatures.

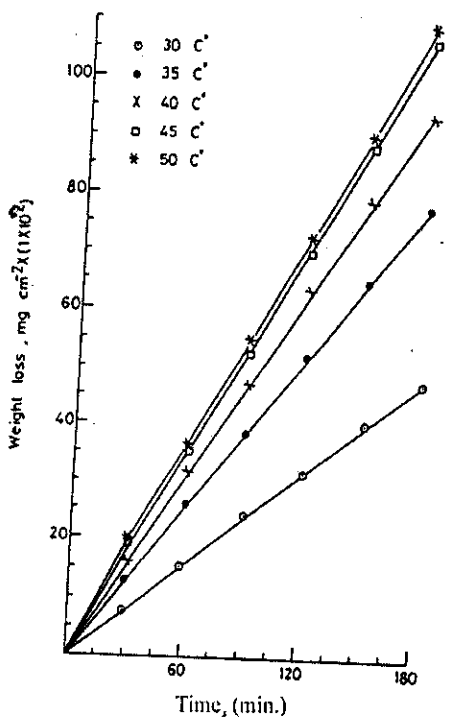


Fig. (3.60): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}M$ compound (III) at different temperatures.

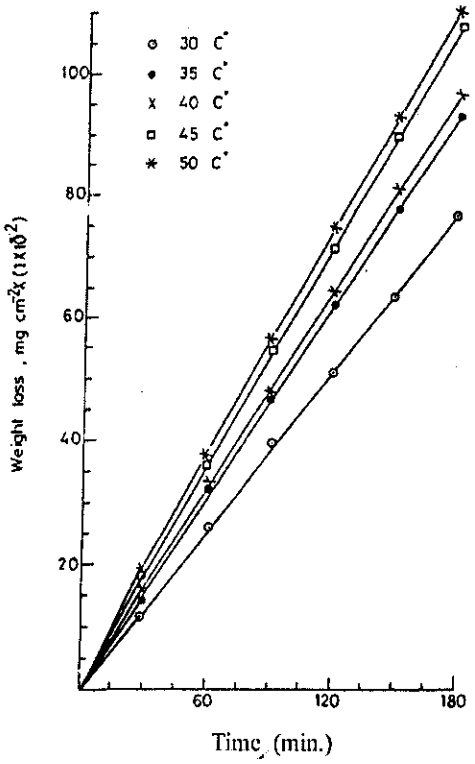


Fig. (3.61): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}M$ compound (III) at different temperatures.

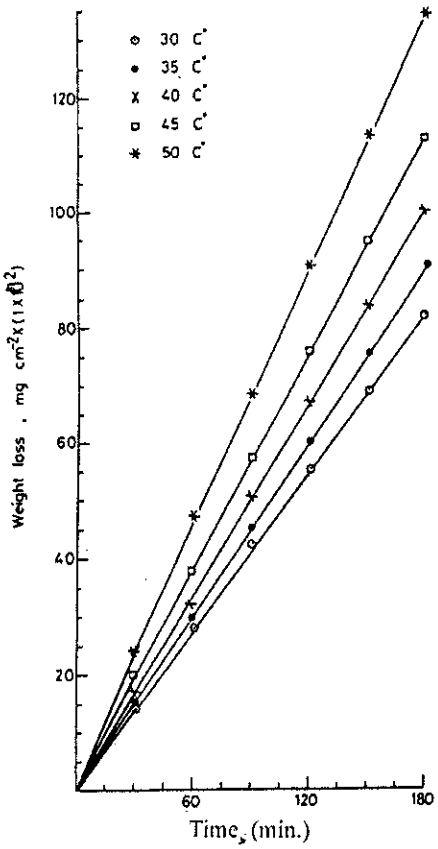


Fig. (3.62): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}M$ compound (III) at different temperatures.

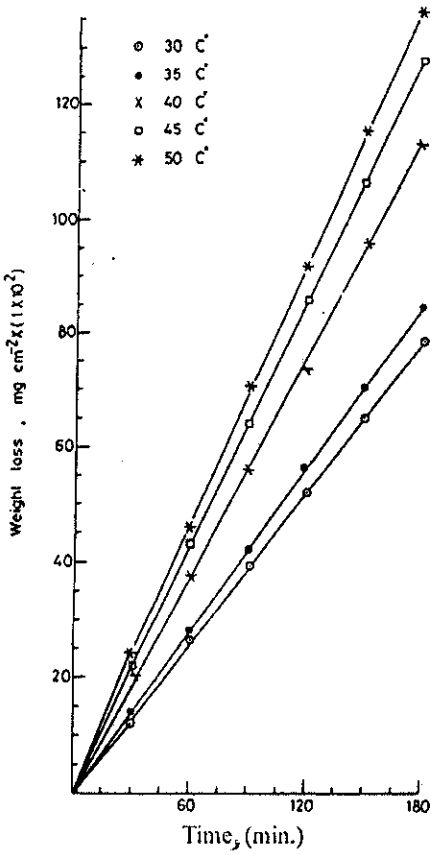


Fig. (3.63): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (III) at different temperatures.

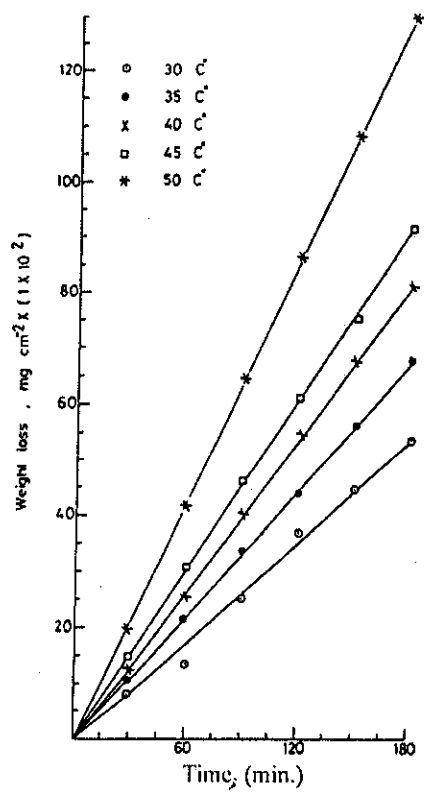


Fig. (3.64): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-4}$M compound (IV) at different temperatures.

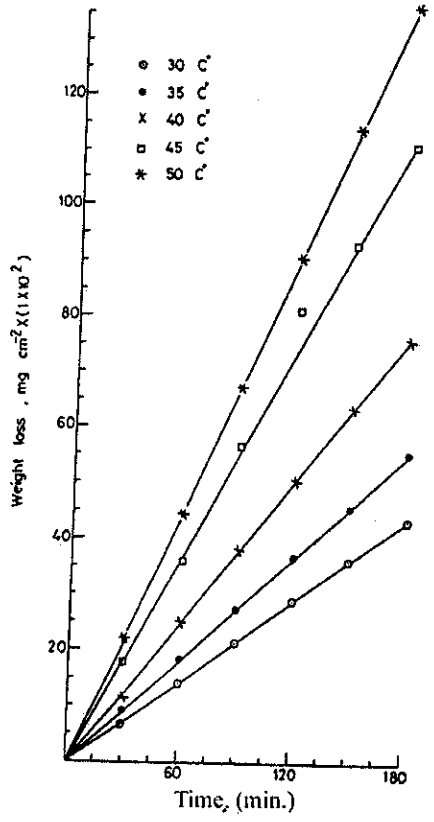


Fig. (3.65): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-5}$M compound (IV) at different temperatures.

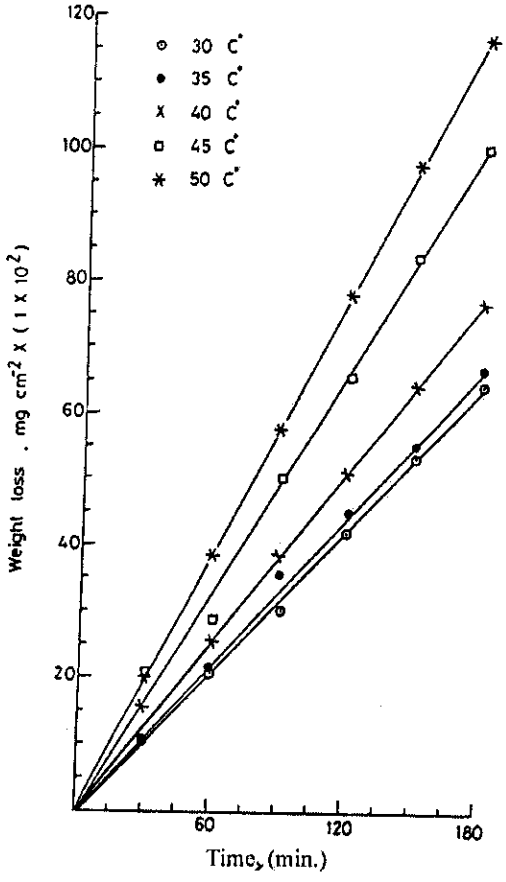


Fig. (3.66): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-6}$M compound (IV) at different temperatures.

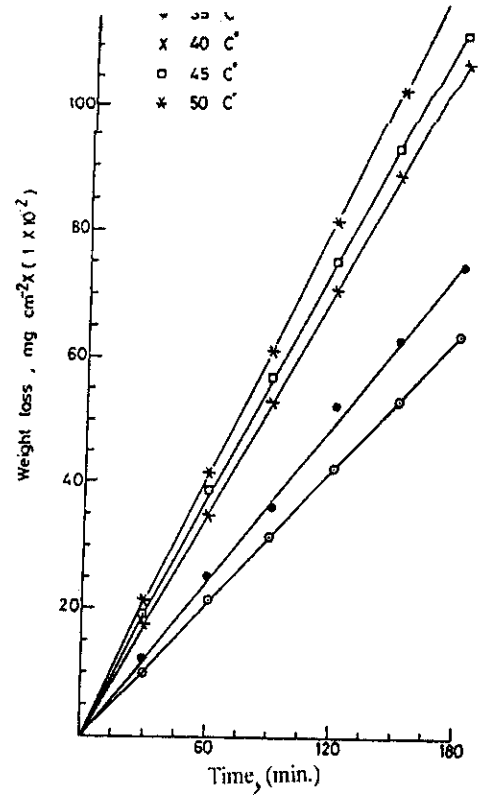


Fig. (3.67): weight loss – time curves for copper in 0.1 M HCl in presence of $1X10^{-7}$M compound (IV) at different temperatures.

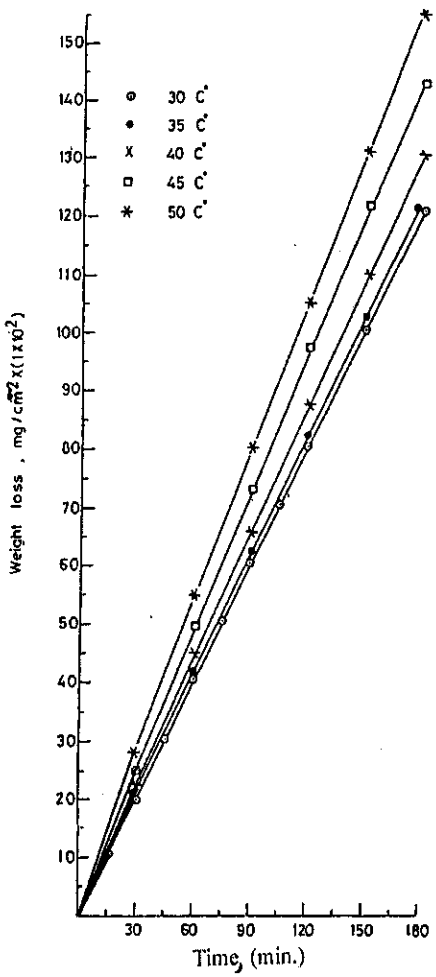


Fig. (3.68): weight loss – time curves for copper in 0.1 M HCl at different temperatures.

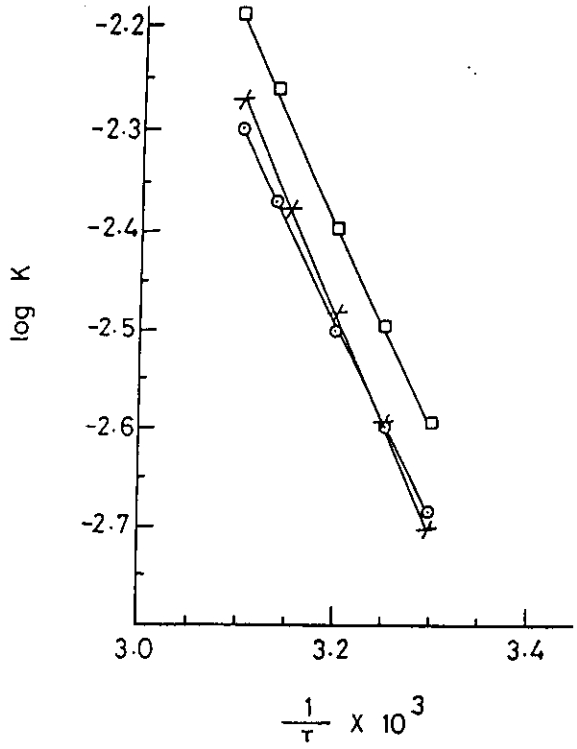


Fig. (3.69): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-4}$) M compound (□)1, (⊙)2, (X)3.

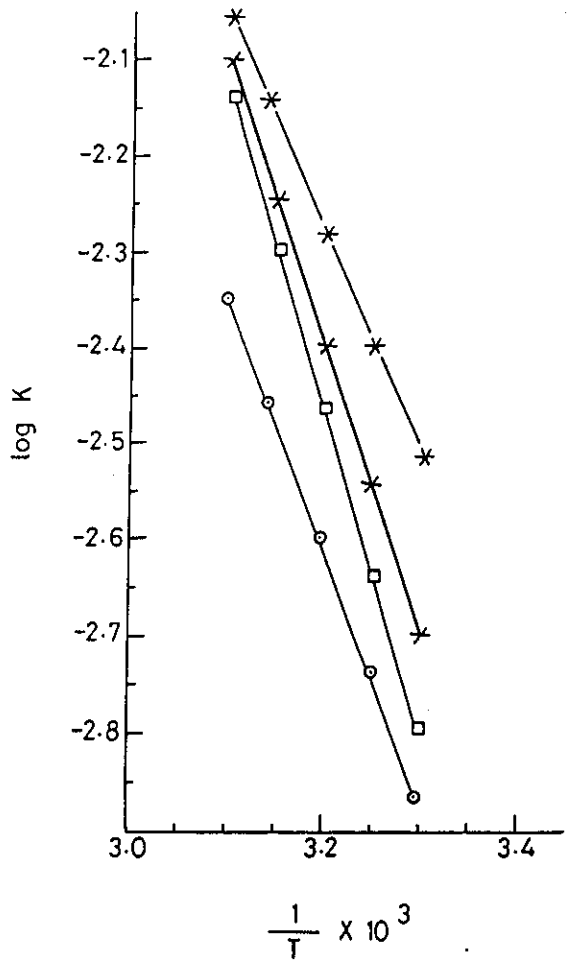


Fig. (3.70): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-4}$) M compound, (⊕)a, (□)b, (X)c, (*)d.

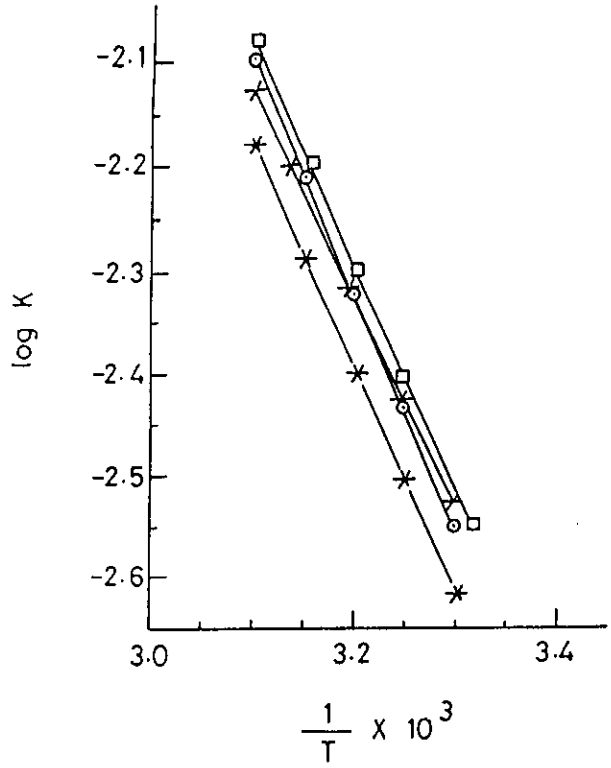


Fig. (3.71): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-4}$) M compound, (⊙) I, (X) II, (□) III and (*) IV.

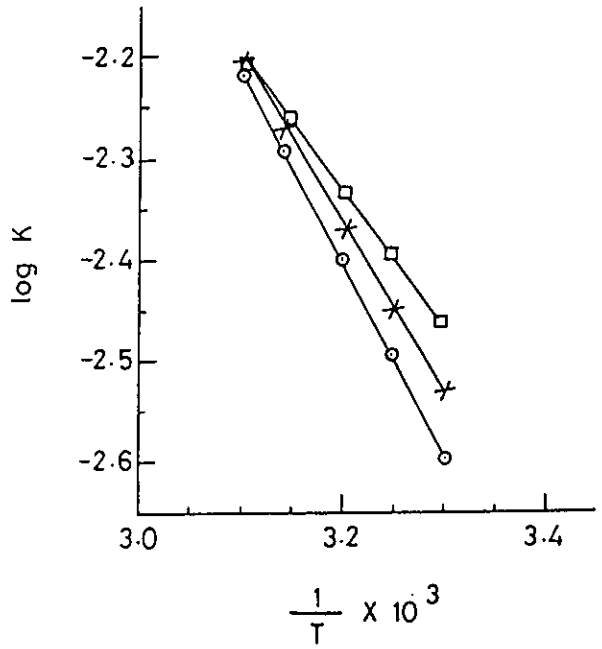


Fig. (3.72): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-5}$) M compound (□)1, (⊙)2, (X)3.

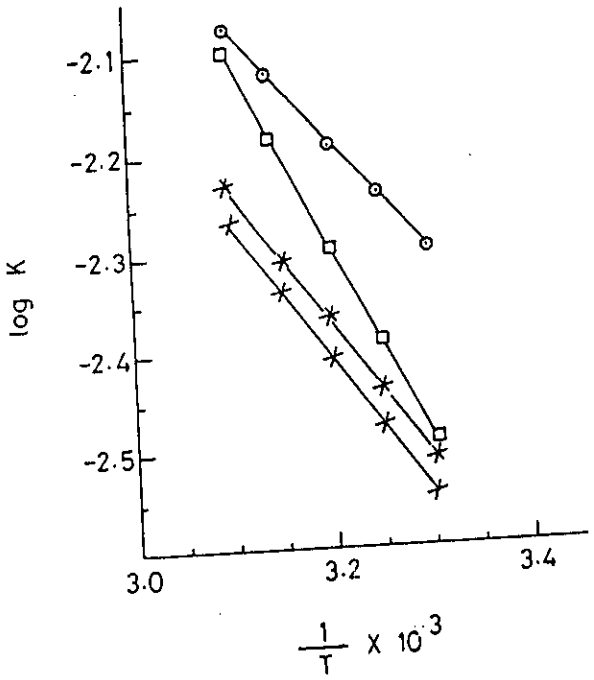


Fig. (3.73): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-6}$) M compound (□)1, (⊙)2, (X)3.

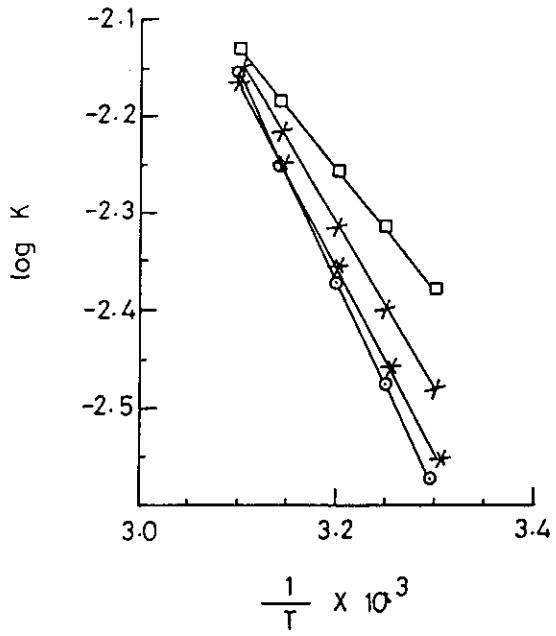


Fig. (3.74): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-7}$) M compound (□)1, (O)2, (X)3.

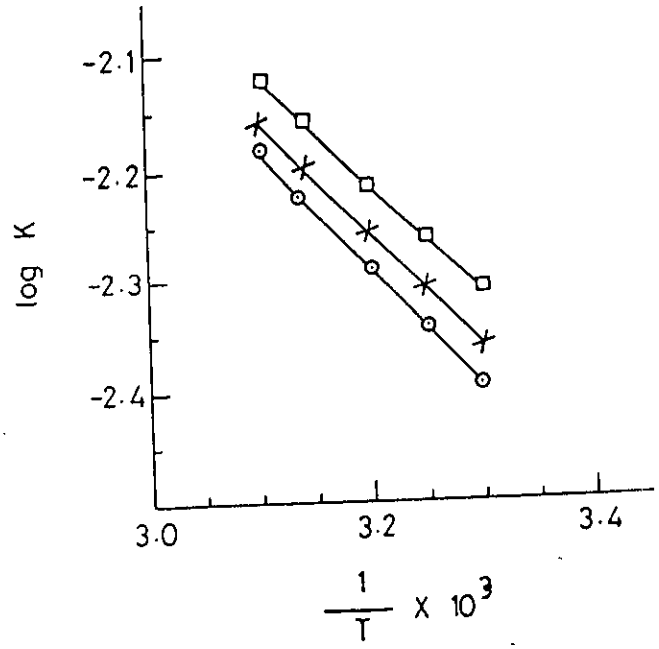


Fig. (3.75): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-5}$) M compound, (⊙)a, (□)b, (X)c, (*)d.

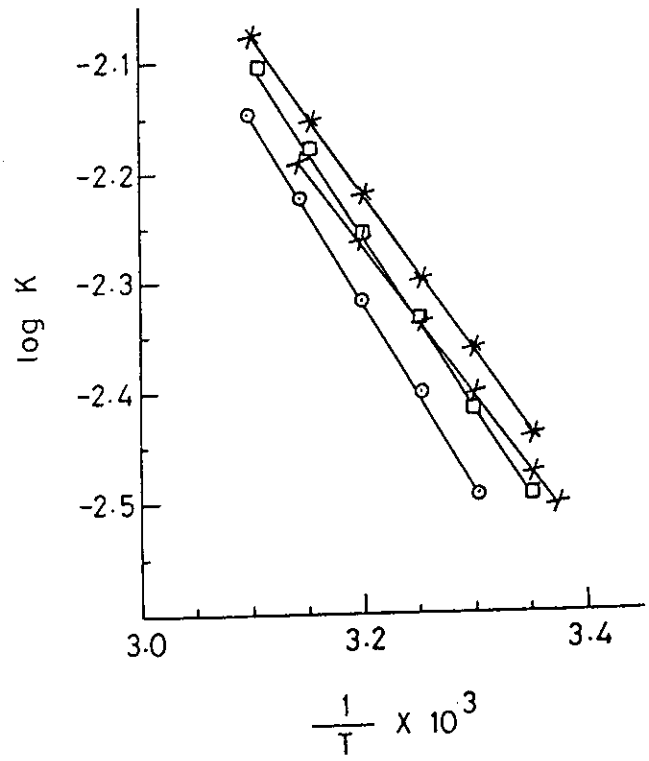


Fig. (3.76): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-6}$) M compound, (⊙)a, (□)b, (X)c, (*)d.

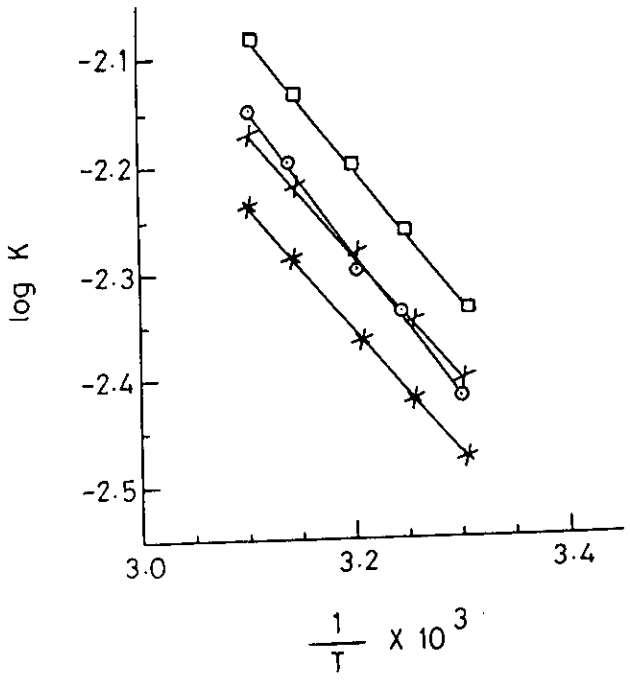


Fig. (3.77): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-7}$) M compound, (⊙)a, (□)b, (X)c, (*)d.

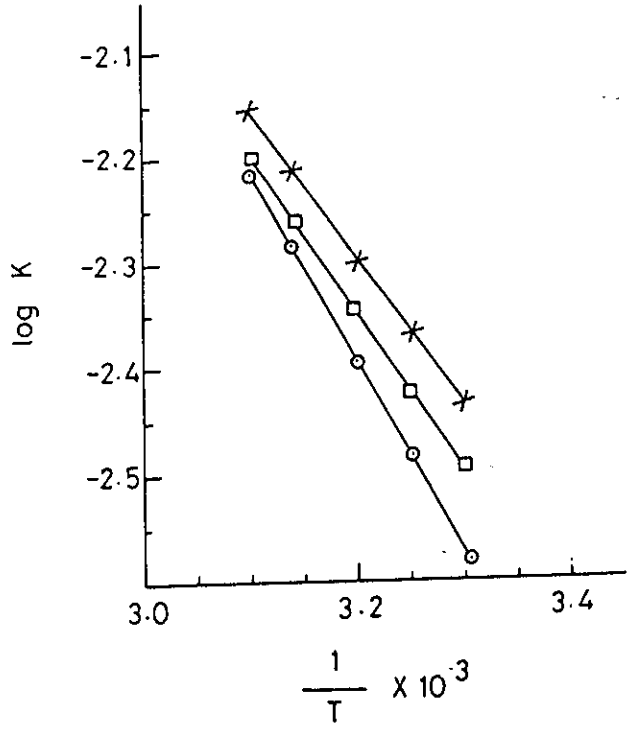


Fig. (3.78): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-5}$) M compound, (⊙) I, (X) II, (□) III and (*) IV.

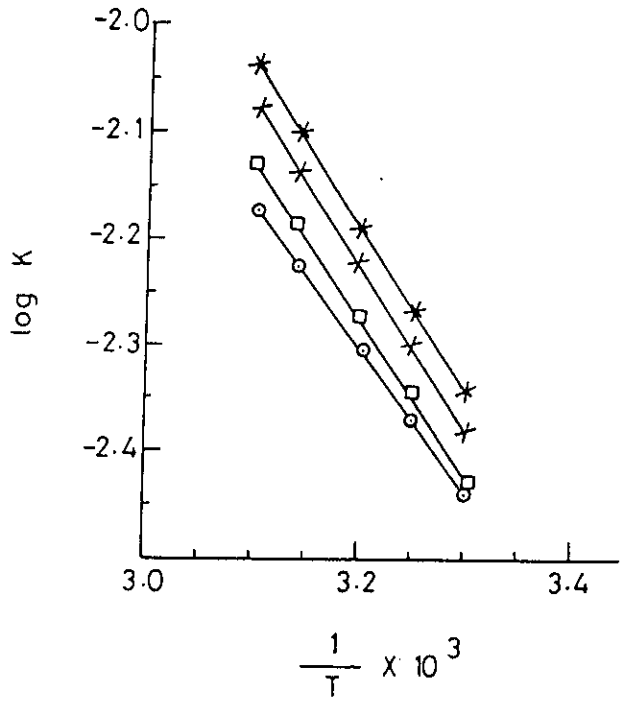


Fig. (3.79): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-6}$) M compound, (⊙) I, (X) II, (□) III and (*) IV.

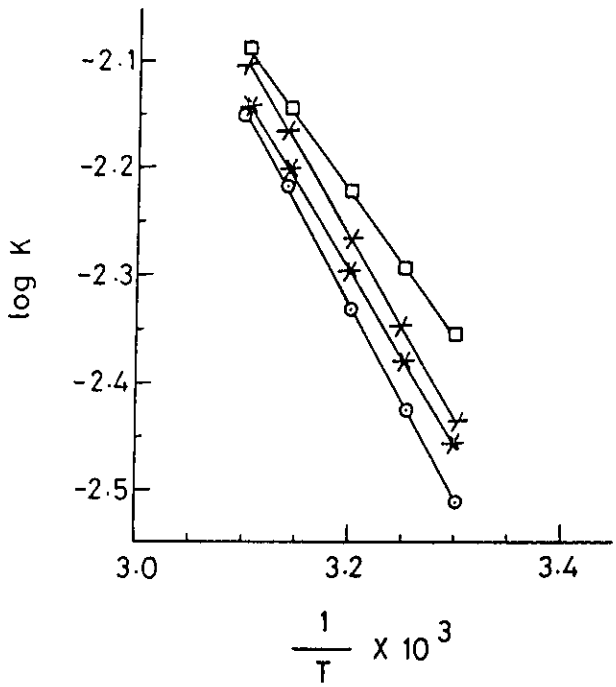


Fig. (3.80): log K –1/T curves for copper dissolution in presence and absence of ($1X10^{-7}$) M compound, (⊙) I, (X) II, (□) III and (*) IV.

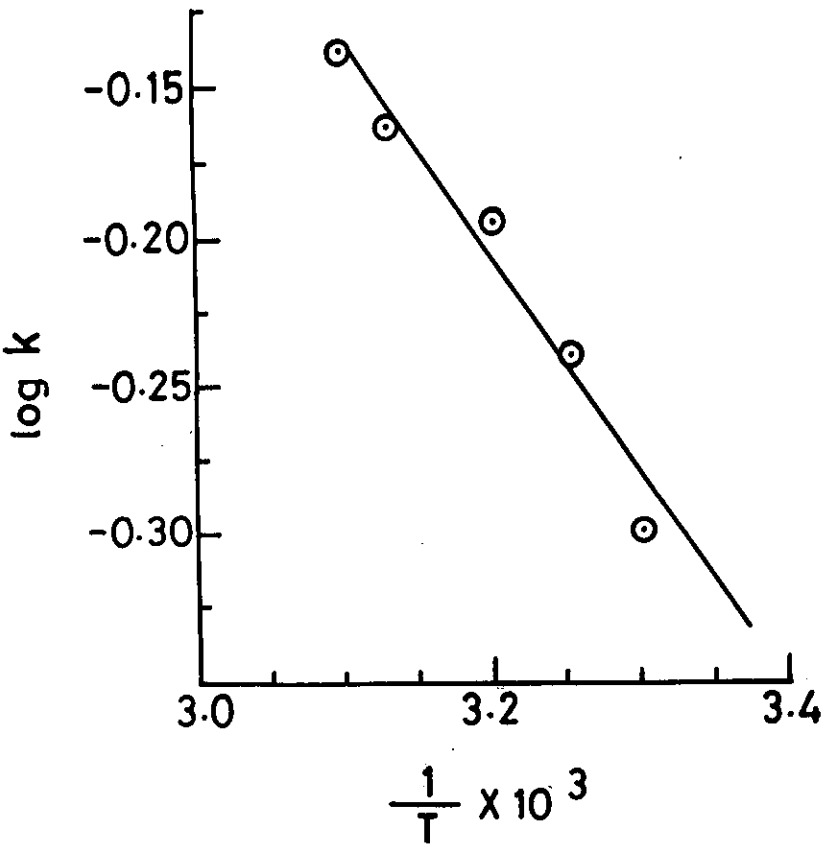


Fig.(3.81): log K – 1/T curves for copper dissolutionin0.1M HCl.

3.2- Electrochemical Measurements

3.2.1- Potentiostatic Polarization:

Electrochemical techniques are based on current and potential measurements. According to the choice of the technique accurate and confidential data, concerning the corrosion process, can be obtained.

Potentiostatic polarization curves of copper in 0.1M hydrochloric acid in the absence and presence of different concentrations of the first, second and third serieses compounds at 30°C are illustrated in Figs. (3.82-3.92) and Tables (3.7a-3.17a). The results show that the addition of inhibitors induced an increase in both cathodic and anodic overvoltages which depends upon concentration. The compounds influence both cathodic and anodic processes in HCl solutions. This indicates that compounds act as mixed type inhibitor. The slopes of anodic and cathodic Tafel lines is approximately constant and independent of the inhibitor concentration. This behaviour suggestes that the inhibitor molecules have no effect on the mechanism of dissolution of copper. The adsorbed molecules mechanically screen the coated part of the electrode and protect it against acid attack.

The polarization curves are shifted in the negative and positive directions depending on the magnitude of concentration of the added inhibitor. This indicates that the compounds have a clear inhibition effect on the dissolution of copper.

The results indicate that the order of increased inhibition efficiency for the additives is:

First series: 2 > 3 > 1 (Table 3.19a)

Second series: a > b > C > d (Table 3.20a)

Third series: I > II > III > IV (Table 3.21a)

Which is given from the following:

$$\% I = [i_{corr.\,(free)} - i_{corr.\,(inh.)} / i_{corr.\,(free)}] X\ 100 \qquad (3.3)$$

The potentiostatic polarization curves of copper in 0.1 M hydrochloric acid solution containing different concentrations of KI ($1X10^{-6}$- $1X\ 10^{-3}$M) and at constant concentration of the additives ($1X10^{-4}$M) at 30°C are shown in Figs. (3.93 - 3.104) and the data obtained are summarized in Tables (3.7b – 3.17b). It was found that the addition of different concentrations of KI to the corrosive medium reduces both cathodic and anodic current densities. This behaviour supports that the inhibition efficiency of the additive compounds increases by the presence of a synergistic effect between iodide ions and the used additives. The same order of increased inhibition efficiency was also obtained by adding different concentrations of KI ($1X10^{-6}$-$1X\ 10^{-3}$ M) to the concentration of the additives ($1X\ 10^{-4}$M) Tables (3.19b – 3.21b). Apparently, the results obtained from the potentionstatic technique give further support to the results obtained from the weight loss measurement. These results confirm the pervious suggestion that these compounds are adsorbed on the metal surface.

Table (3.7a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (1).

Conc., M	E_{corr} mV	$i_{corr.}$ μAcm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	95	5.00	196.0	195.0	37.5	0.38
$5 X 10^{-7}$	95	4.00	198.0	192.3	50.0	0.50
$1 X 10^{-6}$	95	3.20	194.0	198.0	60.0	0.60
$5 X 10^{-6}$	95	2.14	200.0	196.0	73.0	0.73
$1 X 10^{-5}$	95	1.86	193.0	194.0	77.0	0.77
$5 X 10^{-5}$	95	1.55	194.0	195.0	80.6	0.80
$1 X 10^{-4}$	95	1.48	196.0	197.0	81.8	0.81

Table (3.7b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M of compound (1) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	95	1.15	196.0	197.0	85.6	0.86
$1 X 10^{-5}$	95	0.93	196.0	200.0	88.4	0.88
$1 X 10^{-4}$	95	0.87	192.3	194.0	89.0	0.89
$1 X 10^{-3}$	95	0.69	198.0	196.0	91.0	0.91

Table (3.8a): Data from polarization of copper in 1 M HCl containing various concentrations of compound (2).

Conc., M	E_{corr} mV	$i_{corr.}$ μA cm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
1 X 10^{-7}	93	3.76	195.6	194.0	53.0	0.53
5 X 10^{-7}	93	2.95	200.0	196.0	63.0	0.63
1 X 10^{-6}	93	2.70	199.0	198.0	66.3	0.66
5 X 10^{-6}	93	1.70	198.0	197.0	79.0	0.79
1 X 10^{-5}	95	1.45	197.0	195.0	82.0	0.82
5 X 10^{-5}	95	1.40	200.0	194.0	82.5	0.83
1 X 10^{-4}	95	1.39	192.3	196.0	82.6	0.83

Table (3.8b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (2) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ μA cm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
1 X 10^{-6}	100	1.00	193.0	195.0	87.5	0.88
1 X 10^{-5}	100	0.87	192.3	194.0	89.0	0.89
1 X 10^{-4}	100	0.63	197.0	198.0	92.0	0.92
1 X 10^{-3}	95	0.5	200.0	196.0	93.8	0.94

Table (3.9a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (3).

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	95	4.57	197	200.0	43.0	0.43
$5 X 10^{-7}$	94	3.16	198	196.0	61.0	0.61
$1 X 10^{-6}$	90	2.95	192.3	194.0	63.0	0.63
$5 X 10^{-6}$	95	2.00	196.0	195.0	75.0	0.75
$1 X 10^{-5}$	96	1.70	195.0	193.0	78.8	0.79
$5 X 10^{-5}$	93	1.50	197.0	197.0	81.3	0.81
$1 X 10^{-4}$	90	1.45	200.0	198.0	81.9	0.82

Table (3.9b): Data from polarization of copper in 0.1 M HCl + $1 X 10^{-4}$ M compound (3) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ μAcm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	Θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	95	1.07	194.0	193.0	86.6	0.87
$1 X 10^{-5}$	100	0.93	192.3	194.0	88.4	0.88
$1 X 10^{-4}$	95	0.74	195.0	197.0	90.8	0.91
$1 X 10^{-3}$	100	0.63	196.0	198.0	92.0	0.92

Table (3.10a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (a).

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	95	4.27	197.0	196.0	47.0	0.47
$5 X 10^{-7}$	95	2.88	198.0	195.0	64.0	0.64
$1 X 10^{-6}$	95	2.69	200.0	197.0	66.0	0.66
$5 X 10^{-6}$	95	2.51	195.0	193.0	69.0	0.69
$1 X 10^{-5}$	95	2.00	196.0	194.0	75.0	0.75
$5 X 10^{-5}$	95	1.58	195.0	192.3	80.3	0.80
$1 X 10^{-4}$	95	1.35	198.0	197.0	83.0	0.83

Table (3.10b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (a) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	95	0.79	195.0	192.0	90.0	0.900
$1 X 10^{-5}$	95	0.63	197.0	195.0	92.0	0.920
$1 X 10^{-4}$	100	0.55	194.0	193.0	93.0	0.930
$1 X 10^{-3}$	100	0.44	198.0	200.0	95.0	0.950

Table (3.11a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (b).

Conc., M	E_{corr} mV	$i_{corr.}$ μA cm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
1 X 10^{-7}	95	5.00	195.6	195.6	37.5	0.38
5 X 10^{-7}	95	3.40	196.4	192.3	58.0	0.58
1 X 10^{-6}	95	3.16	195.6	192.3	61.0	0.61
5 X 10^{-6}	95	2.70	200.0	198.0	66.3	0.66
1 X 10^{-5}	95	2.52	194.0	196.0	69.0	0.69
5 X 10^{-5}	95	2.00	192.3	194.0	75.0	0.75
1 X 10^{-4}	95	1.45	188.0	190.0	82.0	0.82

Table (3.11b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (b) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ μA cm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
1 X 10^{-6}	95	0.93	197.0	193.0	88.0	0.880
1 X 10^{-5}	100	0.87	198.0	200.0	89.0	0.890
1 X 10^{-4}	95	0.79	196.0	192.3	90.0	0.900
1 X 10^{-3}	95	0.63	198.0	196.0	92.0	0.920

Table (3.12a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (c).

Conc., M	E_{corr} mV	$i_{corr.}$ μAcm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	92	5.40	197.0	197.0	33.0	0.33
$5 X 10^{-7}$	95	4.00	200.0	192.3	50.0	0.50
$1 X 10^{-6}$	100	3.16	195.7	192.3	61.0	0.61
$5 X 10^{-6}$	100	3.00	195.7	192.3	63.0	0.63
$1 X 10^{-5}$	100	2.80	197.0	196.0	65.0	0.65
$5 X 10^{-5}$	95	2.40	192.0	194.0	70.0	0.70
$1 X 10^{-4}$	95	1.60	195.0	198.0	80.0	0.80

Table (3.12b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (c) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ μAcm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	100	1.00	193.0	195.0	87.5	0.875
$1 X 10^{-5}$	100	0.87	190.0	195.0	89.0	0.890
$1 X 10^{-4}$	100	0.80	200.0	194.0	90.0	0.900
$1 X 10^{-3}$	100	0.74	198.0	195.0	90.8	0.908

Table (3.13a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (d).

Conc., M	E_{corr} mV	$i_{corr.}$ μAcm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	100	5.75	195.0	197.0	28.0	0.28
$5 X 10^{-7}$	96	4.27	197.0	192.3	47.0	0.47
$1 X 10^{-6}$	95	3.98	194.0	196.0	50.3	0.50
$5 X 10^{-6}$	95	3.40	198.0	195.0	58.0	0.58
$1 X 10^{-5}$	92	2.90	197.0	193.0	64.0	0.64
$5 X 10^{-5}$	94	2.60	200.0	194.0	67.5	0.68
$1 X 10^{-4}$	96	1.70	198.0	197.0	78.8	0.79

Table (3.13b): Data from polarization of copper in 0.1 M HCl+1 X 10^{-4} M compound (d) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ μAcm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	95	1.07	197.0	200.0	86.6	0.866
$1 X 10^{-5}$	95	0.93	198.0	196.0	88.4	0.880
$1 X 10^{-4}$	100	0.86	193.0	194.0	89.3	0.890
$1 X 10^{-3}$	100	0.80	198.0	197.0	90.0	0.900

Table (3.14a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (I).

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	95	5.40	195.0	193.0	32.5	0.33
$5 X 10^{-7}$	95	2.50	196.0	194.0	68.8	0.69
$1 X 10^{-6}$	96	2.50	200.0	197.0	68.8	0.69
$5 X 10^{-6}$	94	1.82	198.0	195.0	77.3	0.77
$1 X 10^{-5}$	95	1.15	195.0	193.0	85.6	0.85
$5 X 10^{-5}$	100	1.12	194.0	197.0	86.0	0.86
$1 X 10^{-4}$	98	1.07	197.0	198.0	86.6	0.87

Table (3.14b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (I) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	100	0.93	194.0	197.0	88.4	0.880
$1 X 10^{-5}$	100	0.79	195.0	195.0	90.0	0.900
$1 X 10^{-4}$	100	0.63	197.0	196.0	92.0	0.920
$1 X 10^{-3}$	100	0.47	198.0	200.0	94.0	0.940

Table (3.15a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (II).

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	95	5.75	194.0	195.0	28.0	0.28
$5 X 10^{-7}$	95	3.40	200.0	197.0	58.0	0.58
$1 X 10^{-6}$	96	2.60	193.0	194.0	68.0	0.68
$5 X 10^{-6}$	95	1.82	192.3	198.0	77.3	0.77
$1 X 10^{-5}$	94	1.60	198.0	196.0	80.0	0.80
$5 X 10^{-5}$	95	1.26	197.0	195.0	84.3	0.84
$1 X 10^{-4}$	100	1.15	198.0	197.0	85.6	0.86

Table (3.15b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (II) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	95	1	192.3	195.0	87.5	0.875
$1 X 10^{-5}$	95	0.93	190.0	193.0	88.4	0.884
$1 X 10^{-4}$	95	0.79	195.0	194.0	90.1	0.900
$1 X 10^{-3}$	95	0.74	198.0	200.0	90.4	0.900

Table (3.16a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (III).

Conc., M	E_{corr} mV	$i_{corr.}$ μA cm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
1 X 10^{-7}	95	6.30	194.0	195.0	21.3	0.21
5 X 10^{-7}	100	4.60	195.0	198.0	42.5	0.43
1 X 10^{-6}	100	3.16	193.0	195.0	61.0	0.61
5 X 10^{-6}	100	2.51	192.3	193.0	69.0	0.69
1 X 10^{-5}	95	2.14	195.0	196.0	73.3	0.73
5 X 10^{-5}	95	1.58	197.0	194.0	80.3	0.80
1 X 10^{-4}	95	1.58	200.0	197.0	80.3	0.80

Table (3.16b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (III) with various concentrations of KI .

Conc., M	E_{corr} mV	$i_{corr.}$ μA cm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
1 X 10^{-6}	100	1.07	198.0	198.0	86.6	0.866
1 X 10^{-5}	100	0.93	193.0	193.0	88.4	0.880
1 X 10^{-4}	100	0.87	194.0	194.0	89.0	0.890
1 X 10^{-3}	100	0.79	196.0	196.0	90.0	0.900

Table (3.17a): Data from polarization of copper in 0.1 M HCl containing various concentrations of compound (IV).

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	Θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-7}$	95	6.76	200.0	193.0	16.0	0.16
$5 X 10^{-7}$	100	5.00	200.0	196.0	38.0	0.38
$1 X 10^{-6}$	95	3.16	200.0	198.0	61.0	0.61
$5 X 10^{-6}$	100	2.51	196.0	192.0	69.0	0.69
$1 X 10^{-5}$	90	2.30	192.0	195.0	71.3	0.71
$5 X 10^{-5}$	95	1.82	194.6	193.0	77.3	0.77
$1 X 10^{-4}$	100	1.70	195.0	197.0	78.8	0.79

Table (3.17b): Data from polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (IV) with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ $\mu A\ cm^{-2}$	b_a $mV\ dec^{-1}$	b_c $mV\ dec^{-1}$	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	100	1.14	198.0	200.0	85.8	0.858
$1 X 10^{-5}$	100	0.93	197.0	197.0	88.4	0.880
$1 X 10^{-4}$	95	0.87	192.3	195.0	89.0	0.890
$1 X 10^{-3}$	95	0.85	198.0	193.0	89.4	0.890

Table (3.18): Data from potentiostatic polarization of copper in 0.1 M HCl with various concentrations of KI.

Conc., M	E_{corr} mV	$i_{corr.}$ μAcm^{-2}	b_a mV dec^{-1}	b_c mV dec^{-1}	%I	θ
0.0	100	8.00	193.0	192.3	———	———
$1 X 10^{-6}$	100	5.00	200.0	193.0	37.5	0.38
$1 X 10^{-5}$	100	3.98	192.3	195.0	50.0	0.50
$1 X 10^{-4}$	100	2.69	194.0	196.0	66.4	0.66
$5 X 10^{-3}$	100	1.82	198.0	197.0	77.3	0.77

Table (3.20a): Data from polarization of copper in 0.1 M HCl for various concentrations of the second series compounds at 30°C.

Concentration of compounds, (M)	% Inhibition			
	Inhibitor (a)	Inhibitor (b)	Inhibitor (c)	Inhibitor (d)
1×10^{-7}	47.0	37.5	33.0	28.0
5×10^{-7}	64.0	58.0	50.0	47.0
1×10^{-6}	66.0	61.0	61.0	50.3
5×10^{-6}	69.0	66.3	63.0	58.0
1×10^{-5}	75.0	69.0	65.0	64.0
5×10^{-5}	80.3	75.0	70.0	67.5
1×10^{-4}	83.0	82.0	80.0	78.8

Table (3.20b): Data from polarization of copper in 0.1 M HCl +1 X 10^{-4} M of the second series compounds for various KI concentrations at 30°C.

Concentration of KI (M)	% Inhibition			
	Inhibitor (a)	Inhibitor (b)	Inhibitor (c)	Inhibitor (d)
1×10^{-6}	90.0	88.0	87.5	86.6
1×10^{-5}	92.0	89.0	89.0	88.4
1×10^{-4}	93.0	90.0	90.0	89.3
1×10^{-3}	95	92.0	90.8	90.0

Table (3.21a): Data from polarization of copper in 0.1 M HCl for various concentrations of the third series compounds at 30°C.

Concentration of compounds, (M)	% Inhibition			
	Inhibitor (I)	Inhibitor (II)	Inhibitor (III)	Inhibitor (IV)
1×10^{-7}	32.5	28.0	21.3	16.0
5×10^{-7}	68.8	58.0	42.5	38.0
1×10^{-6}	68.8	68.0	61.0	61.0
5×10^{-6}	77.3	77.3	69.0	69.0
1×10^{-5}	85.6	80.0	73.3	71.3
5×10^{-5}	86.0	84.3	80.3	77.3
1×10^{-4}	86.6	85.6	80.3	78.8

Table (3.21b): Data from polarization of copper in 0.1 M HCl +1 X 10^{-4} M of the third series at 30°C.

Concentration of KI (M)	% Inhibition			
	Inhibitor (I)	Inhibitor (II)	Inhibitor (III)	Inhibitor (IV)
1×10^{-6}	88.4	87.5	86.6	85.8
1×10^{-5}	90.0	88.4	88.4	88.4
1×10^{-4}	92.0	90.1	89.0	89.0
1×10^{-3}	94.0	90.4	90.0	89.4

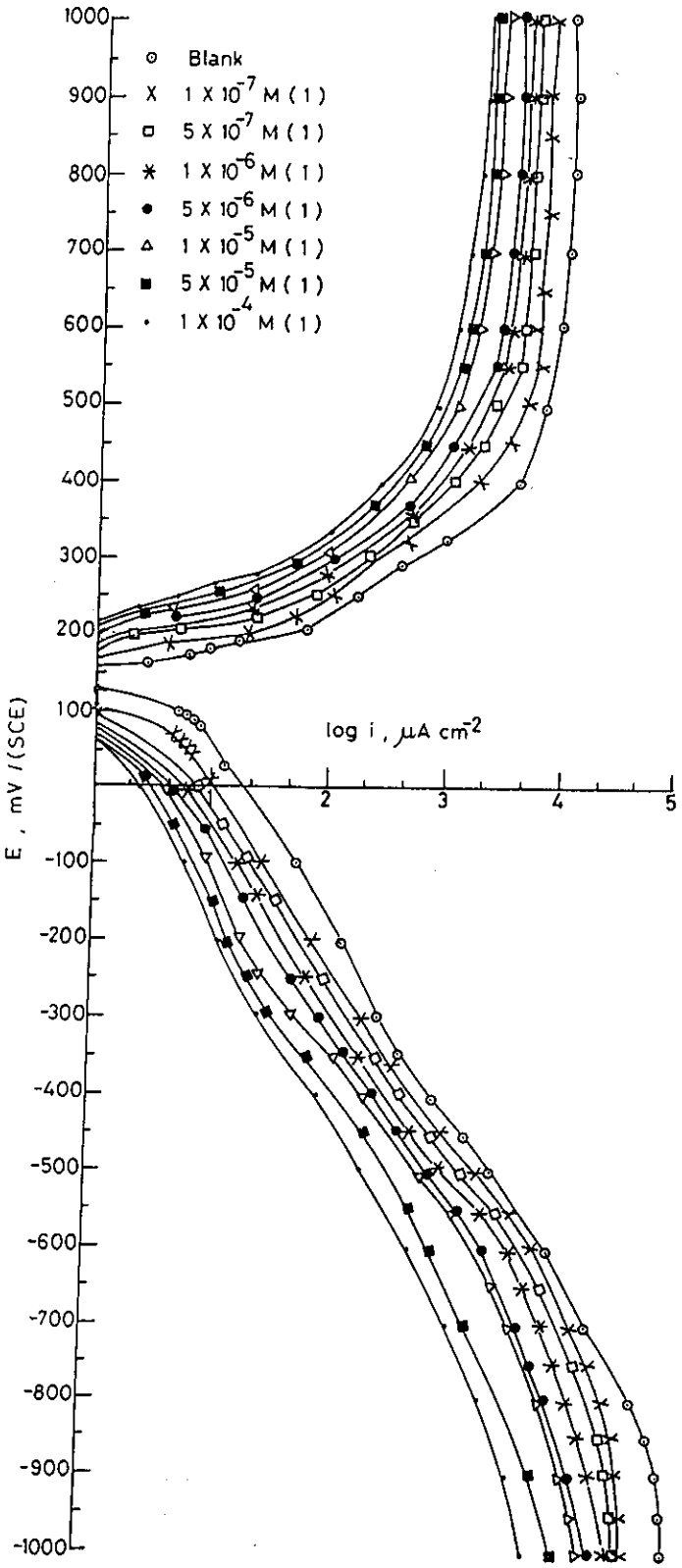


Fig. (3.82): potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (1).

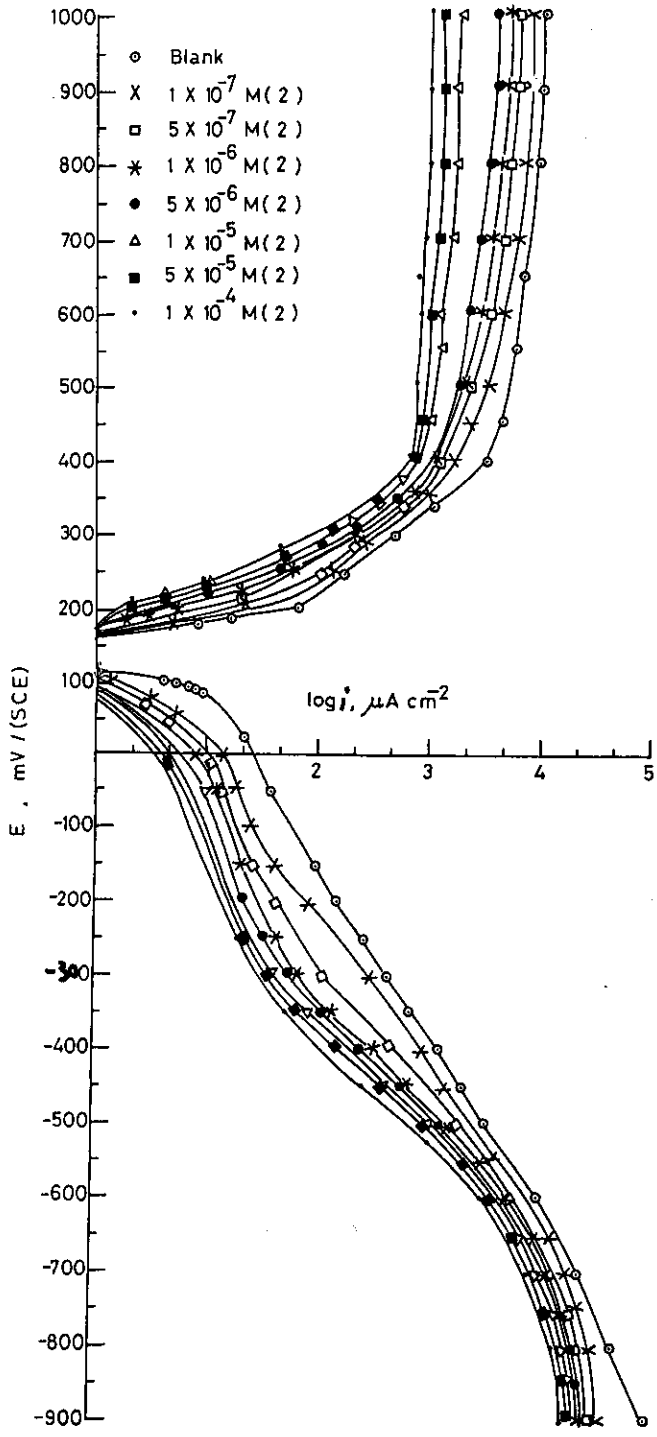


Fig. (3.83): potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (2).

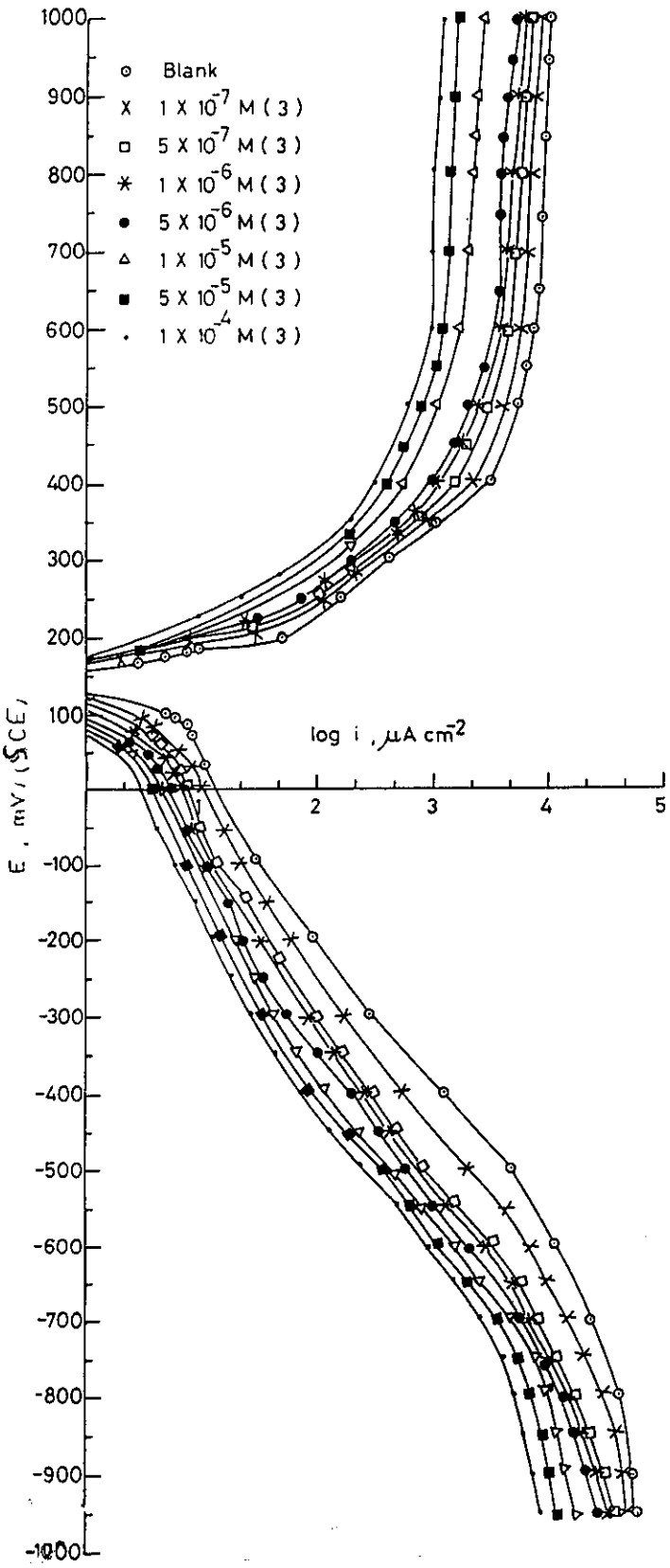


Fig. (3.84): potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (3).

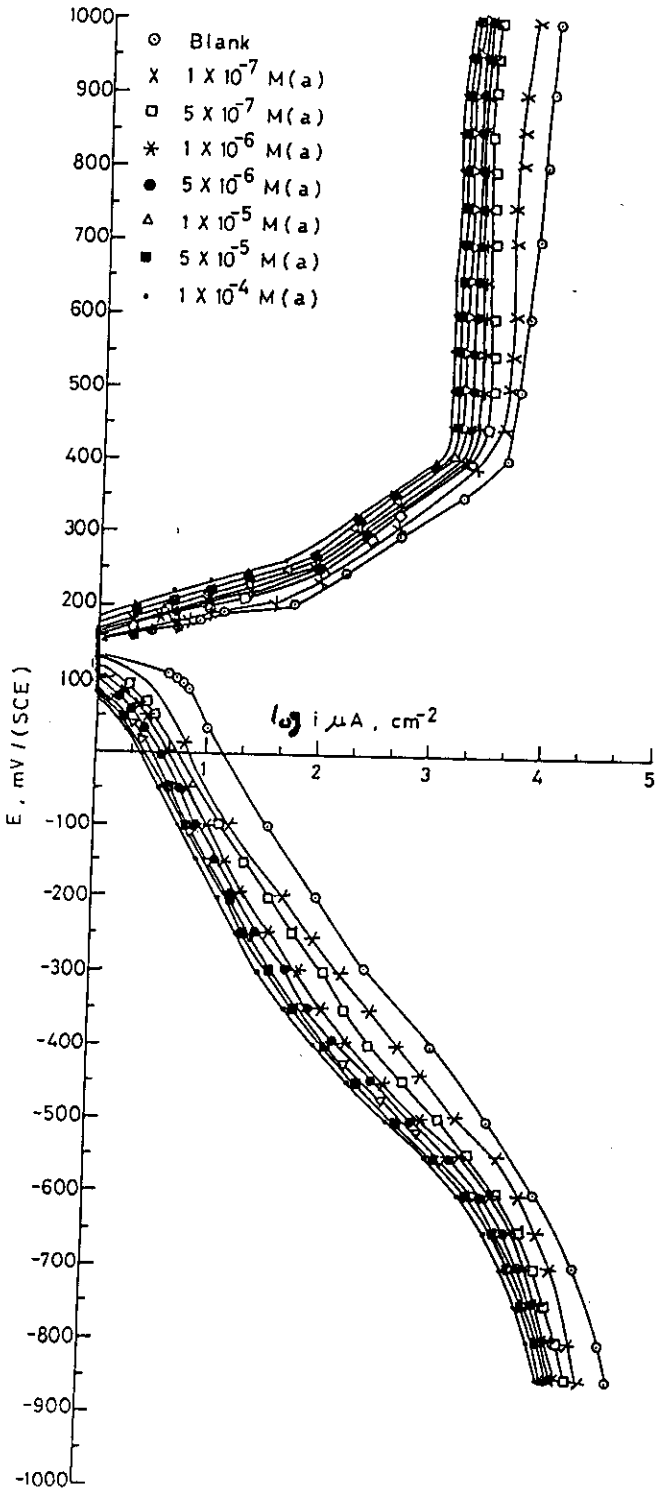


Fig. (3.85): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (a).

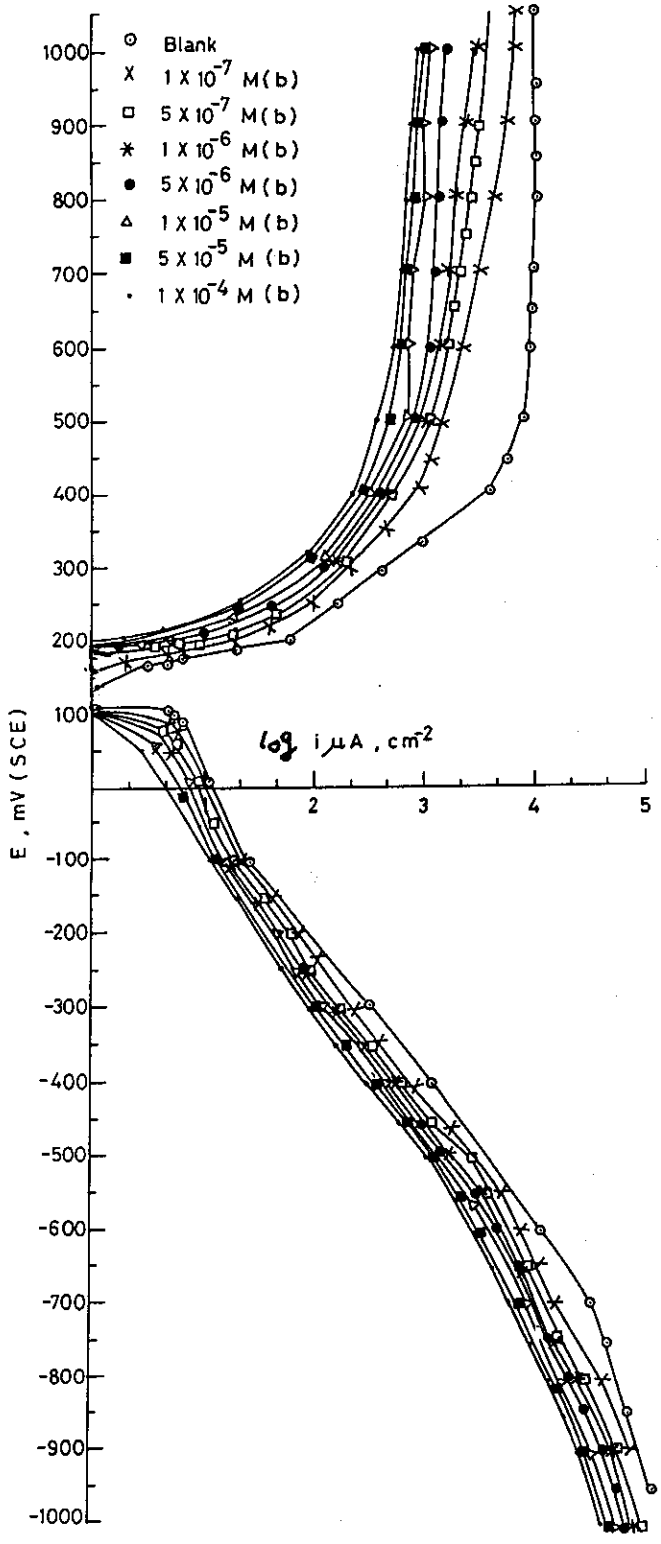


Fig.(3.86): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (b).

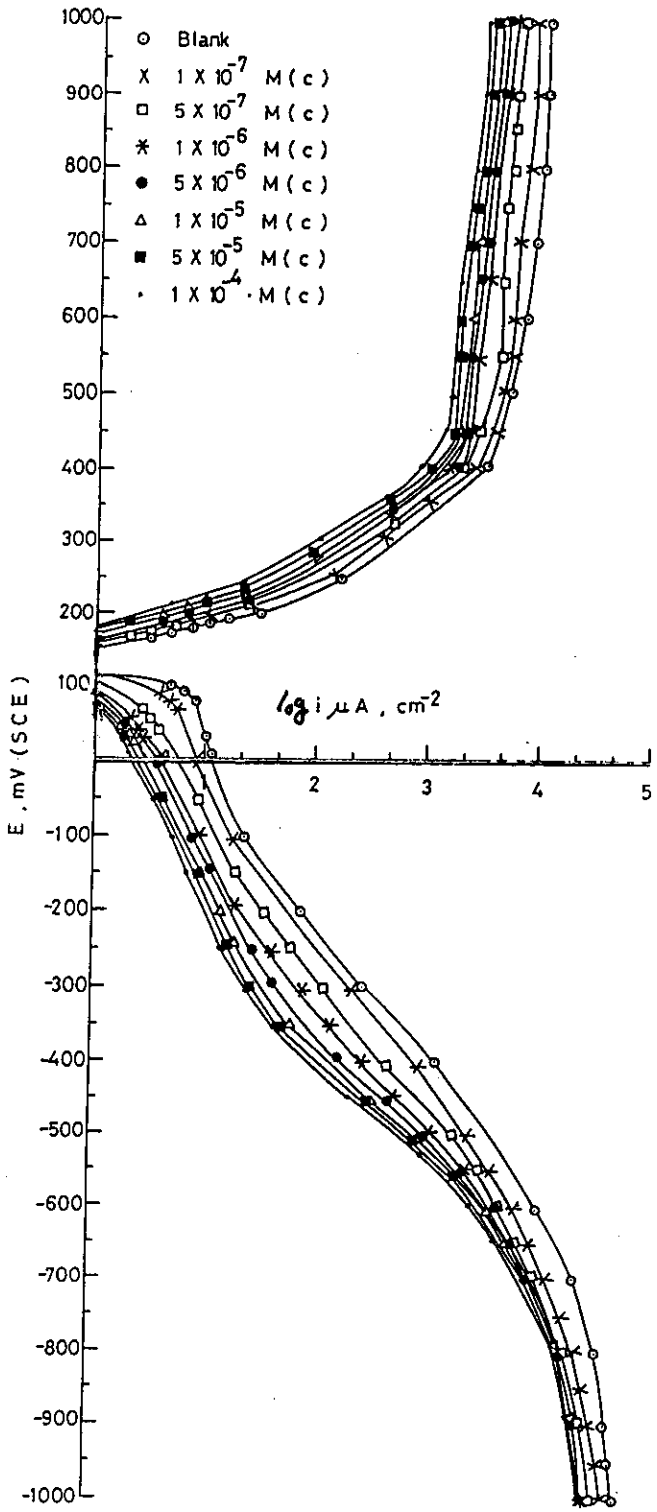


Fig.(3.87): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (c).

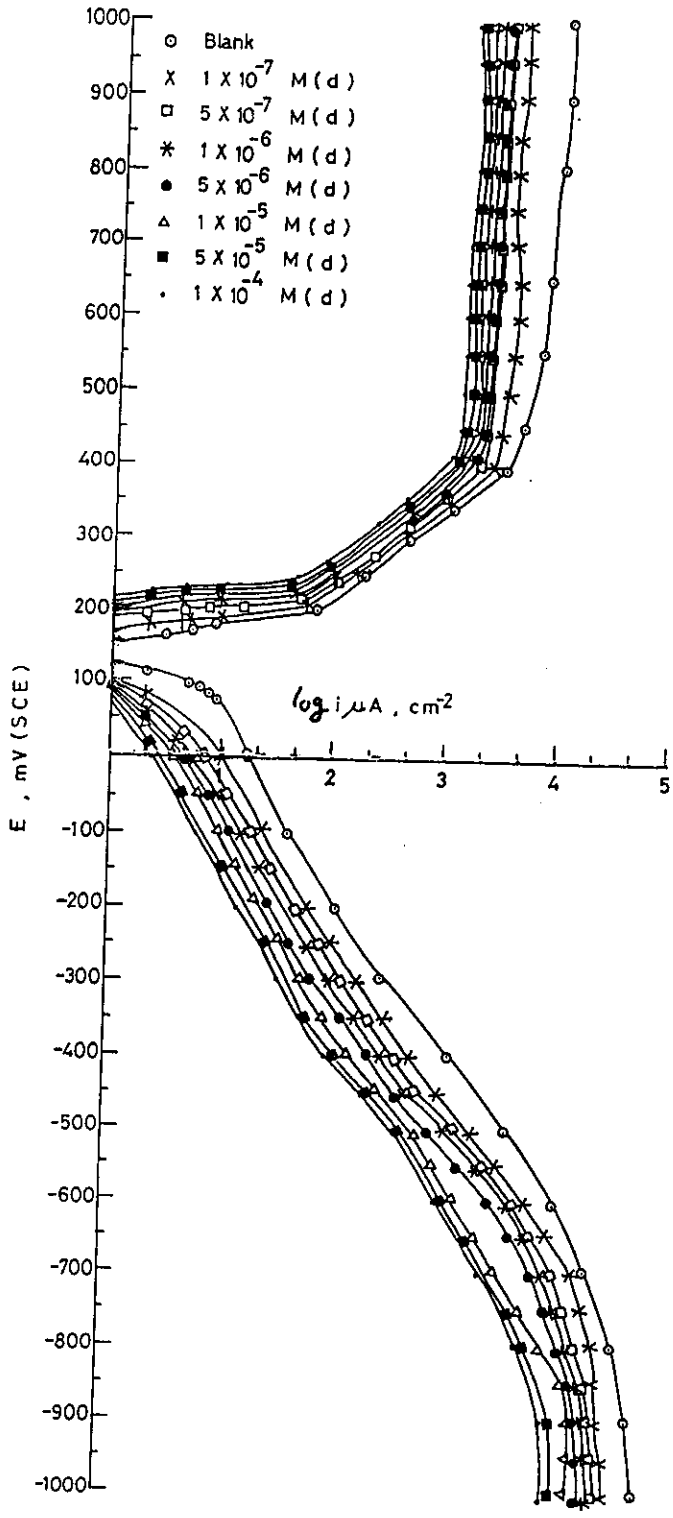


Fig. (3.88): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (d).

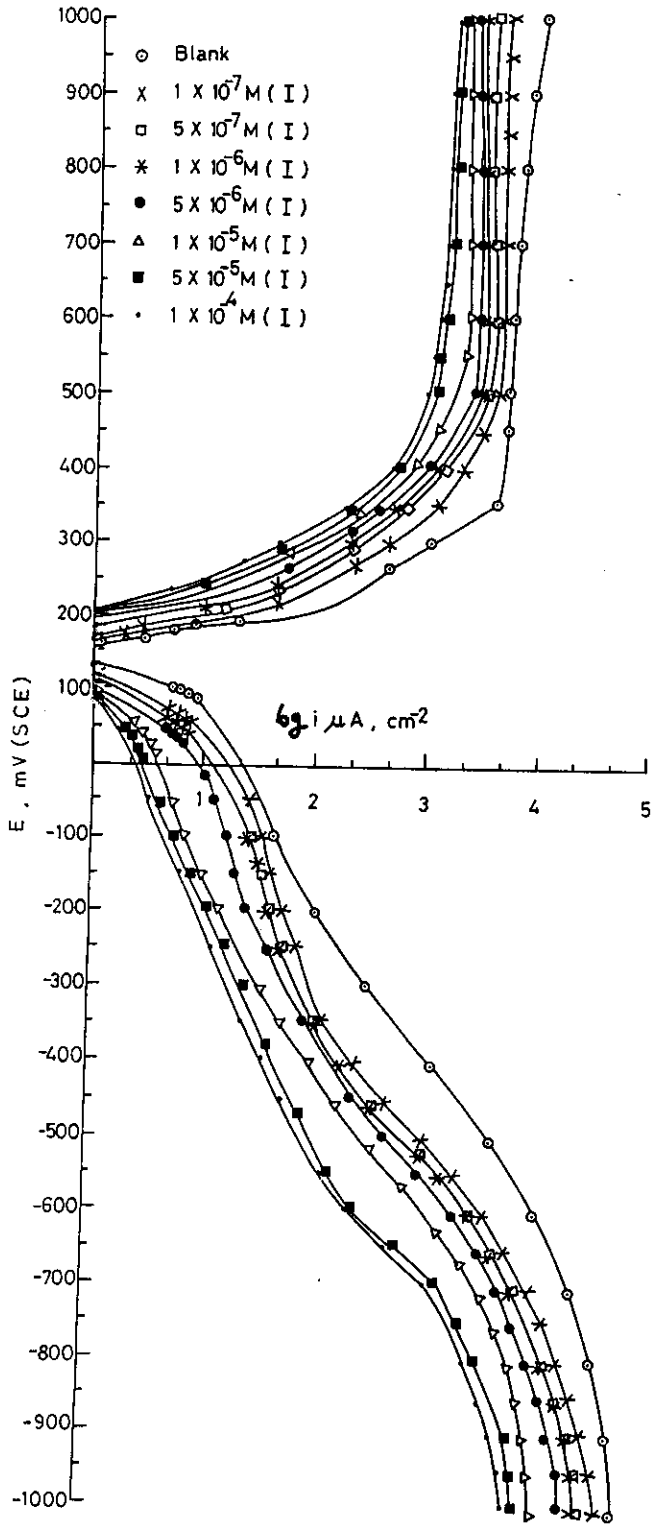


Fig. (3.89): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (I).

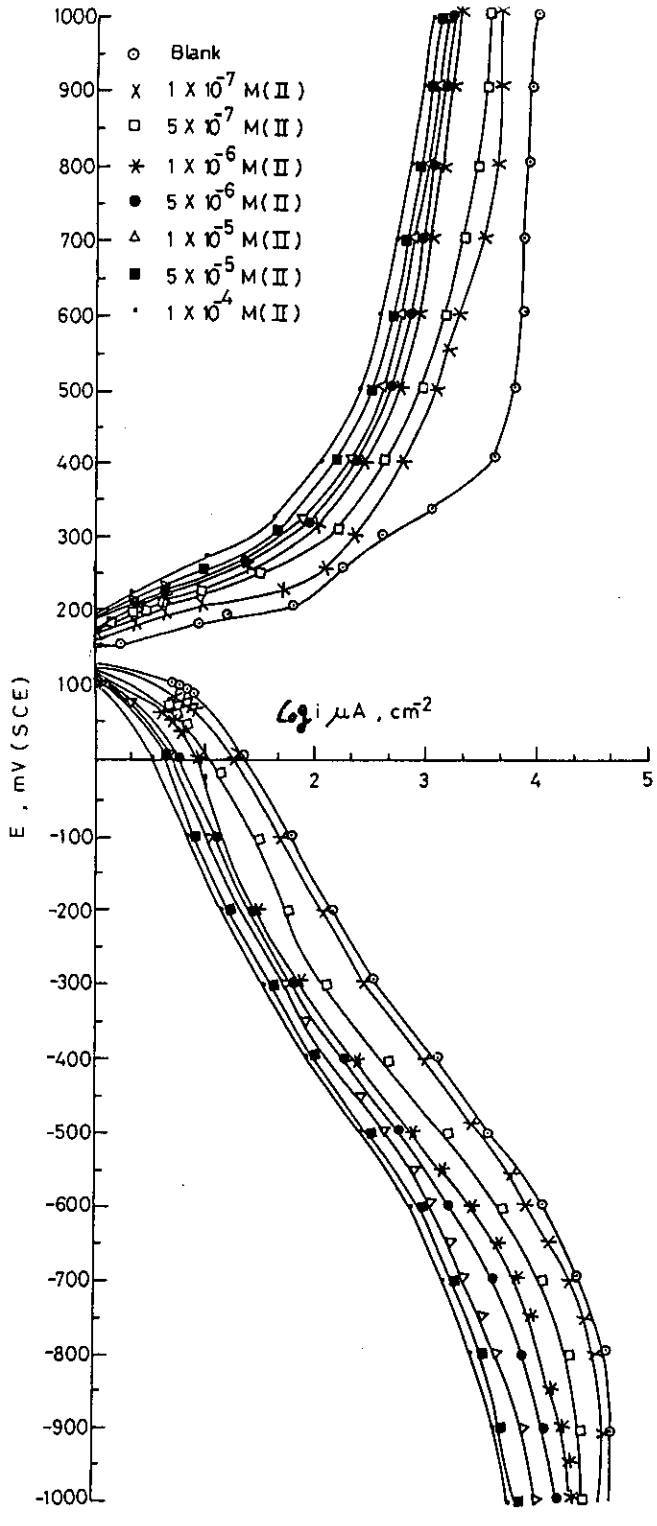


Fig. (3.90): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (II).

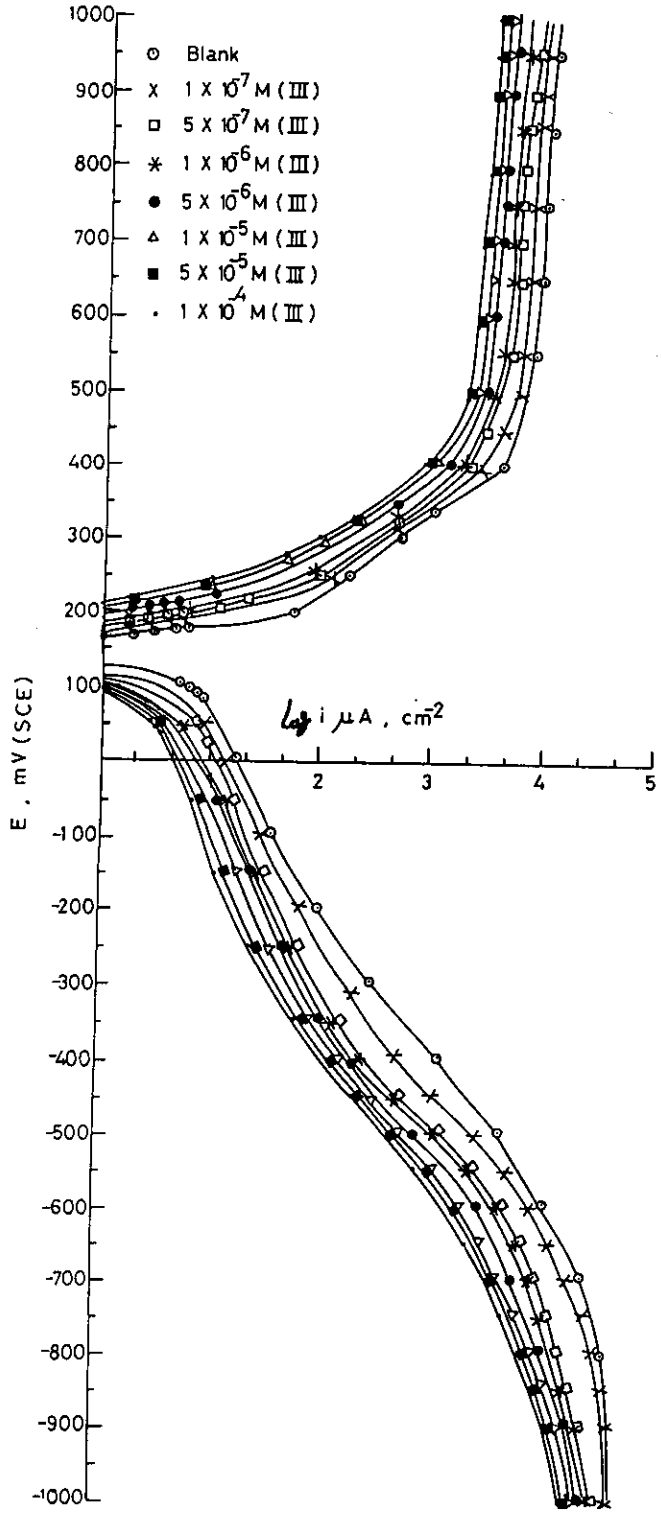


Fig. (3.91): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (III).

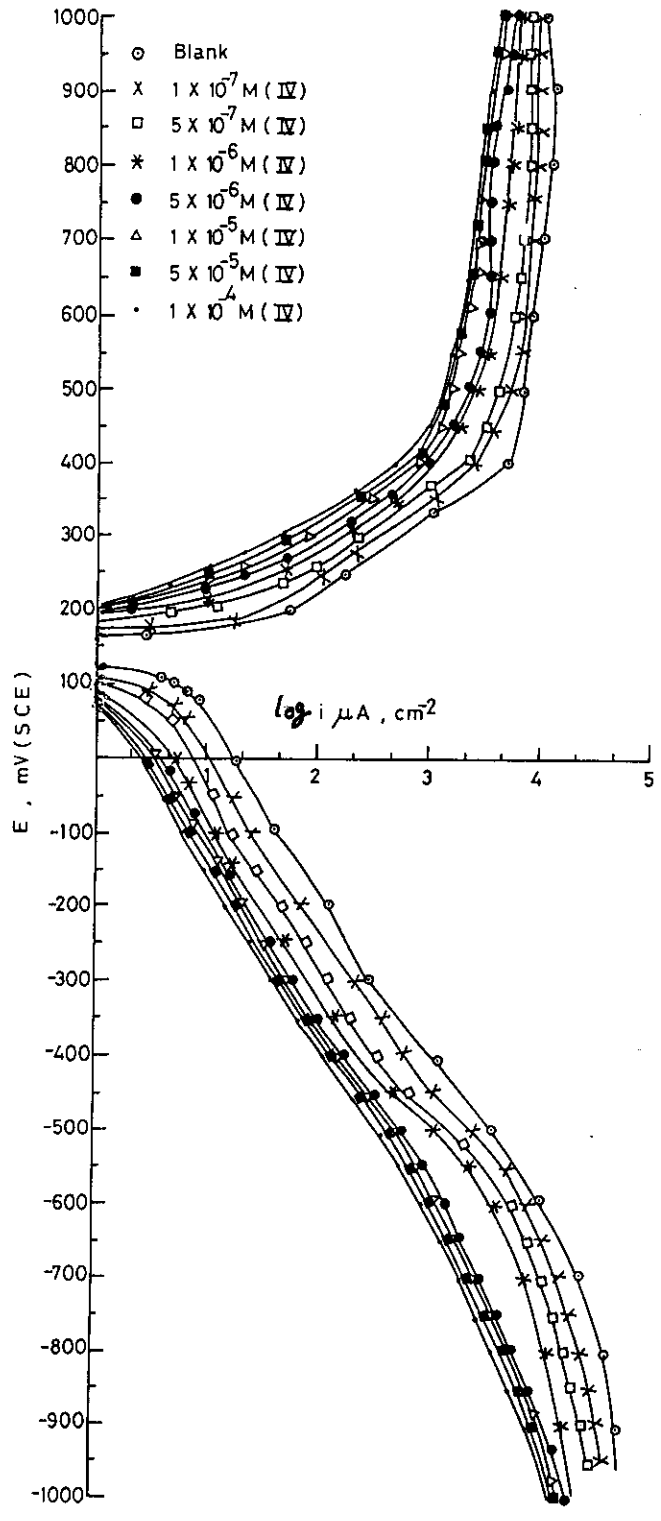


Fig. (3.92): Potentiostatic polarization curves of copper in 0.1 M HCl alone and containing different concentrations of compound (IV).

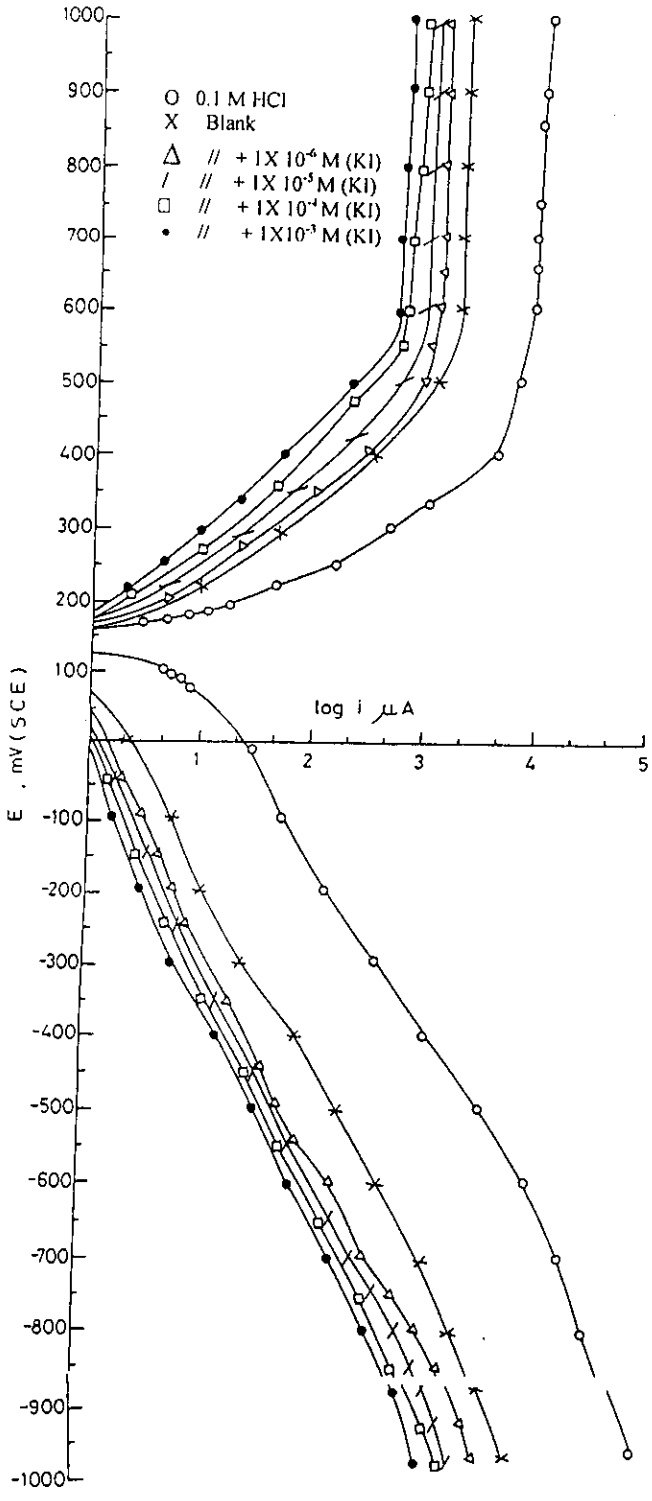


Fig. (3.93): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (1) (Blank) and containing different concentrations of KI.

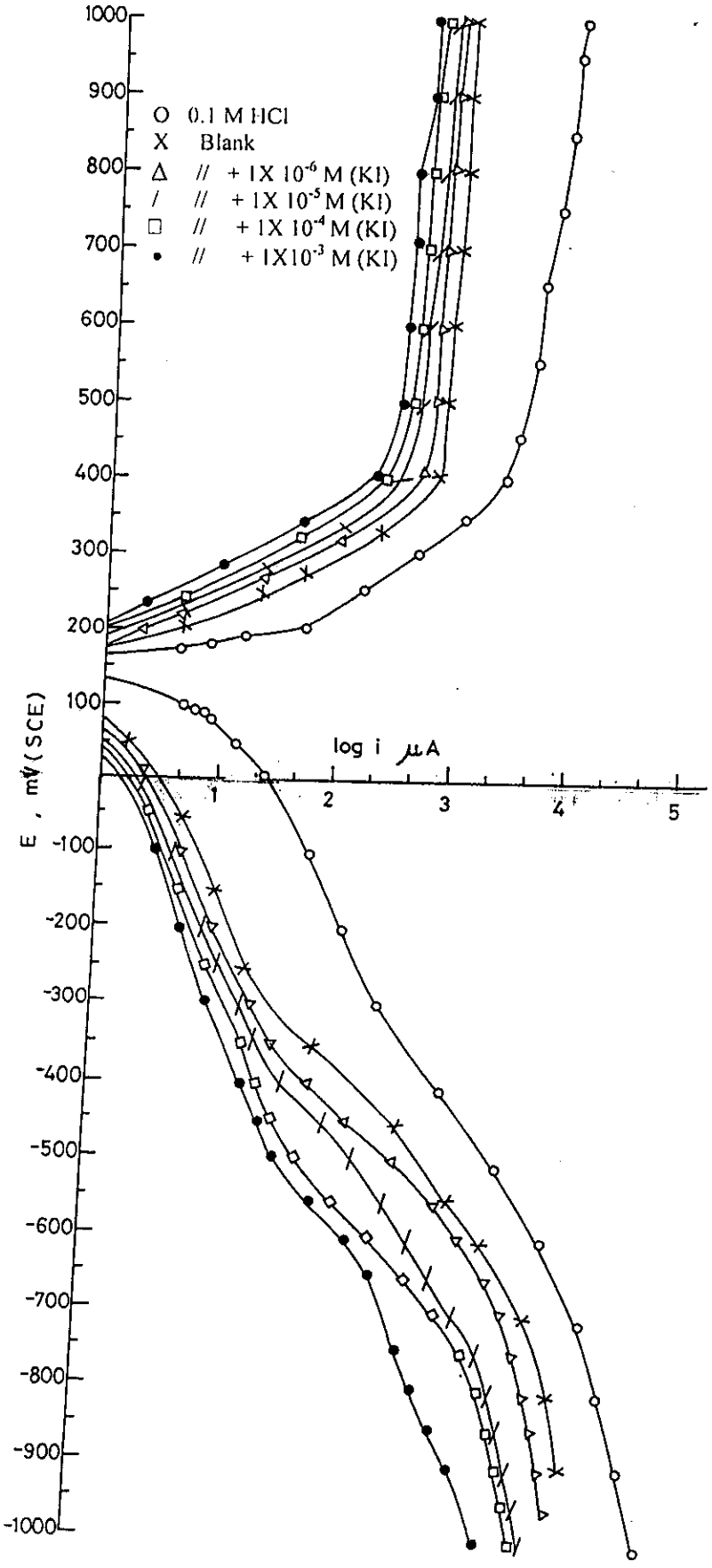


Fig. (3.94): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (2) (Blank) and containing different concentrations of KI.

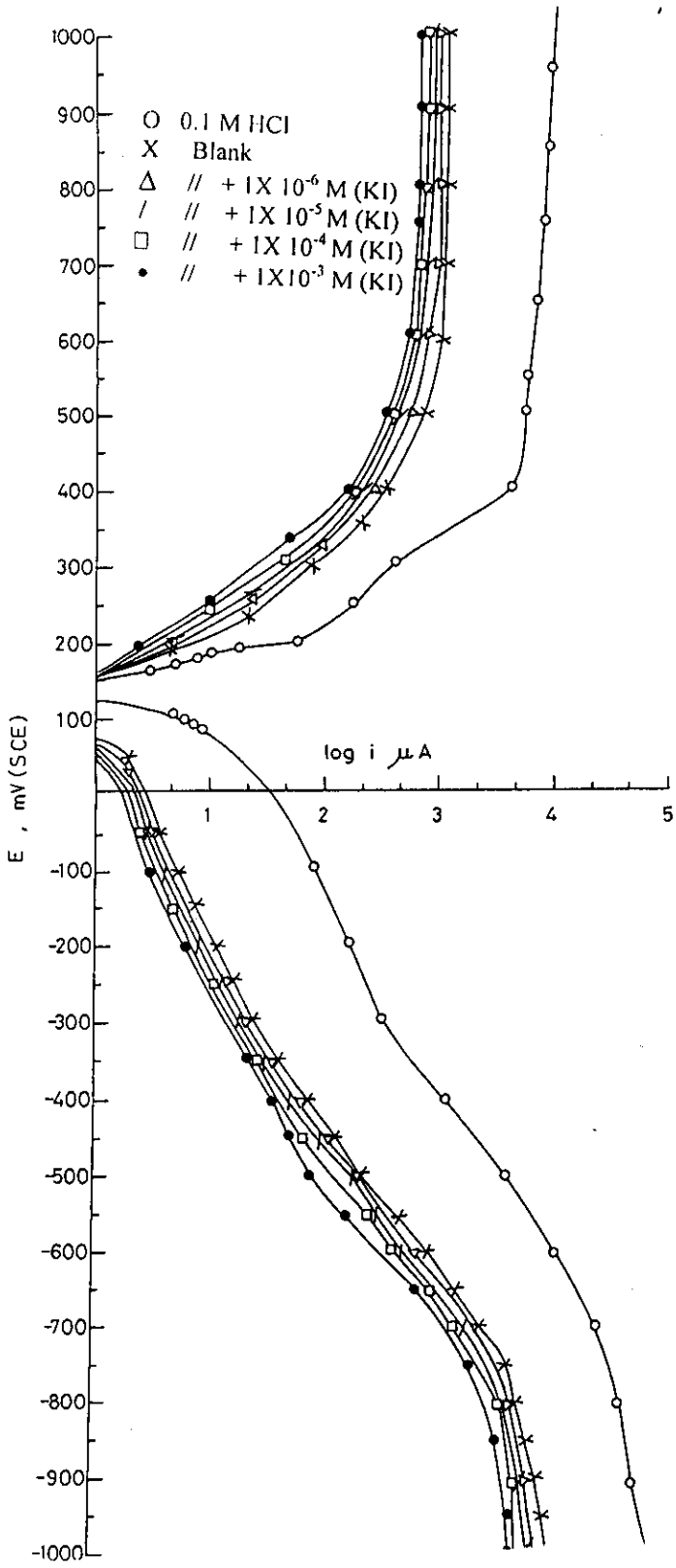


Fig. (3.95): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (3) (Blank) and containing different concentrations of KI.

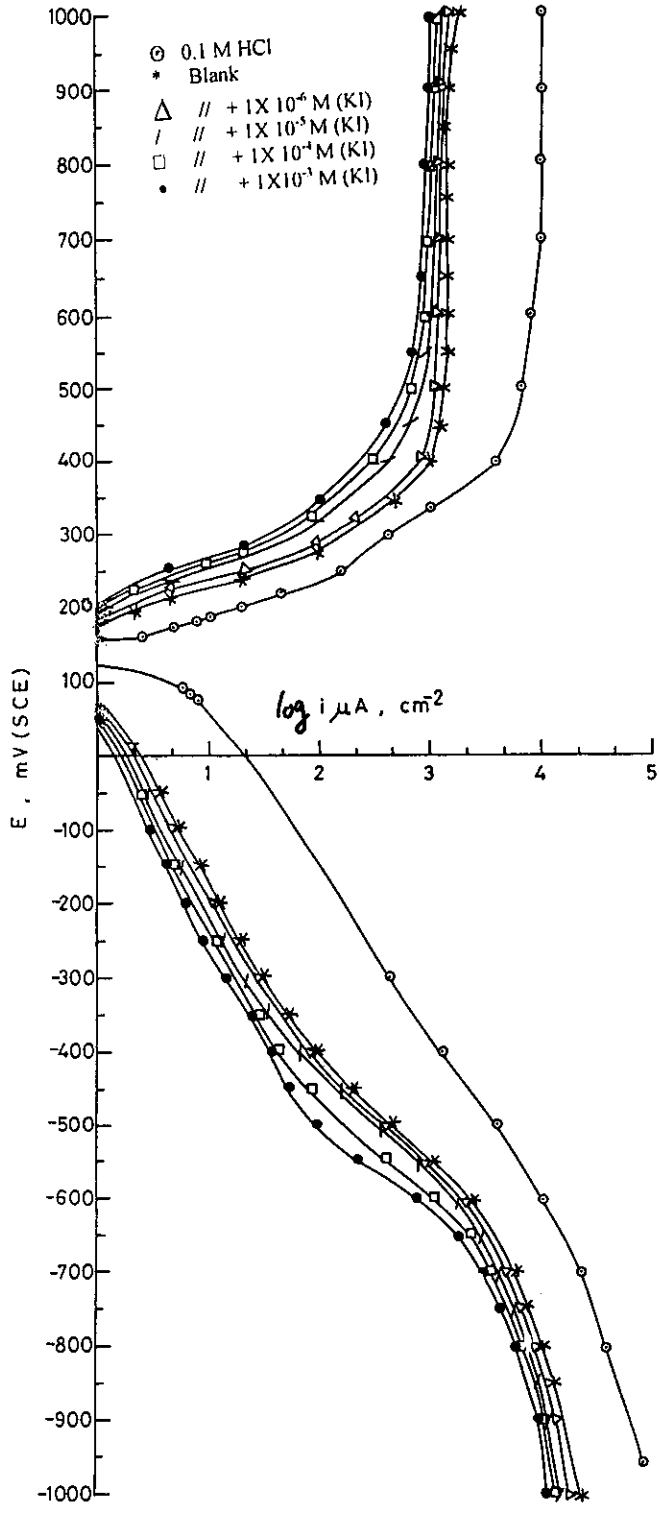


Fig. (3.96): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (a) (Blank) and containing different concentrations of KI.

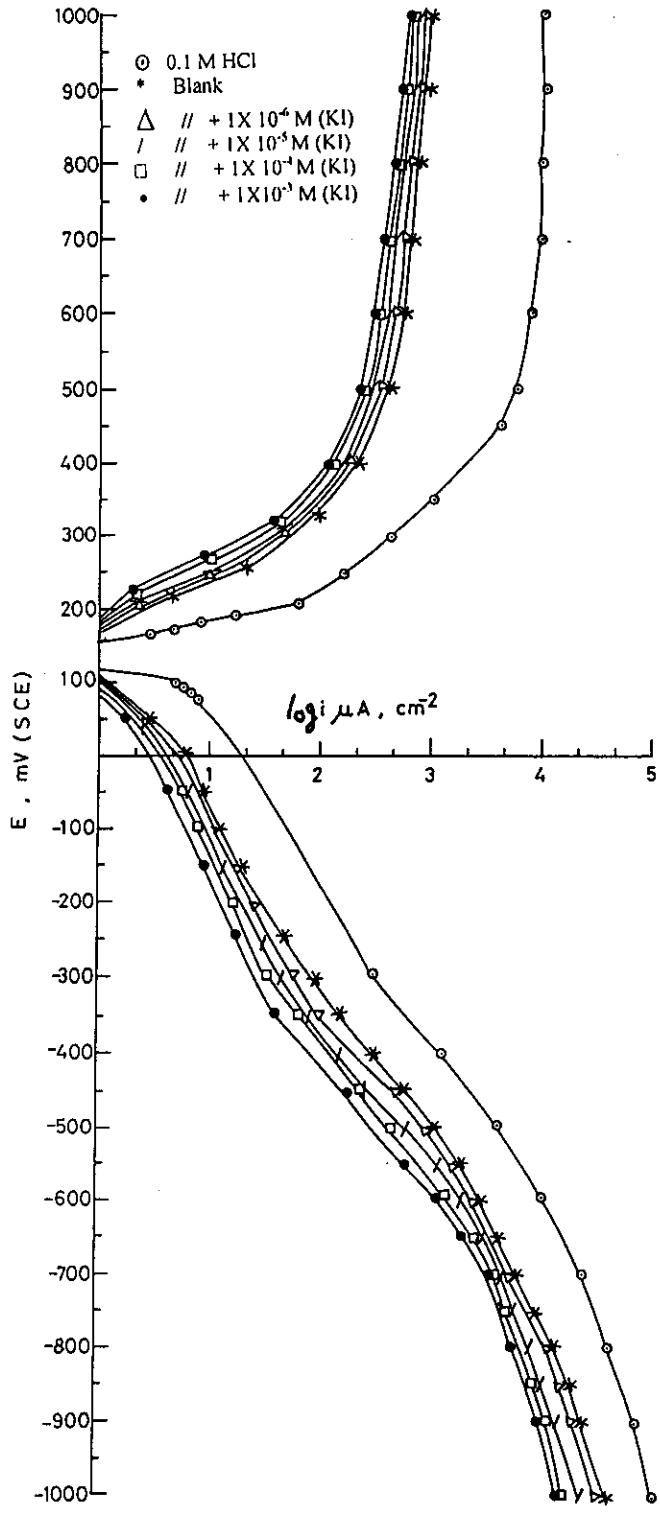


Fig. (3.97): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}$M compound (b) (Blank) and containing different concentrations of KI.

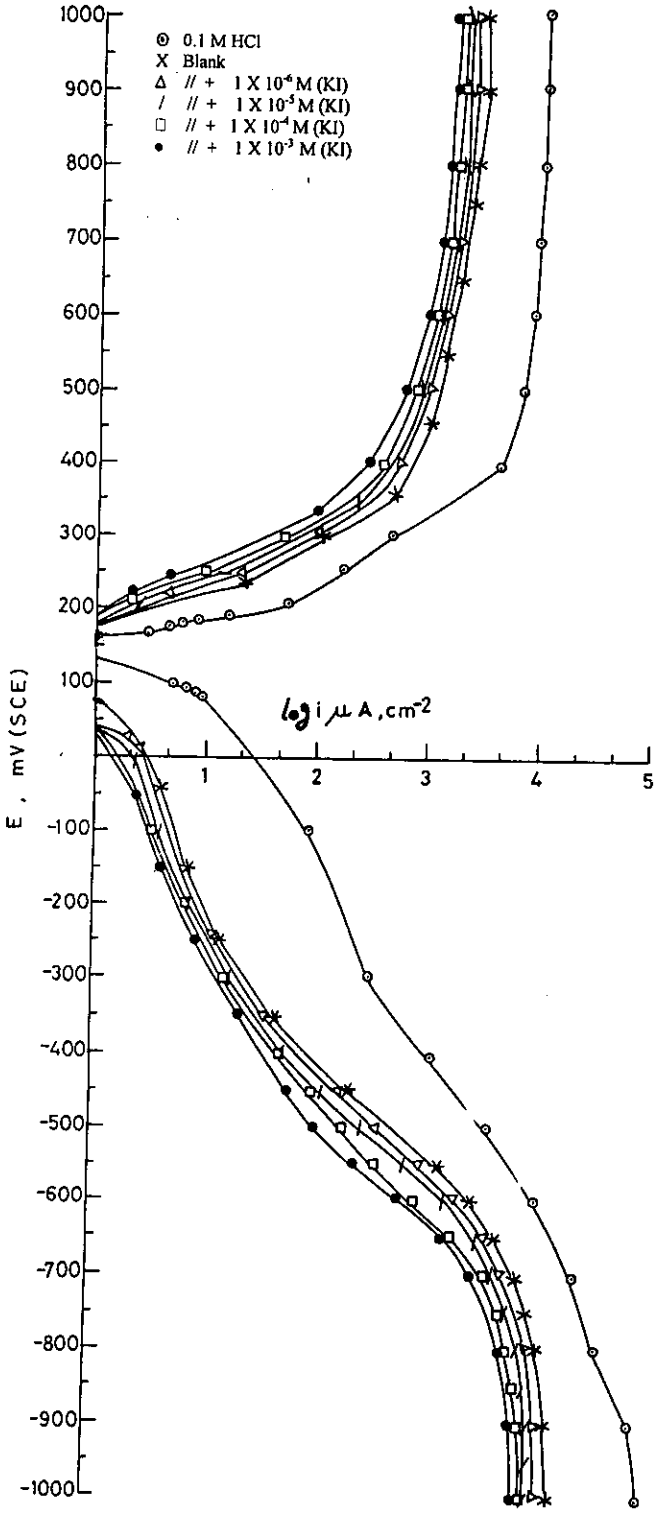


Fig.(3.98): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (c) (Blank) and containing different concentrations of KI.

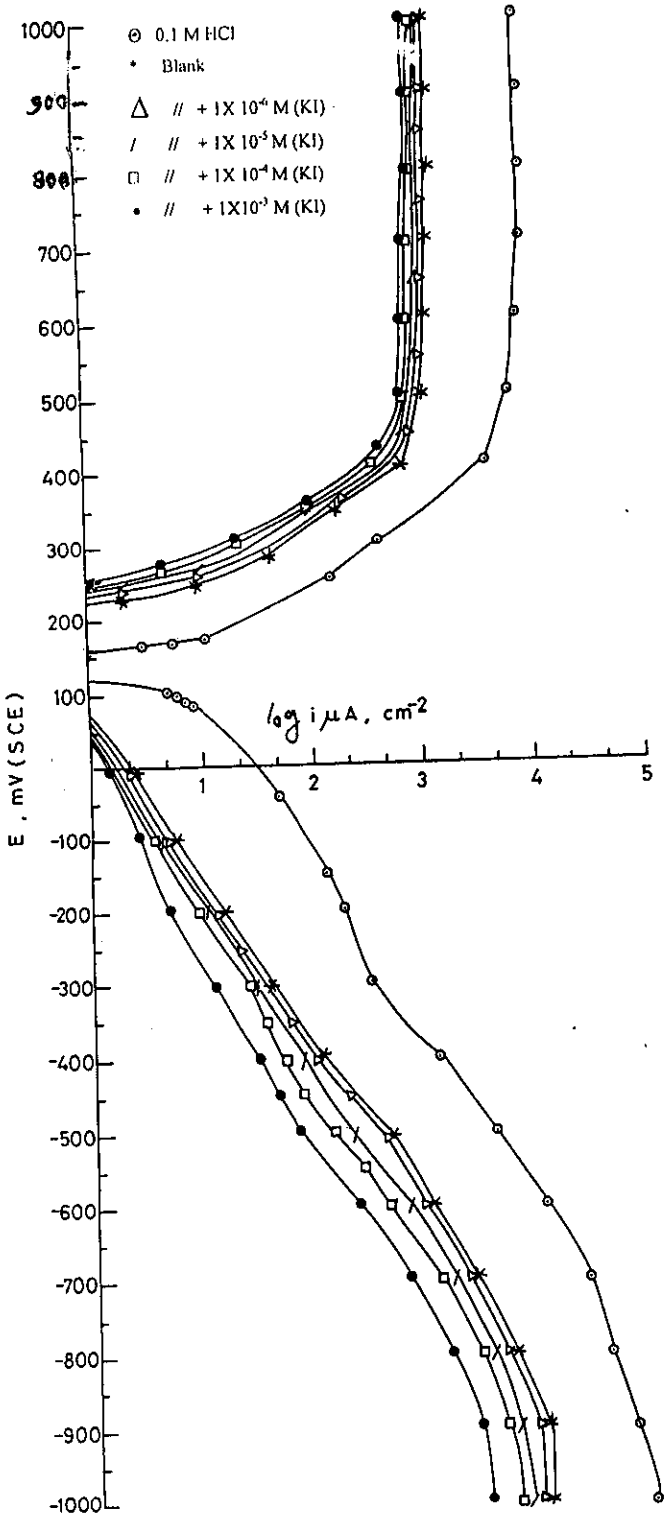


Fig. (3.99): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (d) (Blank) and containing different concentrations of KI.

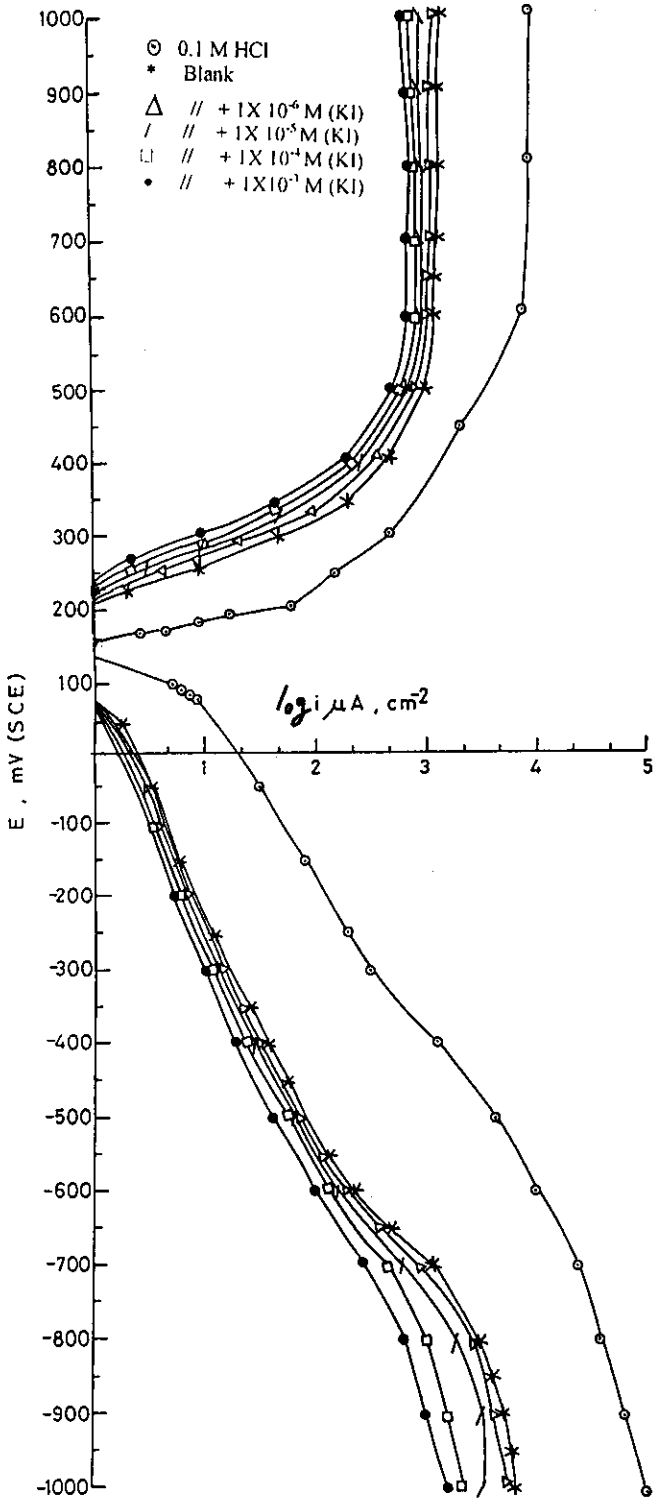


Fig.(3.100): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (I) (Blank) and containing different concentrations of KI.

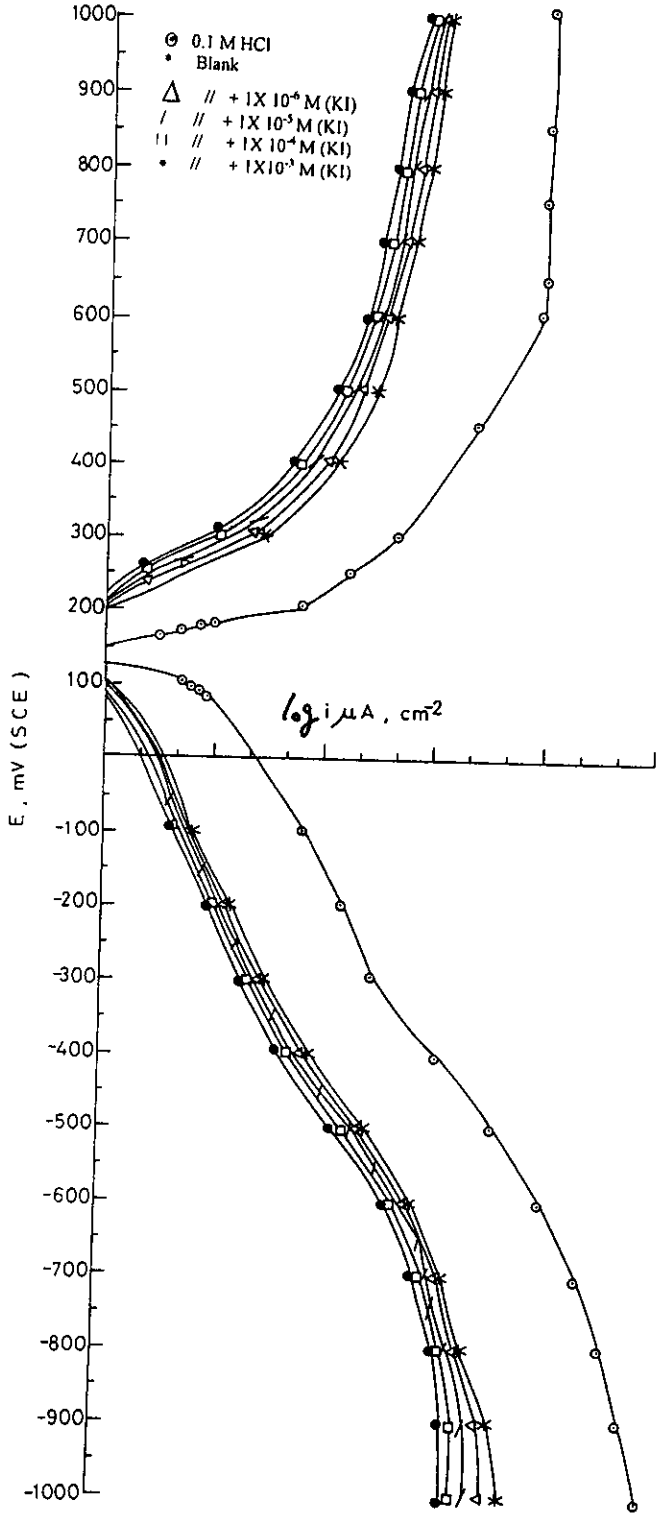


Fig.(3.101): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (II) (Blank) and containing different concentrations of KI.

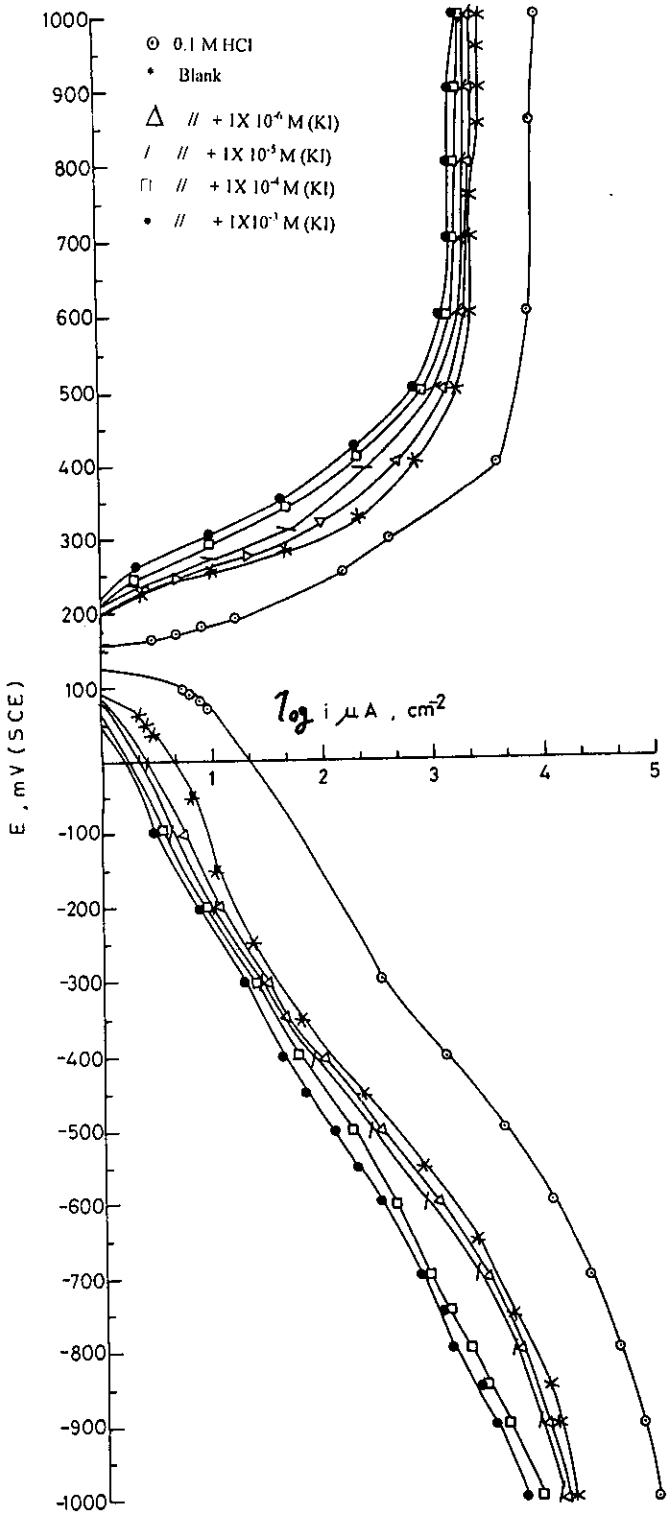


Fig.(3.102): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}$M compound (III) (Blank) and containing different concentrations of KI.

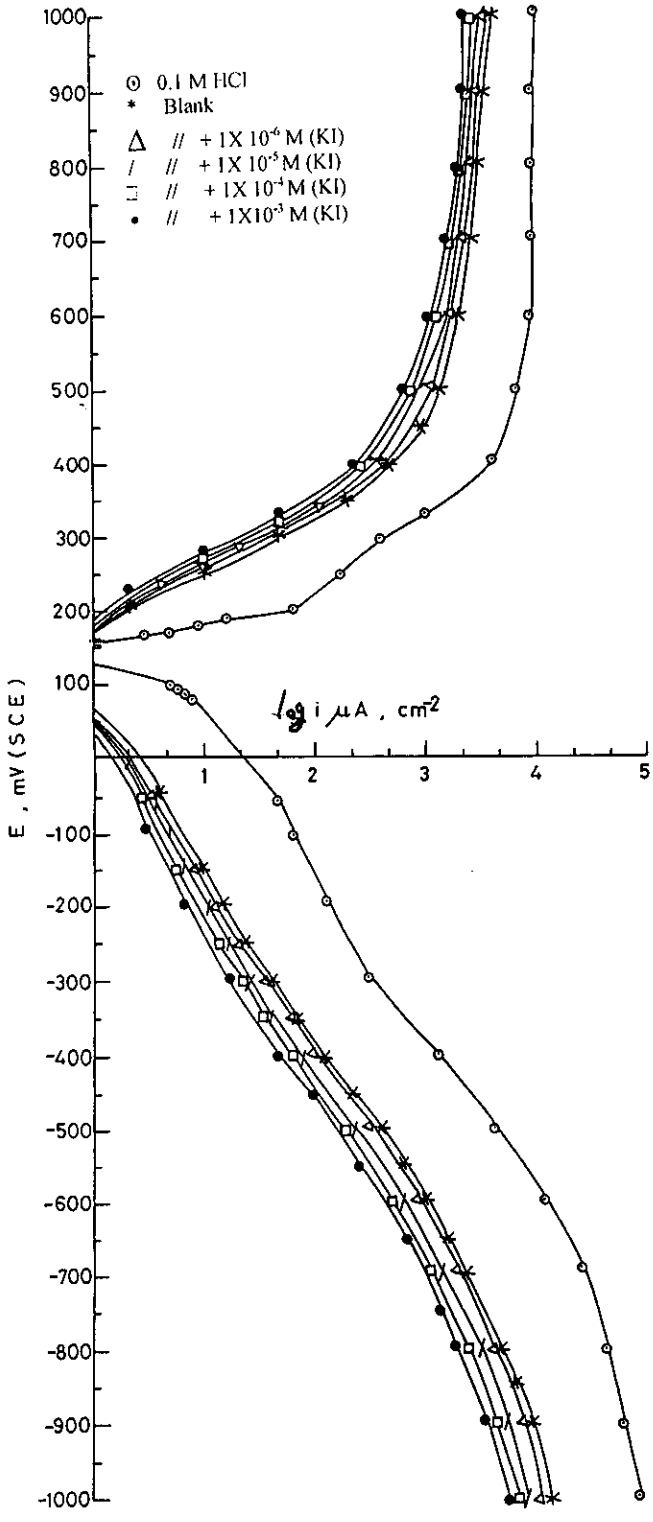


Fig.(3.103): Potentiostatic polarization curves of copper in 0.1 M HCl + $1X10^{-4}M$ compound (IV) (Blank) and containing different concentrations of KI.

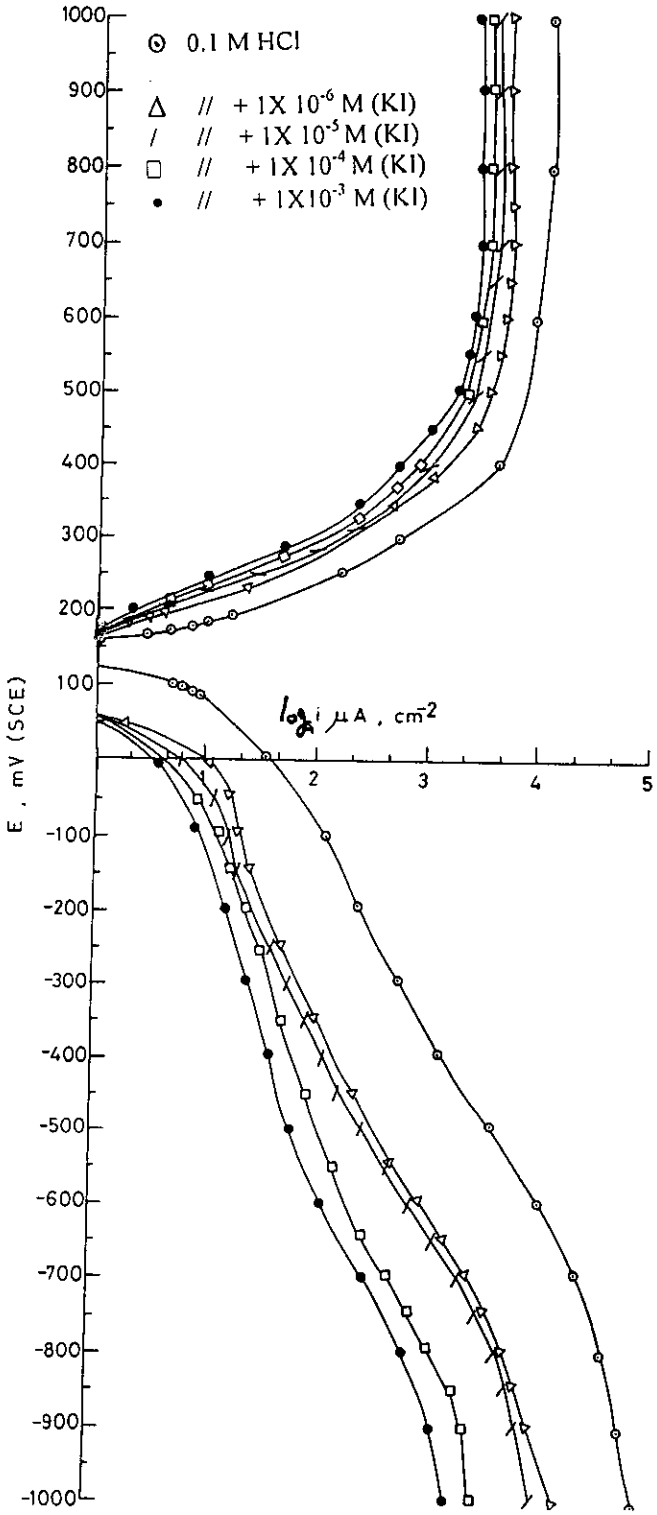


Fig. (3.104): Potentiostatic polarization of copper in 0.1 M HCl alone and containing different concentrations of KI.

3.2.2) Linear Polarization Method:

In this method an imposed potential, E, in the range of ± 25 mV from the steady state potential, $E_{corr.}$, is applied to the working electrode with a scan rate of 0.1 mV/Sec. The relation between E and i is a straight line, the slope of this line ($\Delta E/ \Delta i$) is the linear polarization resistance, Rp is a general term, which is considered as a measure of the kinetic facility at the electrode/ electrolyte interface or measure the resistance of a substance to oxidation. The corrosion rate is directly related to this term and can be calculated from its values by equation:

$$i_{corr.} = \frac{b_a \, b_c}{2.3(b_a + b_c)} \cdot \frac{1}{R_P} = \frac{B}{R_P} \qquad (3.4)$$

where, b_a = anodic Tafel slope.

b_c = cathodic Tafel Slope.

R_p = is the polarization resistance.

In most corroding systems the corrosion resistance is equal to the linear polarization resistance. The degree of surface coverage, (θ), and the inhibition efficiency, (%I) of an inhibitor are obtained from the respective linear polarization resistance, R_p, according to the following equations.

$$\theta = 1 - \frac{(R_P)_{Free}}{(R_P)_{add.}} \qquad (3.5)$$

$$\%I = \left[1 - \frac{(R_P)_{Free}}{(R_P)_{add.}}\right] \times 100 \qquad (3.6)$$

where, $(R_P)_{Free}$ = The linear polarization resistance in absence of additive

$(R_P)_{add.}$ = The linear polarization resistance in presence of additive

The results obtained in the absence and presence of inhibitors are illustrated in Figs. (3.105 – 3.115). Tables (3.22a – 3.32a) show values of polarization resistance and percentage inhibition efficiency obtained from this techniques. Table (3.22b – 3.32b) and Figs. (3.116 – 3.127) show the

linear polarization plots for the corrosion of copper in 0.1M HCl acid solution at different concentrations of KI ($1X10^{-6} - 1X10^{-4}M$) and constant concentration of the additives ($1X10^{-4}M$).

From the linear polarization measurements, the effectiveness of the additives as corrosion inhibitors without and with iodide ions vary according the following order:

First series: 2 > 3 > 1 (Tables 3.34a , 3.34b)

Second series: a > b> c> d (Tables 3.35a , 3.35b)

Third series: I > II > III > IV (Tables 3.36a , 3.36b)

This order agrees well with those obtained from weight loss and potentiostatic techniques.

Table (3.22a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (1).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.300	———
$1 X 10^{-7}$	0.270	25.0
$5 X 10^{-7}$	0.240	33.0
$1 X 10^{-6}$	0.180	50.0
$5 X 10^{-6}$	0.170	53.0
$1 X 10^{-5}$	0.130	64.0
$5 X 10^{-5}$	0.130	64.0
$1 X 10^{-4}$	0.089	75.3

Table (3.22b): Data from linear polarization of copper in 0.1 M HCl + $1X10^{-4}$ M compound (1) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
$1 X 10^{-6}$	0.083	77.0
$1 X 10^{-5}$	0.080	78.0
$1 X 10^{-4}$	0.068	81.0
$1 X 10^{-3}$	0.067	81.3

Table (3.23a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (2).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
$1 X 10^{-7}$	0.240	33.0
$5 X 10^{-7}$	0.180	50.0
$1 X 10^{-6}$	0.150	58.3
$5 X 10^{-6}$	0.120	67.0
$1 X 10^{-5}$	0.100	72.0
$5 X 10^{-5}$	0.083	77.0
$1 X 10^{-4}$	0.063	82.5

Table (3.23b): Data from linear polarization of copper in 0.1 M HCl + $1X10^{-4}M$ compound (2) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
$1 X 10^{-6}$	0.060	83.0
$1 X 10^{-5}$	0.059	84.0
$1 X 10^{-4}$	0.053	85.0
$1 X 10^{-3}$	0.050	86.0

Table (3.24a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (3).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
1×10^{-7}	0.280	22.0
5×10^{-7}	0.200	44.0
1×10^{-6}	0.160	55.6
5×10^{-6}	0.140	61.0
1×10^{-5}	0.130	64.0
5×10^{-5}	0.120	67.0
1×10^{-4}	0.083	76.9

Table (3.24b): Data from linear polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (3) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
1×10^{-6}	0.080	78.0
1×10^{-5}	0.077	79.0
1×10^{-4}	0.067	81.0
1×10^{-3}	0.062	83.0

Table (3.25a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (a).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-7}	0.200	44.0
5×10^{-7}	0.180	50.0
1×10^{-6}	0.150	58.0
5×10^{-6}	0.140	61.0
1×10^{-5}	0.130	64.0
5×10^{-5}	0.100	72.0
1×10^{-4}	0.080	78.0

Table (3.25b): Data from linear polarization of copper in 0.1 M HCl + $1X10^{-4}M$ compound (a) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-6}	0.080	78.0
1×10^{-5}	0.075	80.0
1×10^{-4}	0.070	80.5
1×10^{-3}	0.067	81.4

Table (3.26a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (b).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-7}	0.200	33.0
5×10^{-7}	0.180	50.0
1×10^{-6}	0.180	50.0
5×10^{-6}	0.160	56.0
1×10^{-5}	0.150	58.0
5×10^{-5}	0.130	64.0
1×10^{-4}	0.120	67.0

Table (3.26b): Data from linear polarization of copper in 0.1 M HCl + $1X10^{-4}M$ compound (b) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-6}	0.100	72.0
1×10^{-5}	0.089	75.0
1×10^{-4}	0.075	79.0
1×10^{-3}	0.068	81.0

Table (3.27a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (c).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-7}	0.260	28.0
5×10^{-7}	0.25	31.0
1×10^{-6}	0.200	44.0
5×10^{-6}	0.200	44.0
1×10^{-5}	0.160	56.0
5×10^{-5}	0.140	61.0
1×10^{-4}	0.120	67.0

Table (3.27b): Data from linear polarization of copper in 0.1 M HCl + $1X10^{-4}M$ compound (c) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-6}	0.110	69.0
1×10^{-5}	0.100	72.0
1×10^{-4}	0.075	79.0
1×10^{-3}	0.067	81.0

Table (3.28a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (d).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
$1 X 10^{-7}$	0.300	17.0
$5 X 10^{-7}$	0.280	22.0
$1 X 10^{-6}$	0.250	31.0
$5 X 10^{-6}$	0.240	33.0
$1 X 10^{-5}$	0.240	33.0
$5 X 10^{-5}$	0.200	44.0
$1 X 10^{-4}$	0.200	44.0

Table (3.28b): Data from linear polarization of copper in 0.1 M HCl + 1 $X10^{-4}M$ compound (d) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
$1 X 10^{-6}$	0.160	55.0
$1 X 10^{-5}$	0.150	58.0
$1 X 10^{-4}$	0.140	61.0
$1 X 10^{-3}$	0.08	78.0

Table (3.30a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (II).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-7}	0.220	39.0
5×10^{-7}	0.200	44.0
1×10^{-6}	0.200	44.0
5×10^{-6}	0.170	53.0
1×10^{-5}	0.150	58.0
5×10^{-5}	0.140	61.0
1×10^{-4}	0.120	67.0

Table (3.30b): Data from linear polarization of copper in 0.1 M HCl + $1X10^{-4}M$ compound (II) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	——
1×10^{-6}	0.100	72.0
1×10^{-5}	0.089	75.3
1×10^{-4}	0.080	78.0
1×10^{-3}	0.067	81.0

Table (3.31a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (III).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
1×10^{-7}	0.230	36.0
5×10^{-7}	0.225	38.0
1×10^{-6}	0.220	39.0
5×10^{-6}	0.200	44.0
1×10^{-5}	0.180	50.0
5×10^{-5}	0.160	56.0
1×10^{-4}	0.130	64.0

Table (3.31b): Data from linear polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (III) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
1×10^{-6}	0.120	67.0
1×10^{-5}	0.100	72.0
1×10^{-4}	0.086	76.0
1×10^{-3}	0.075	79.0

Table (3.32a): Data from linear polarization of copper in 0.1 M HCl containing various concentrations of compound (IV).

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
1×10^{-7}	0.280	22.0
5×10^{-7}	0.240	33.0
1×10^{-6}	0.240	33.0
5×10^{-6}	0.200	44.0
1×10^{-5}	0.200	44.0
5×10^{-5}	0.170	53.0
1×10^{-4}	0.140	57.0

Table (3.32b): Data from linear polarization of copper in 0.1 M HCl + 1 X 10^{-4} M compound (IV) containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
1×10^{-6}	0.130	64.0
1×10^{-5}	0.100	72.0
1×10^{-4}	0.089	75.0
1×10^{-3}	0.077	79.0

Table (3.33): Data from linear polarization of copper in 0.1M HCl containing various concentrations of KI.

Conc., M	$(1/R_P)\ \Omega^{-1}$	%I
0.0	0.360	———
$1X10^{-6}$	0.170	53.00
$1X10^{-5}$	0.160	56.00
$1X10^{-4}$	0.130	64.00
$1X10^{-3}$	0.125	65.00

Table (3.34 a): Data from linear polarization of copper in 0.1 M HCl for various concentrations of the first series compounds at 30°C.

Concentration of compounds, (M)	% Inhibition		
	Inhibitor (1)	Inhibitor (2)	Inhibitor (3)
$1 X 10^{-7}$	25.0	33.0	22.0
$5 X 10^{-7}$	33.5	50.0	44.0
$1 X 10^{-6}$	50.0	58.3	55.6
$5 X 10^{-6}$	53.0	67.0	61.0
$1 X 10^{-5}$	64.0	72.0	64.0
$5 X 10^{-5}$	64.0	77.0	67.0
$1 X 10^{-4}$	75.3	82.5	76.9

Table (3.34b): Data from linear polarization of copper in 0.1 M HCl + $1 X 10^{-4}$ M of the first series compounds for various KI concentrations at 30°C.

Concentration of KI (M)	% Inhibition		
	Inhibitor (1)	Inhibitor (2)	Inhibitor (3)
$1 X 10^{-6}$	77.0	83.0	78.0
$1 X 10^{-5}$	78.0	84.0	79.0
$1 X 10^{-4}$	81.0	85.0	81.0
$1 X 10^{-3}$	81.3	86.0	83.0

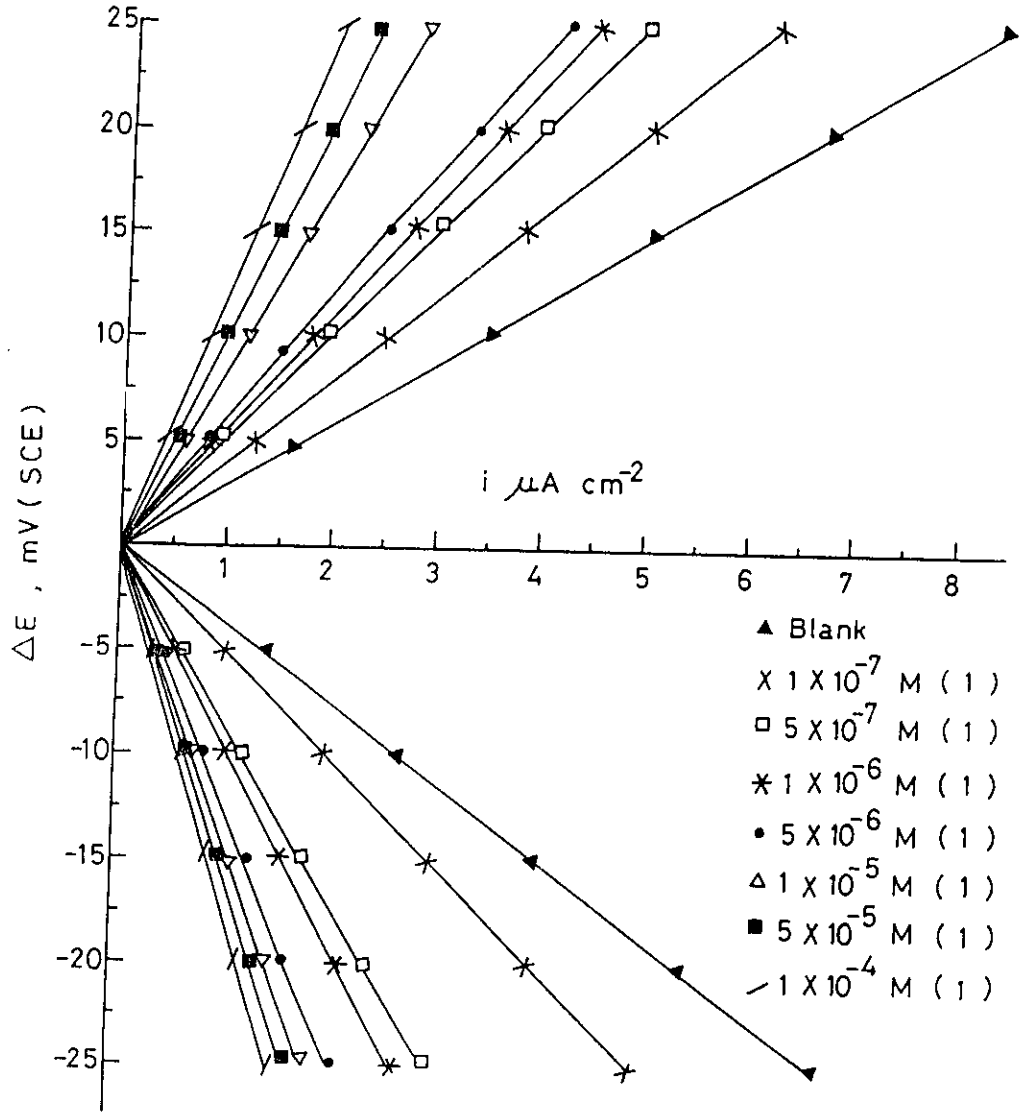


Fig. (3.105): linear polarization curves for copper in 0.1 M HCl in presence of compound (1).

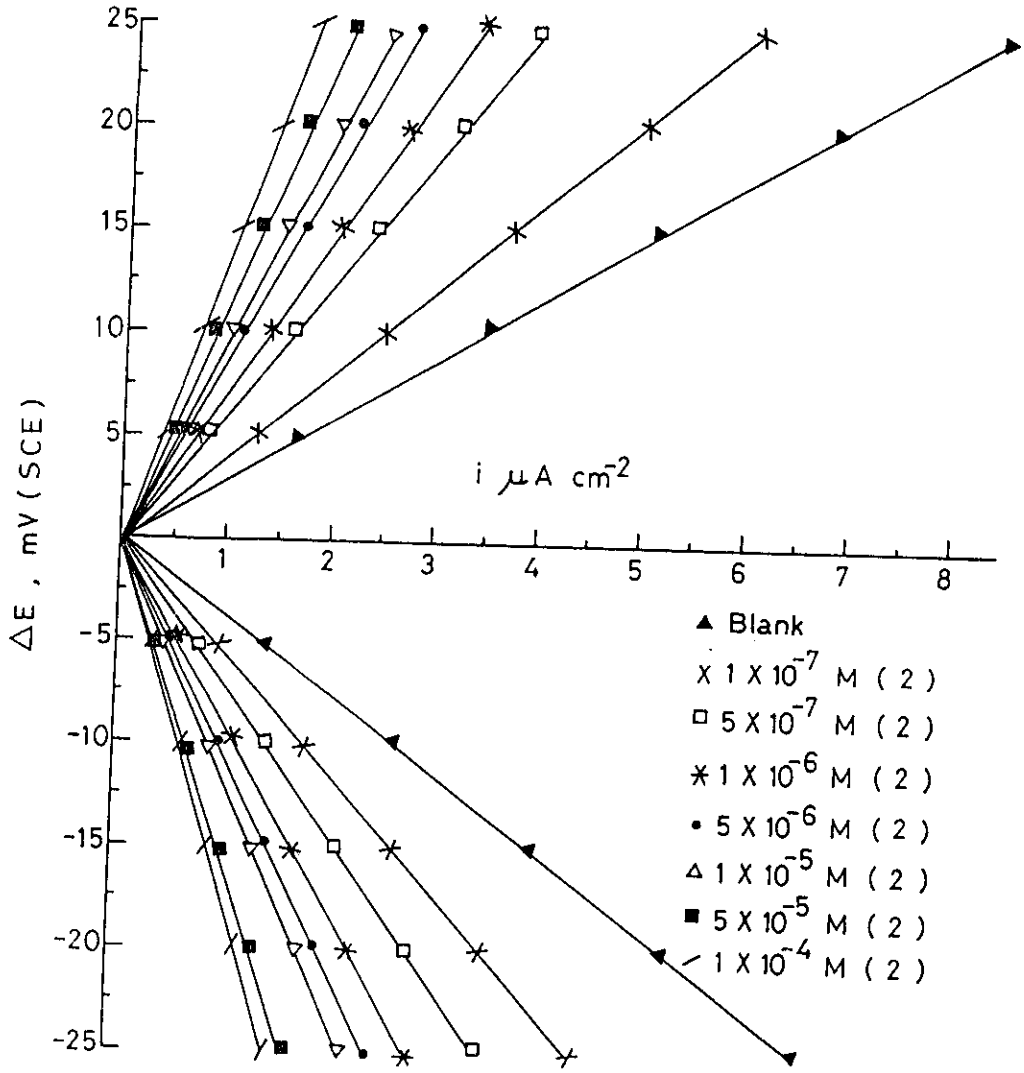


Fig.(3.106): linear polarization curves for copper in 0.1 M HCl in presence of compound (2).

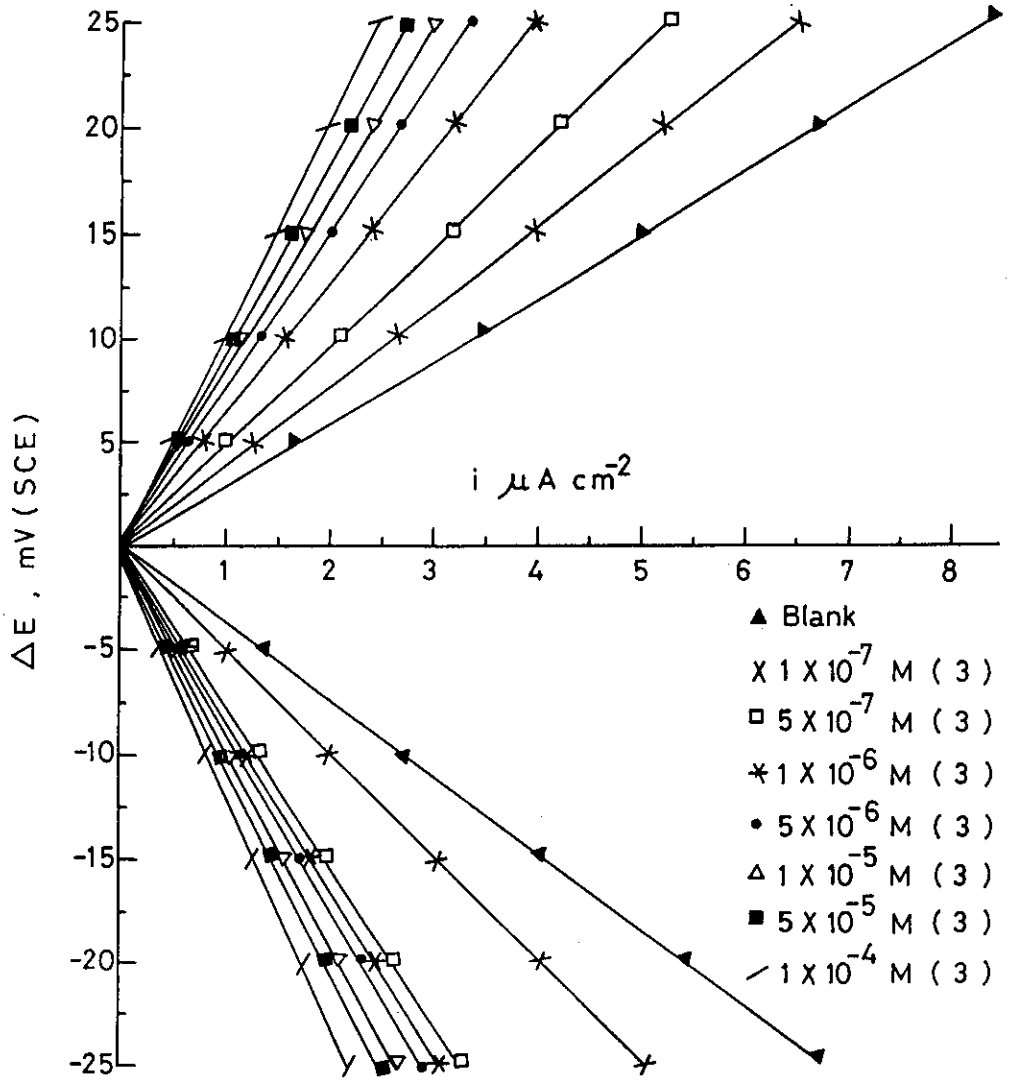


Fig.(3.107): linear polarization curves for copper in 0.1 M HCl in presence of compound (3).

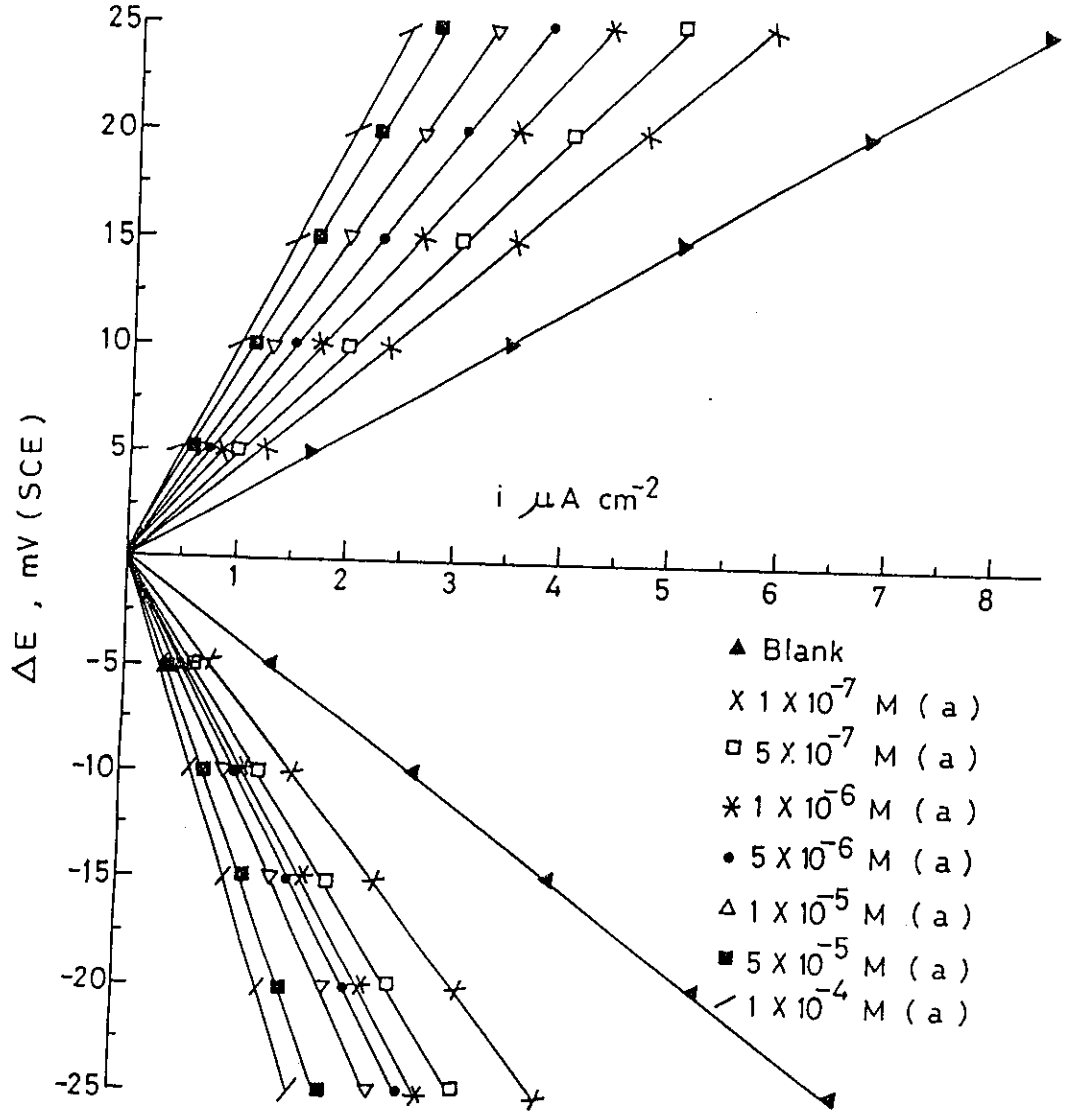


Fig. (3.108): linear polarization curves for copper in 0.1 M HCl in presence of compound (a).

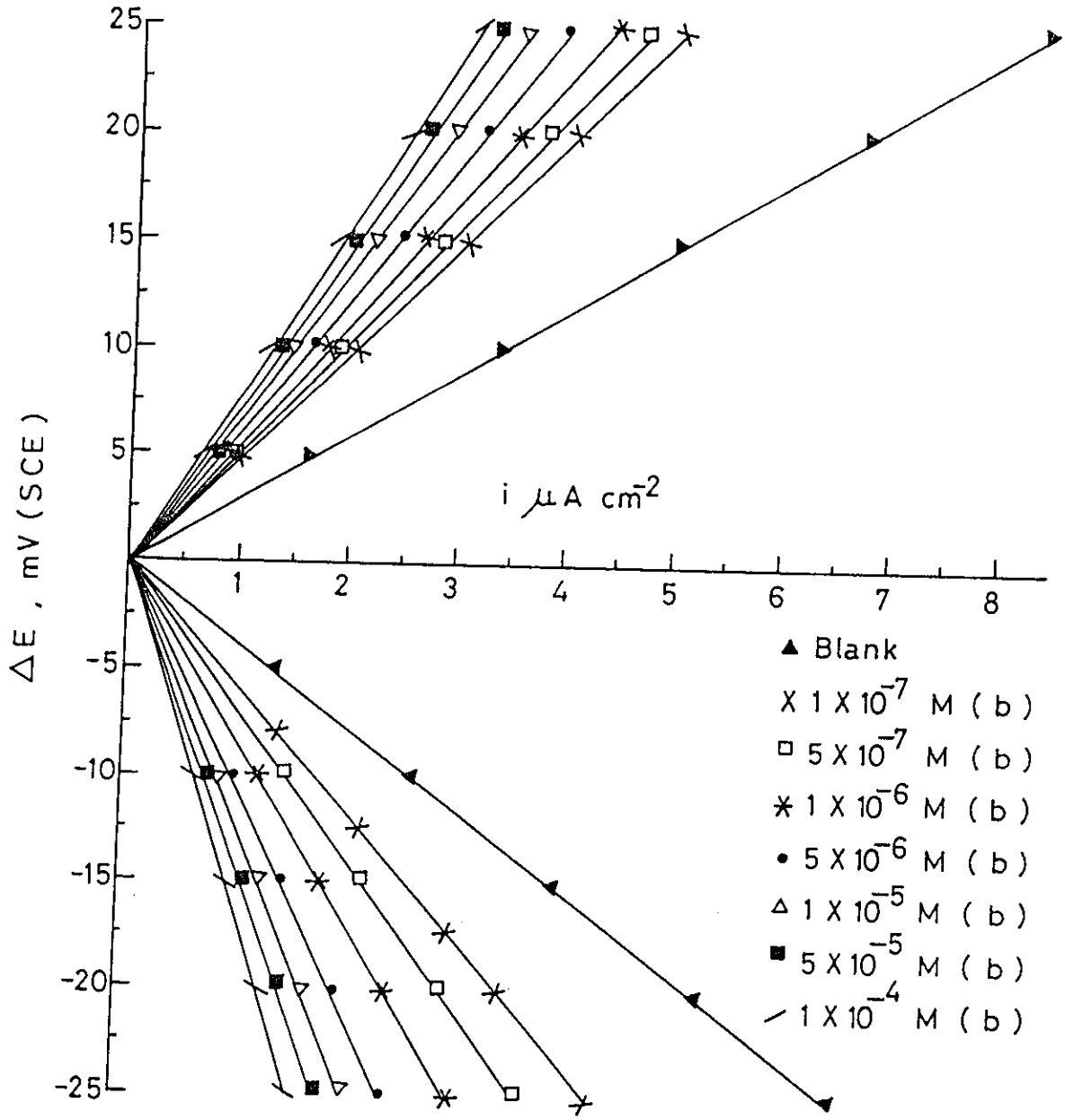


Fig.(3.109): linear polarization curves for copper in 0.1 M HCl in presence of compound (b).

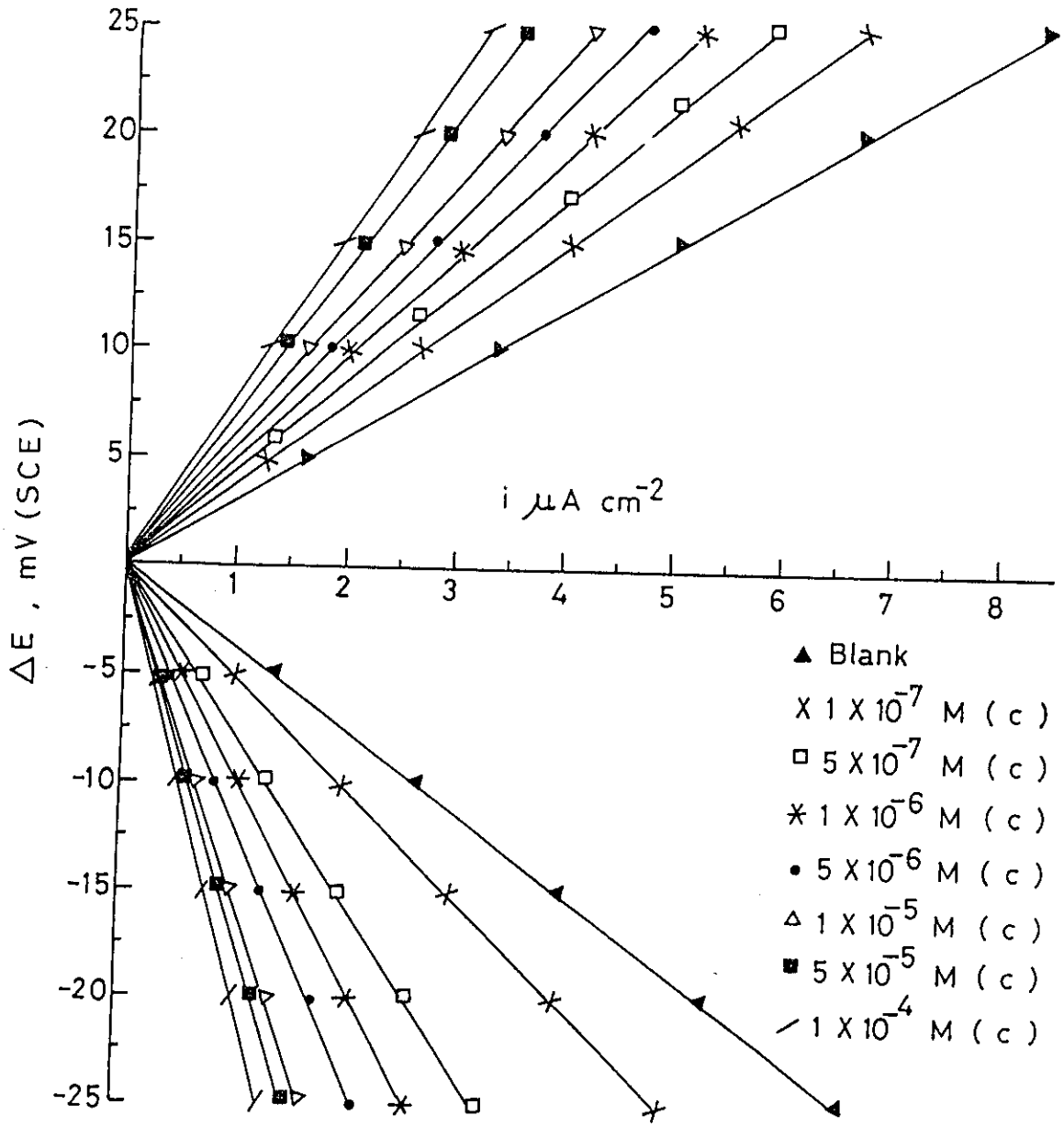


Fig.(3.110): linear polarization curves for copper in 0.1 M HCl in presence of compound (c).

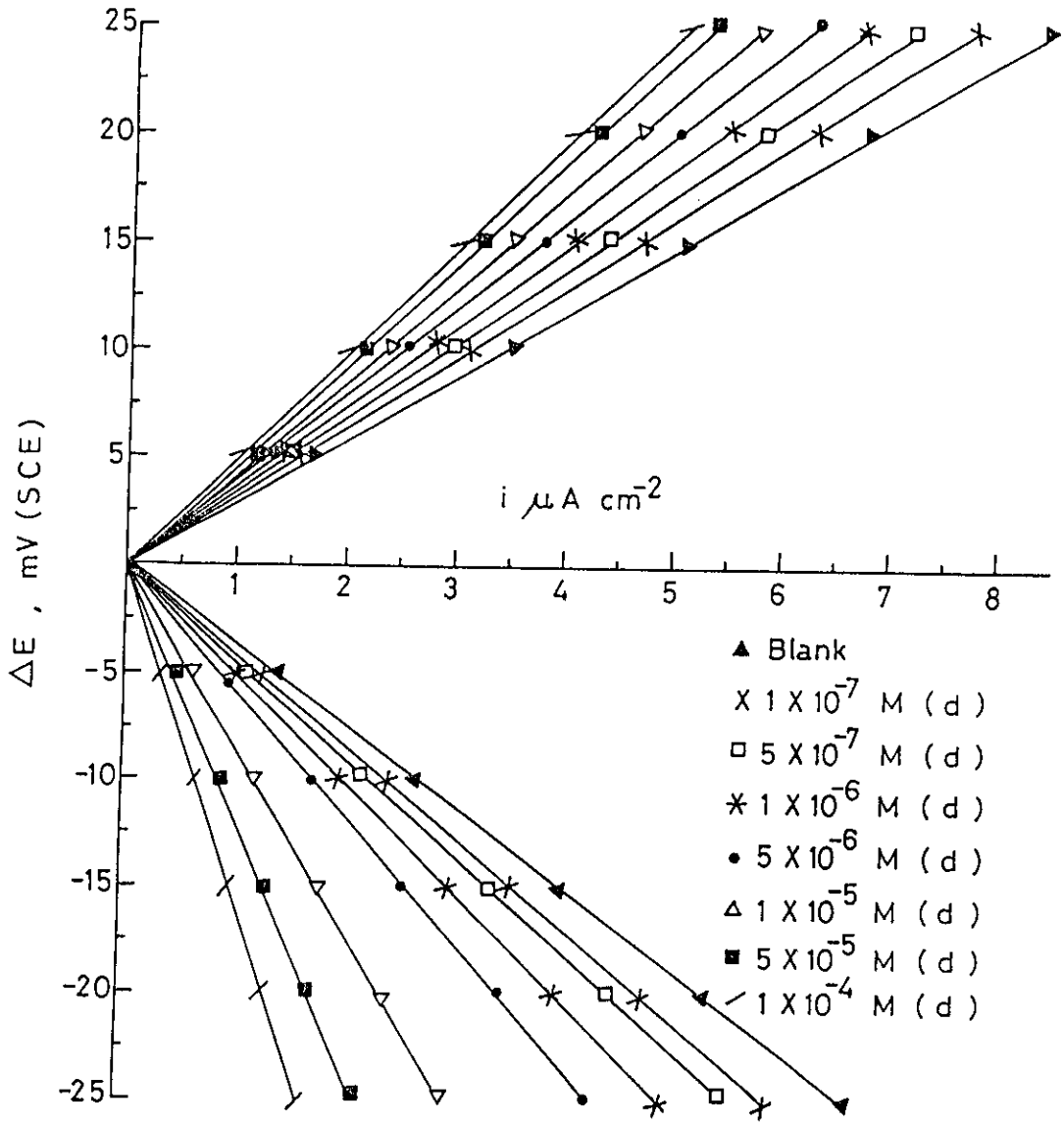


Fig.(3.111): linear polarization curves for copper ir 0.1 M HCl in presence of compound (d).

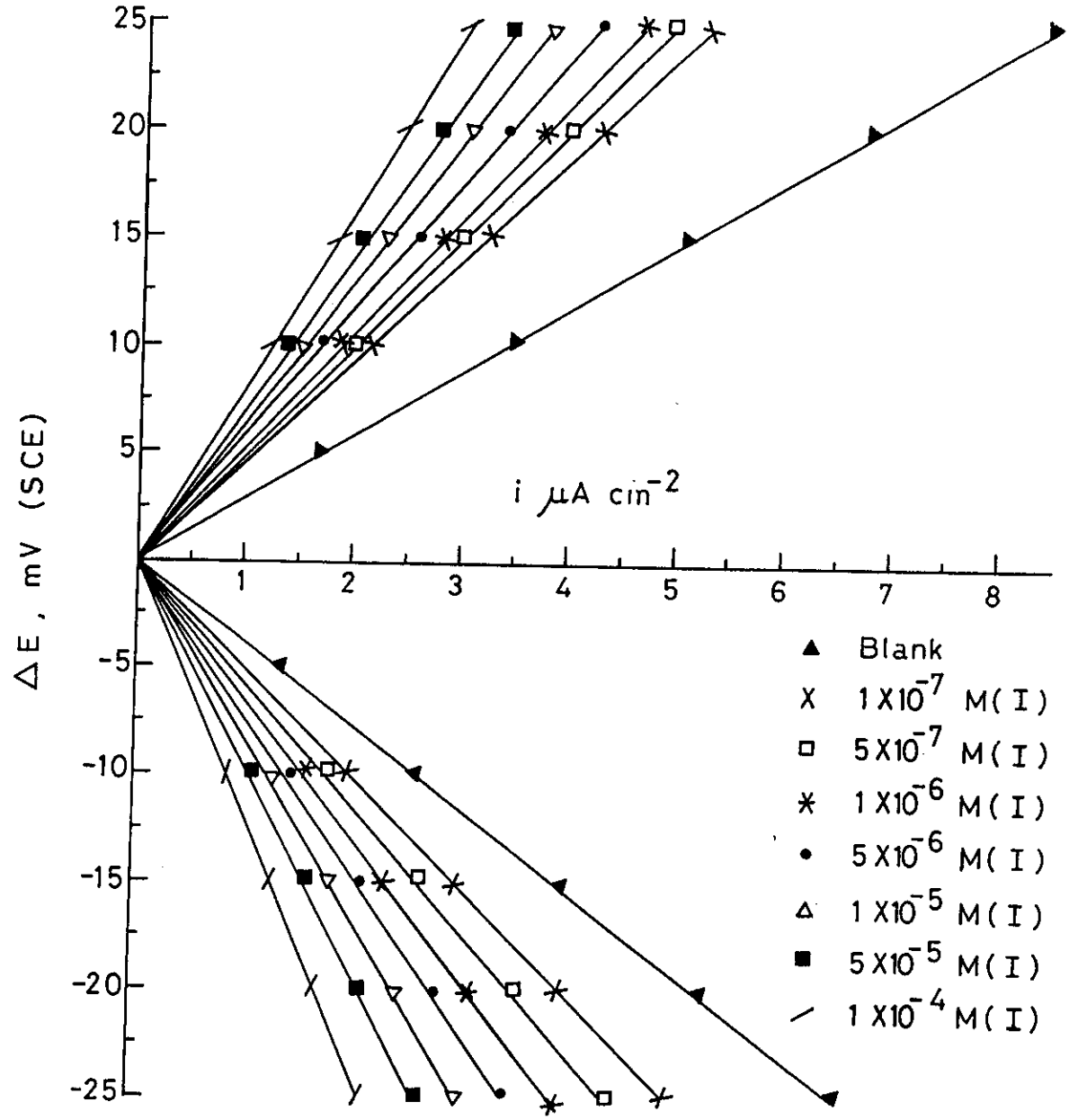


Fig.(3.112): linear polarization curves for copper in 0.1 M HCl in presence of compound (I) at 30°C.

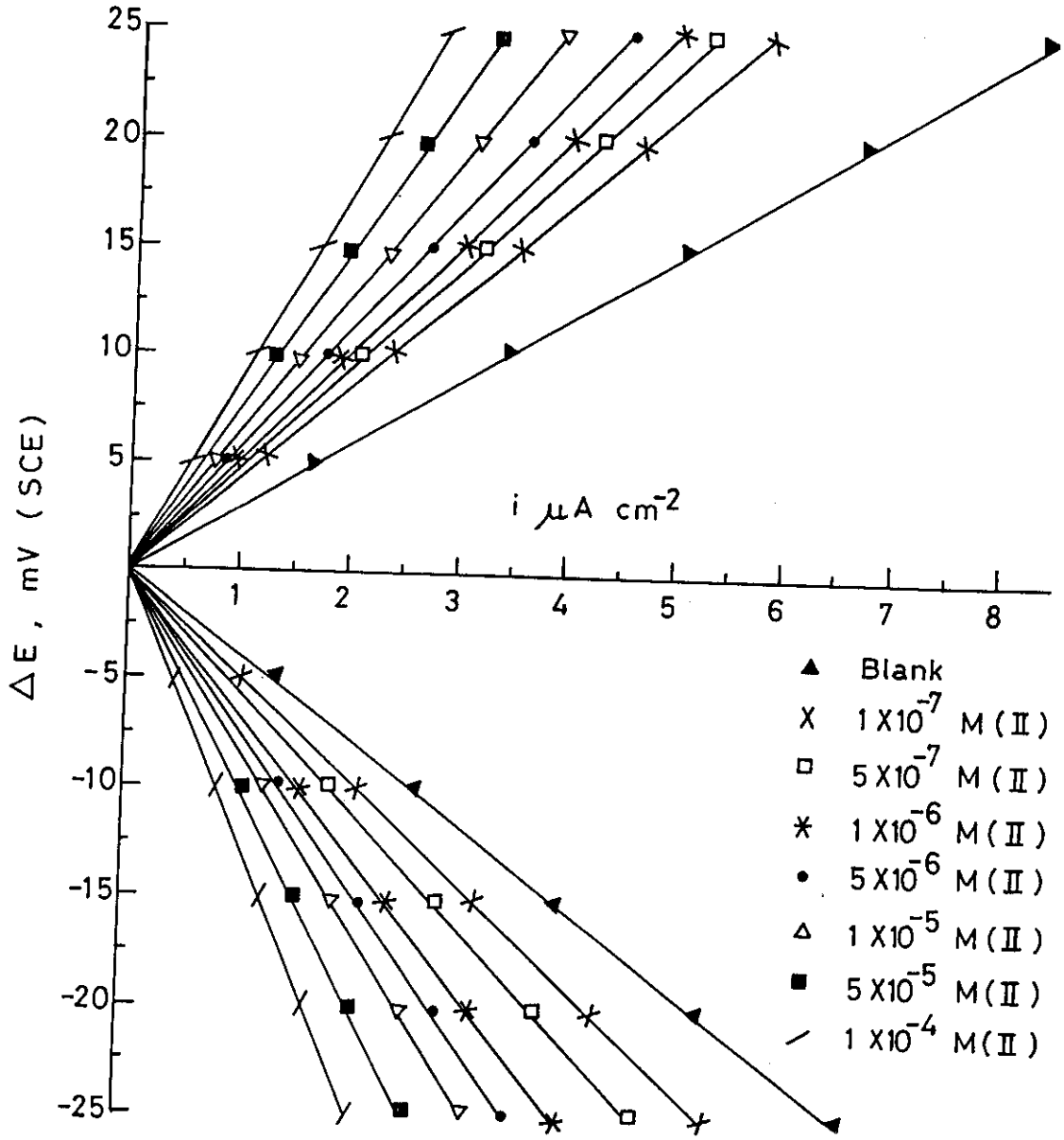


Fig.(3.113): linear polarization curves for copper in 0.1 M HCl in presence of compound (II).

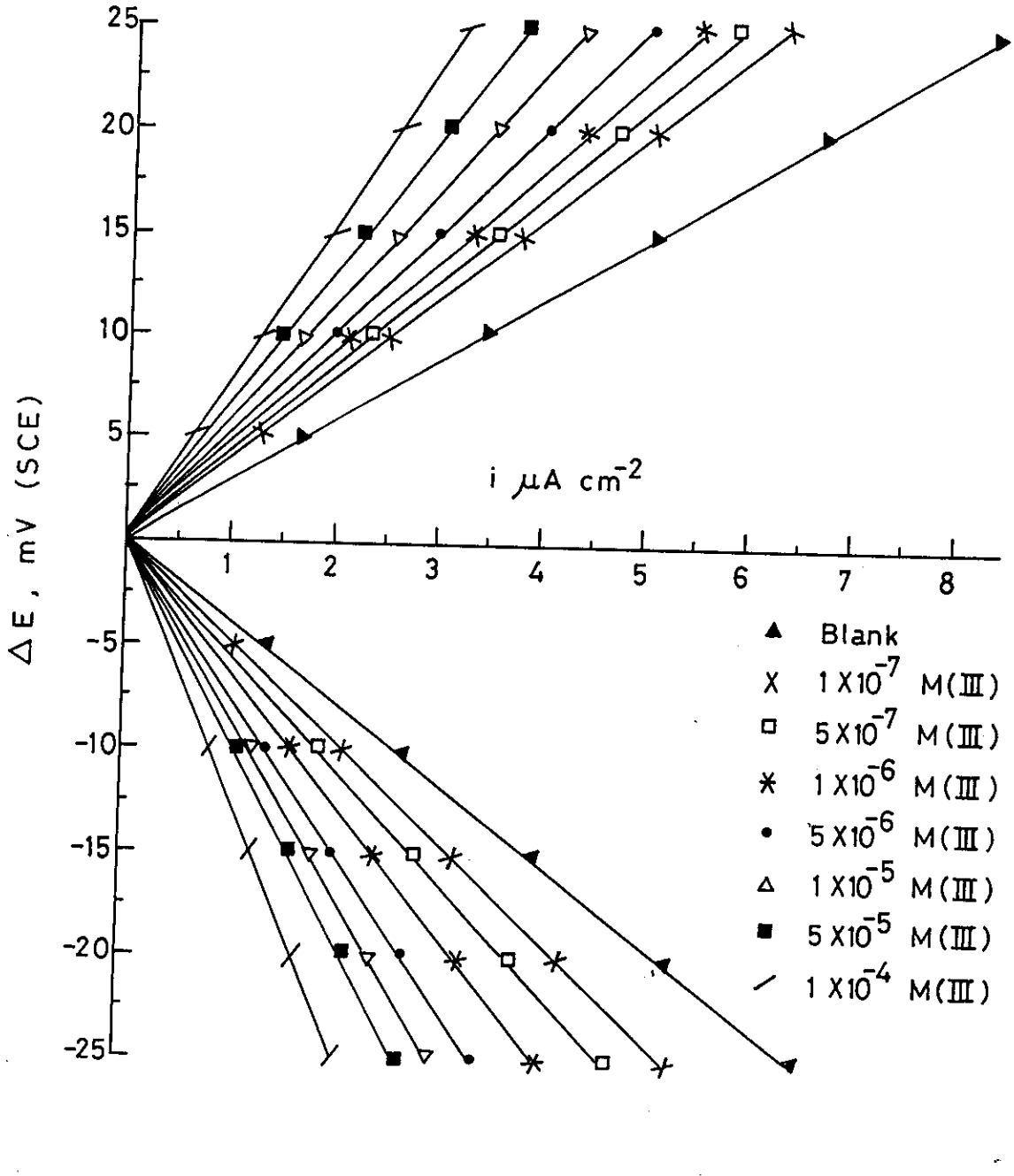
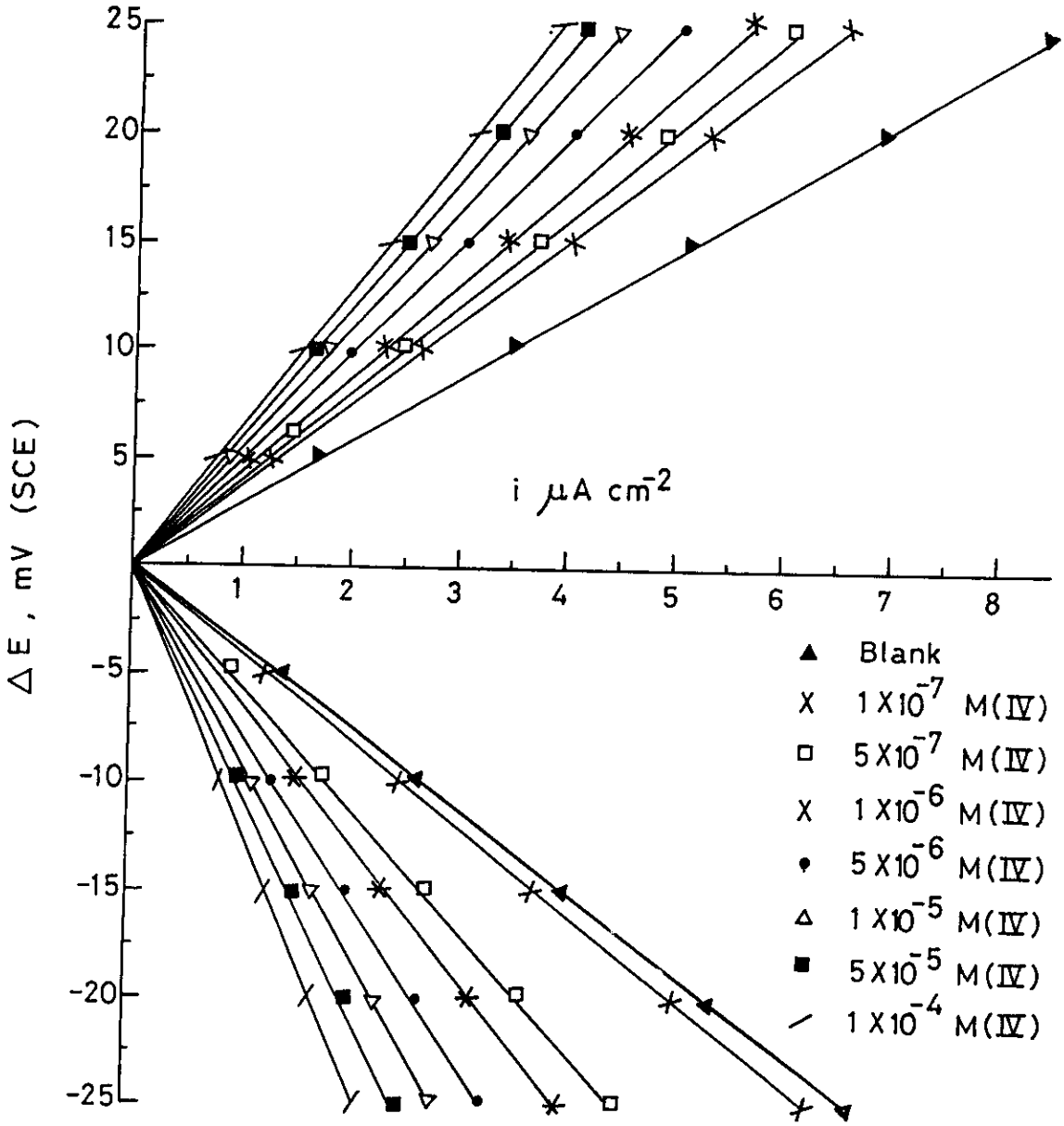


Fig.(3.114): linear polarization curves for copper in 0.1 M HCl in presence of compound (III).



Fig,(3.115): linear polarization curves for copper in 0.1 M HCl in presence of compound (IV).

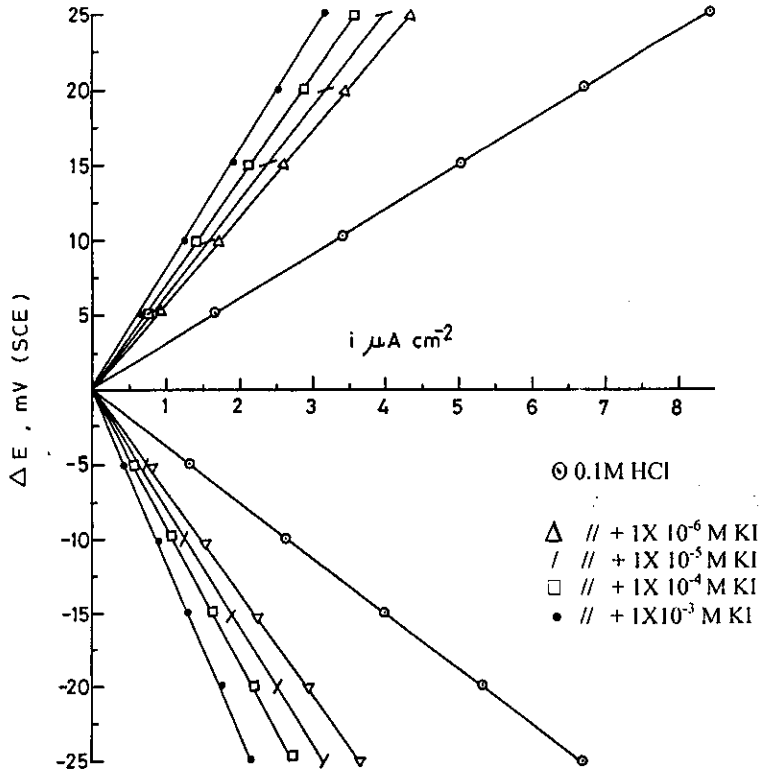


Fig (3.116): linear polarization curves for copper in 0.1 M HCl in presence of various concentrations of KI.

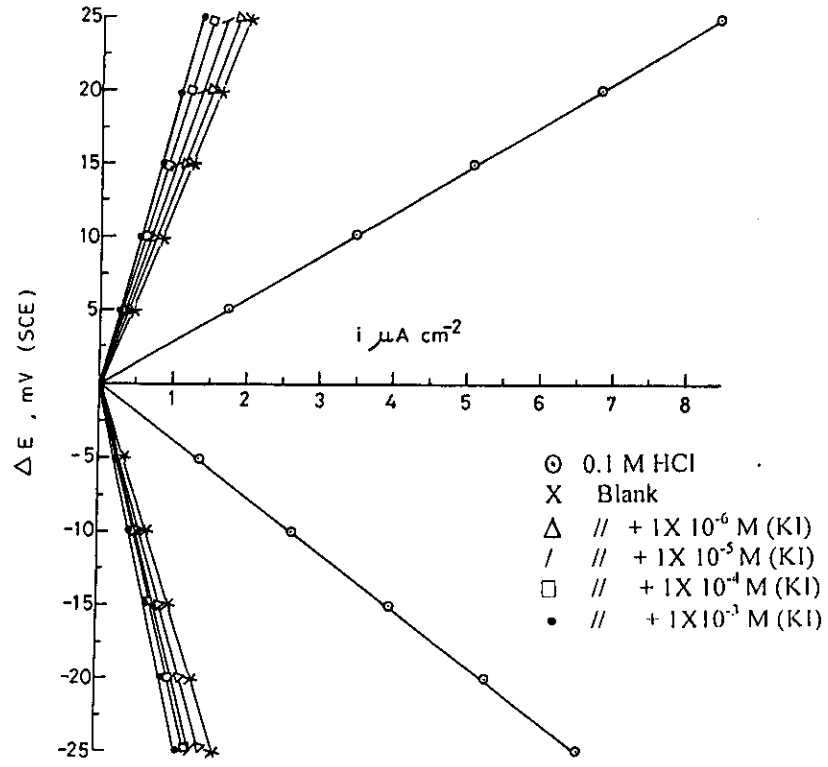


Fig. (3.117): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (1) (Blank) in presence of various concentrations of KI.

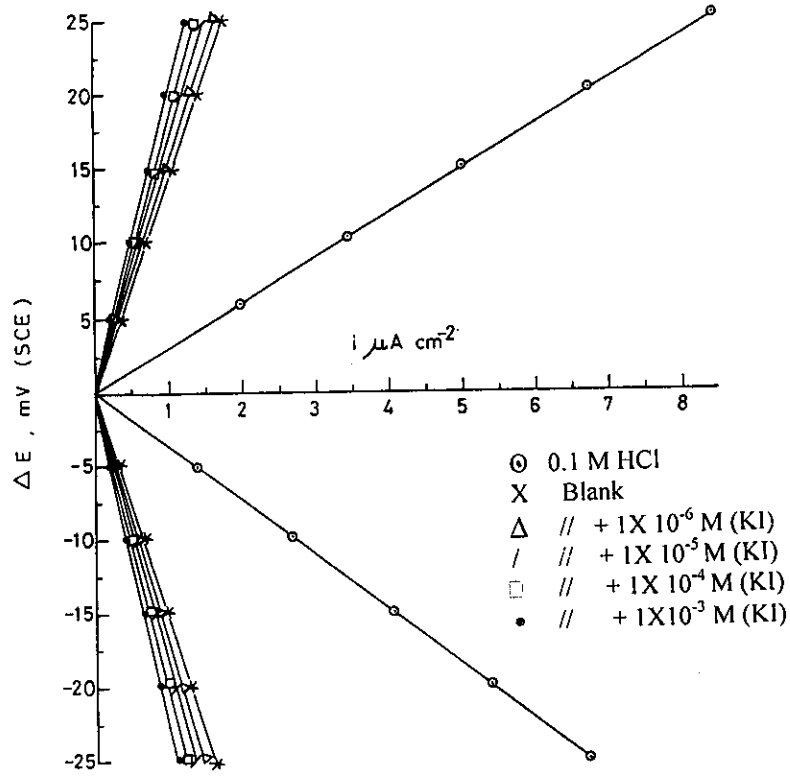


Fig (3.118): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (2) (Blank) in presence of various concentrations of KI.

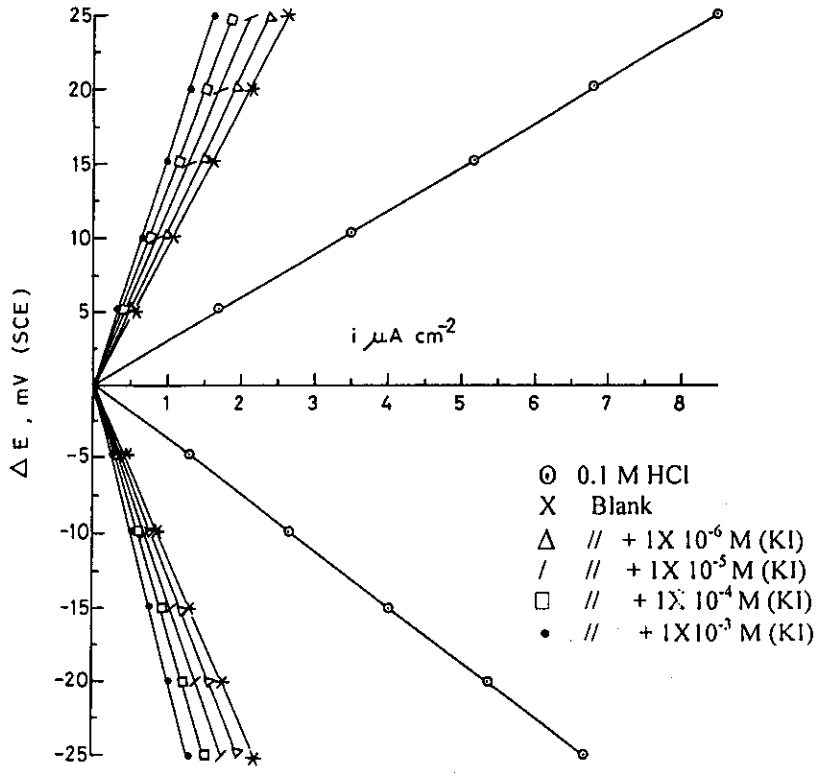


Fig.(3.119): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (3) (Blank) in presence of various concentrations of KI.

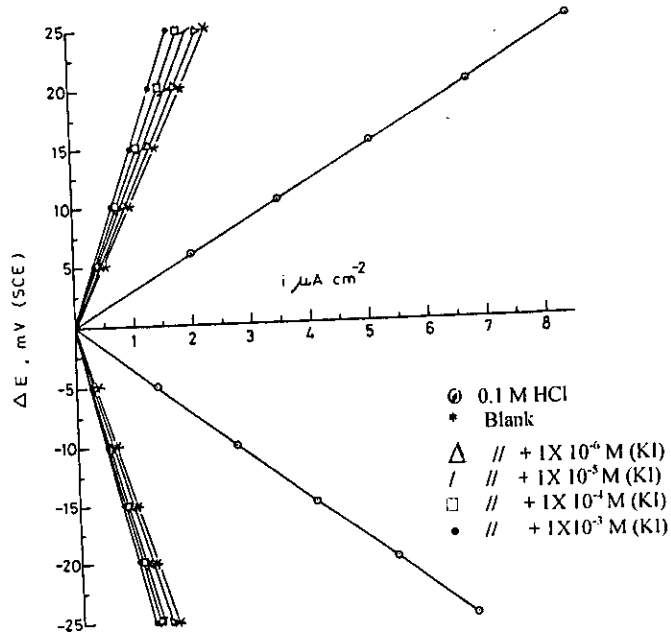


Fig (3.120): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (a) (Blank) in presence of various concentrations of KI at 30°C.

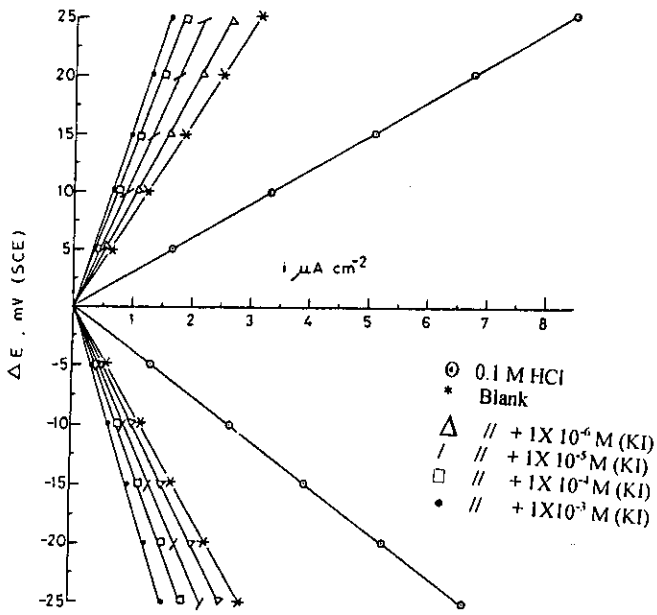


Fig.(3.121): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (b) (Blank) in presence of various concentrations of KI at 30°C.

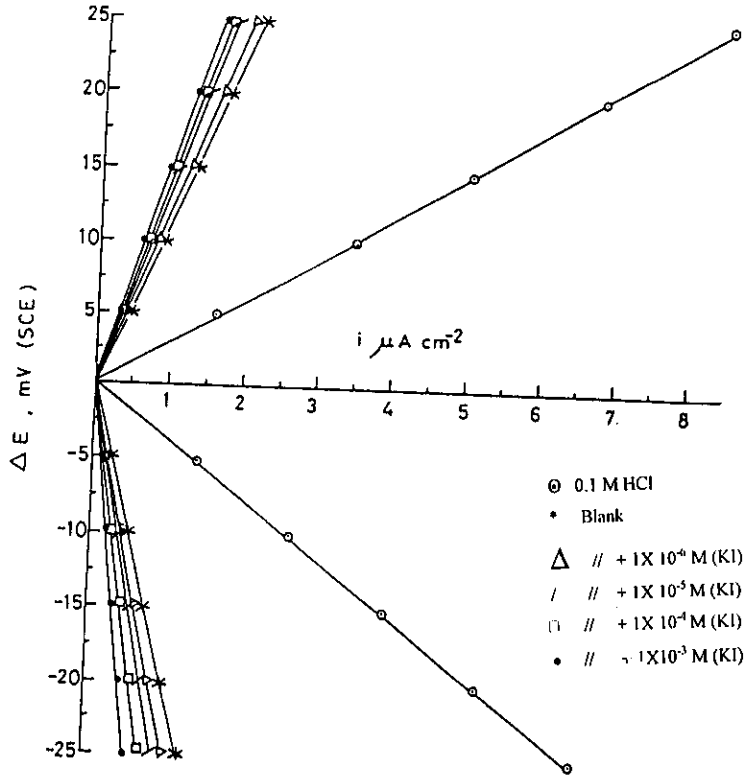
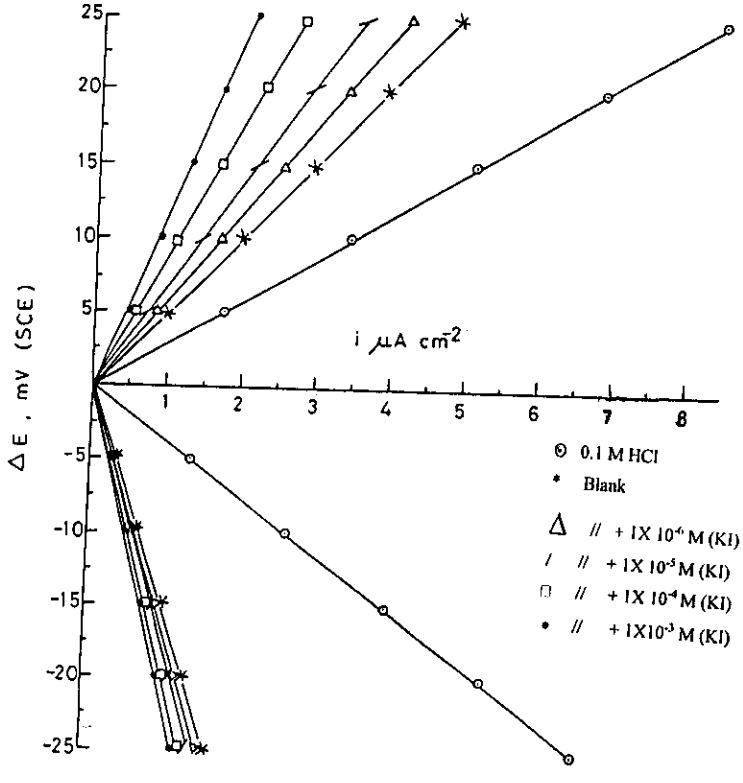


Fig (3.122): linear polarization curves for copper in 0.1 M HCl + 1X10^{-4} M compound (c) (Blank) in presence of various concentrations of KI at 30°C.



Fig,(3.123): linear polarization curves for copper in 0.1 M HCl + 1X10^{-4} M compound (d) (Blank) in presence of various concentrations of KI at 30°C.

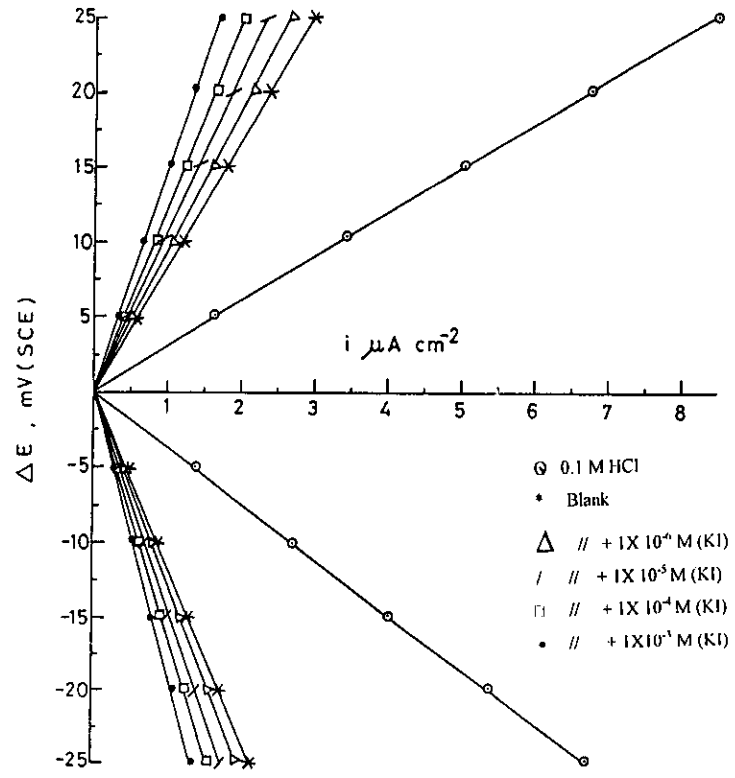


Fig (3.124): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (I) (Blank) in presence of various concentrations of KI at 30°C.

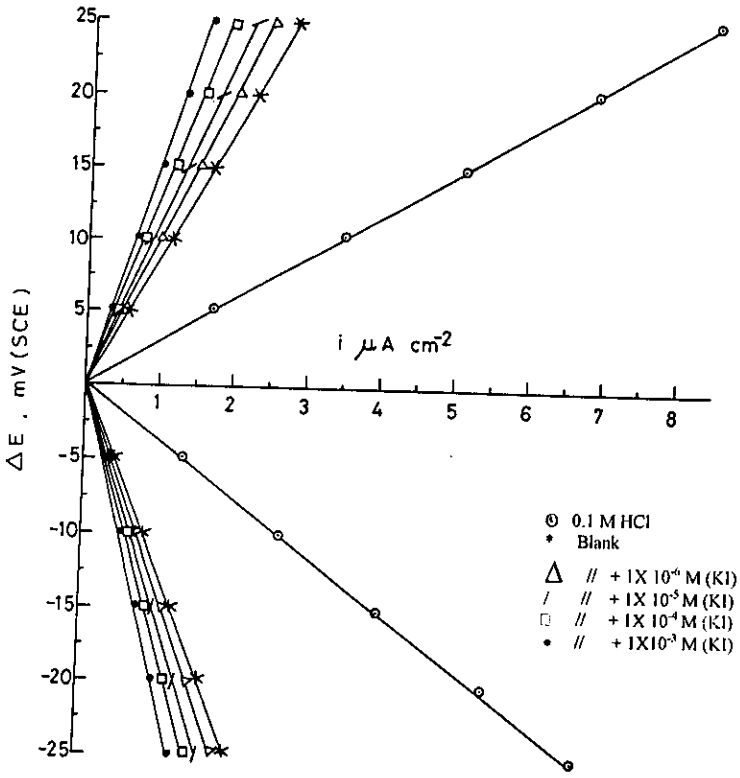


Fig. (3.125): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (II) (Blank) in presence of various concentrations of KI at 30°C.

Adsorption Behaviour of The Inhibitors:-

Figs. (3.128 – 3.138) demonstrate the variation of the degree of surface coverage with bulk concentration of the additives by the three techniques used (polarization, linear polarization, and weight loss). All curves exhibit the S-Shape in θ - log C system of coordinates, Frumkin's approach was considered [171].

The Frumkin isotherm has the formula:

$$KC = (\theta / 1 - \theta)\exp(-f\theta) \qquad (3.7)$$

where C is the concentration of the adsorbed substance in the bulk or the solution and K is the modified equilibrium constant of the adsorption process, which is related to the standard free energy of adsorption according to the following equation:

$$K = \exp(\Delta G^{\circ}_{ads}/RT)\ 1/55.5 \qquad (3.8)$$

These curves include one inflexion referring to one step adsorption processes [172]. This is agreement with the assumption used in the derivation of these isotherms, mobile layers are formed on the adsorption process[173]. This leads to the adsorption of the present inhibitors on the copper surface of a type approaching physical adsorption [174] which is due to electrical interaction between the double layer existing at phase boundary and the adsorbing molecules.

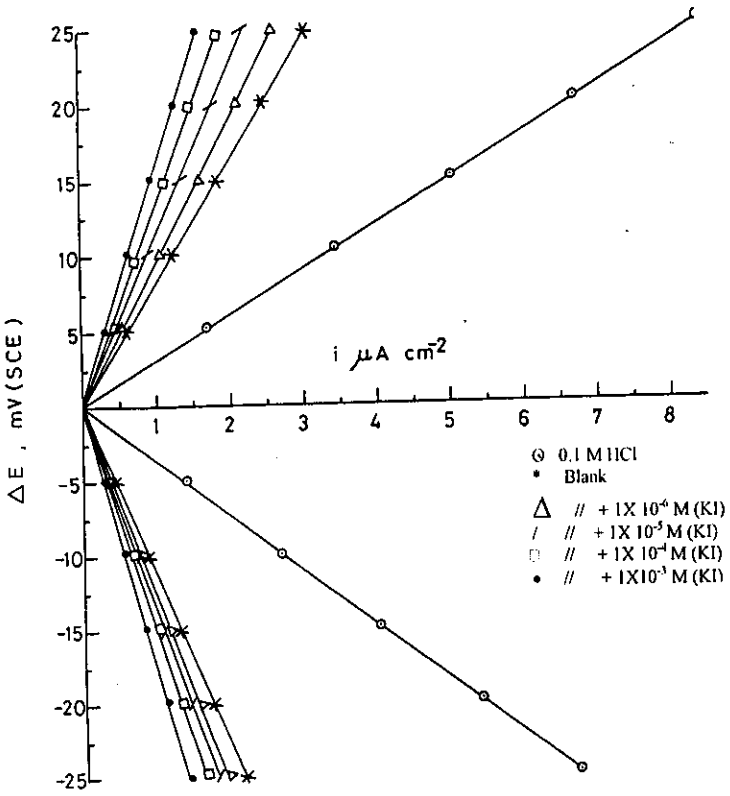


Fig (3.126): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (III) (Blank) in presence of various concentrations of KI at 30°C.

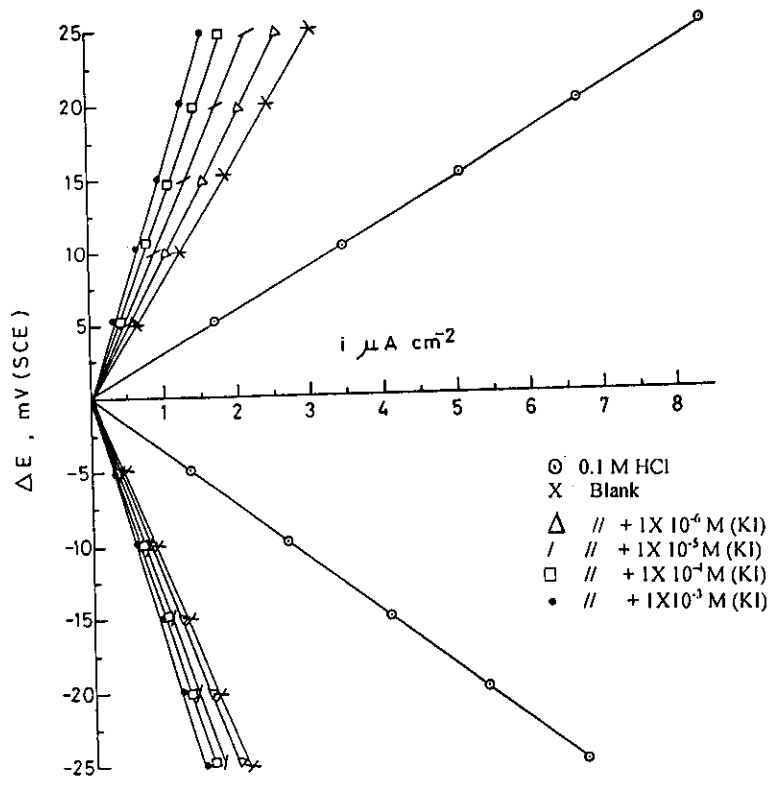


Fig (3.127): linear polarization curves for copper in 0.1 M HCl + $1X10^{-4}$ M compound (IV) (Blank) in presence of various concentrations of KI at 30°C.

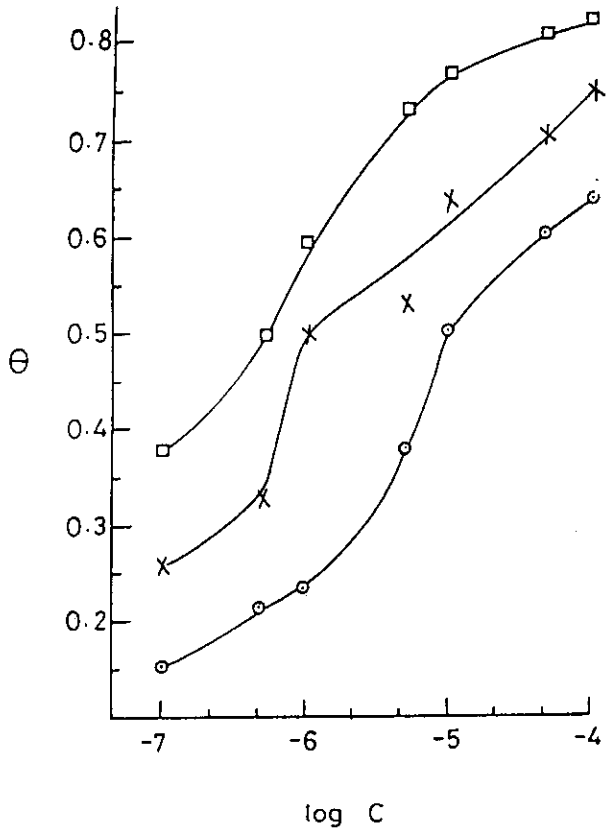


Fig (3.128): Effect of compound (1) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

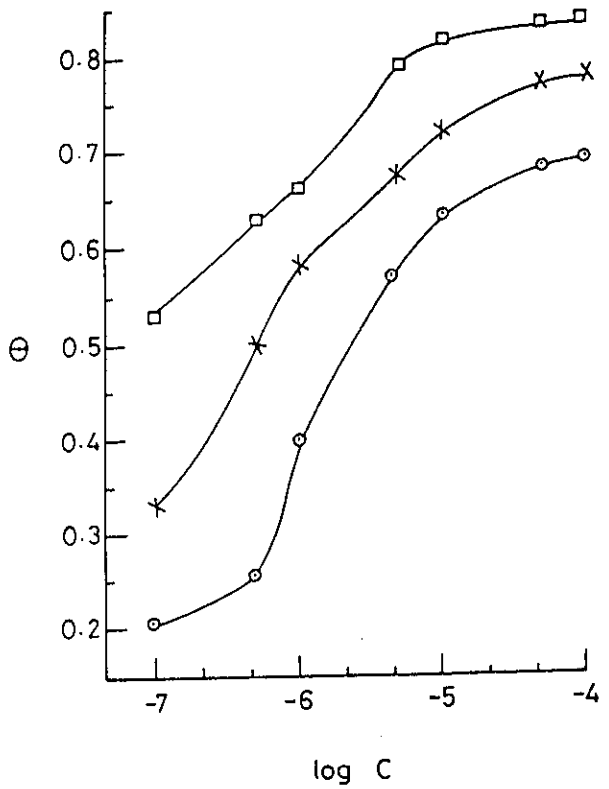


Fig. (3.129): Effect of compound (2) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

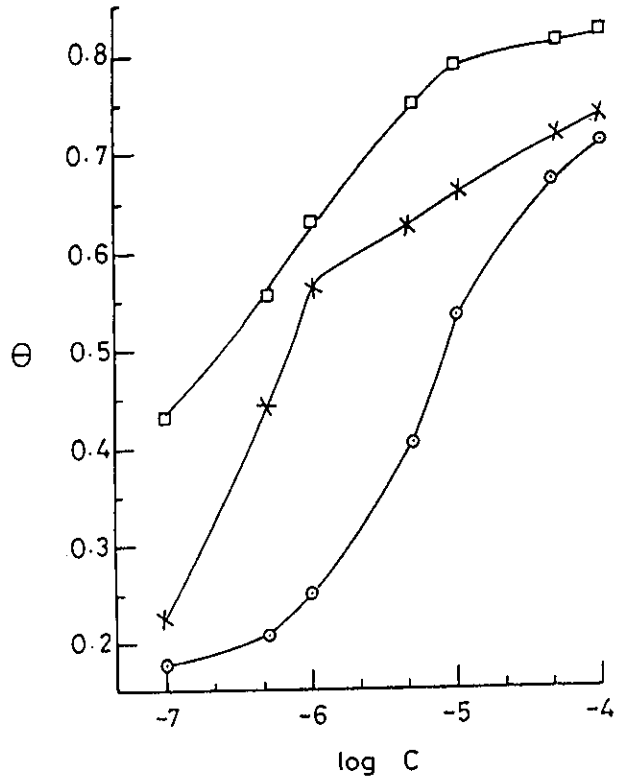


Fig (3.130): Effect of compound (3) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

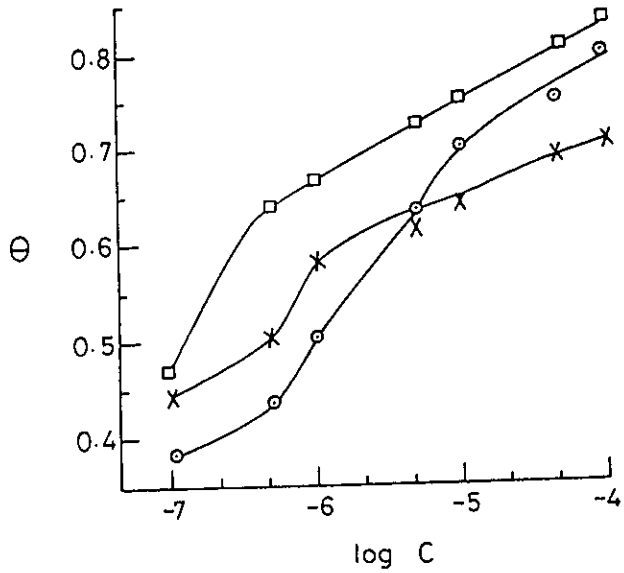


Fig.(3.131): Effect of compound (a) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

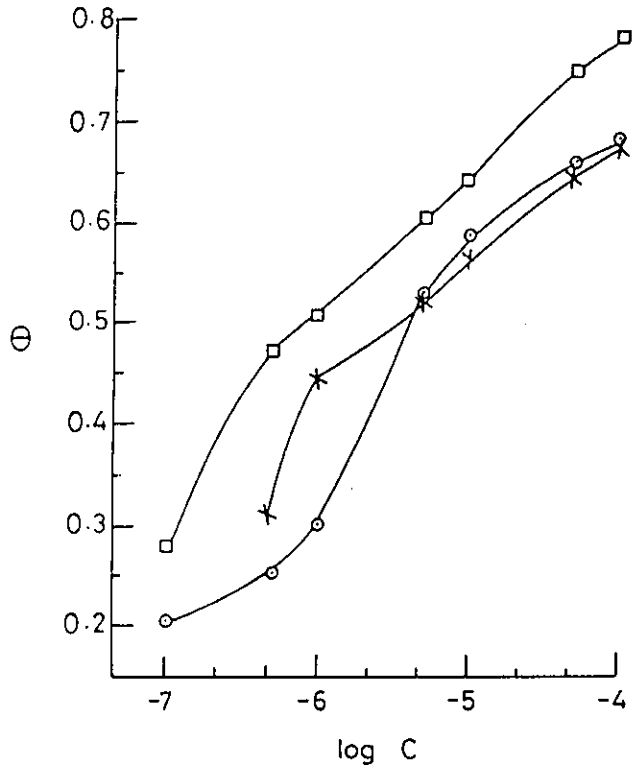


Fig (3.132): Effect of compound (b) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

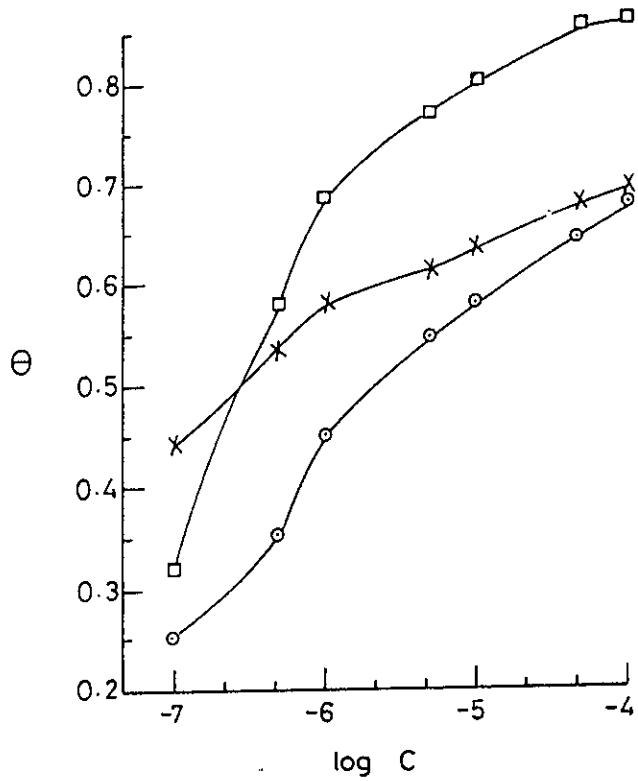


Fig (3.133): Effect of compound (c) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

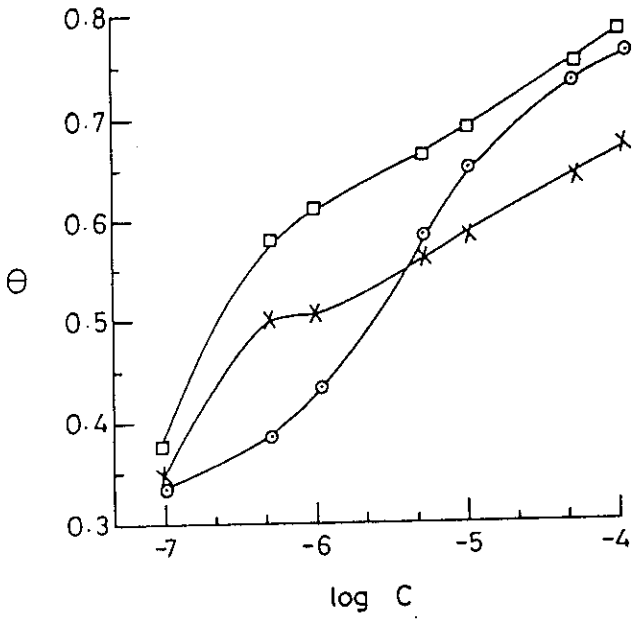


Fig (3.134): Effect of compound (d) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

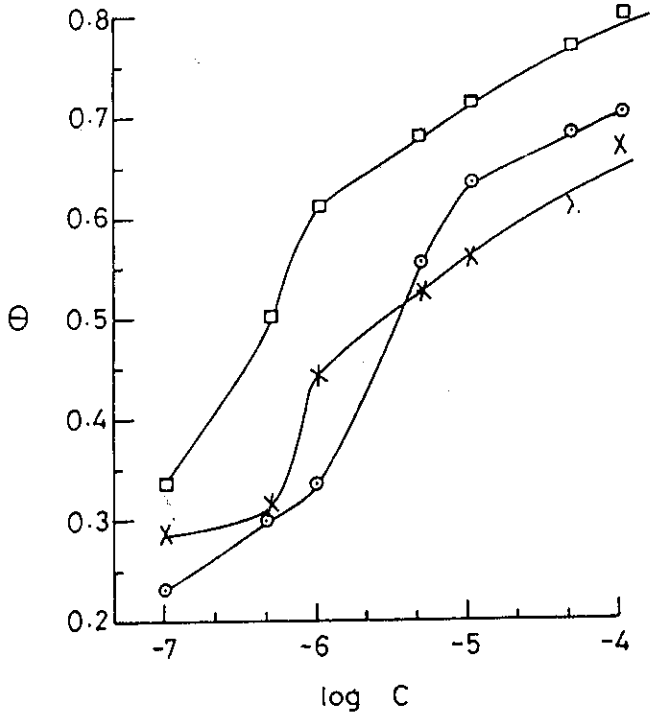


Fig (3.135): Effect of compound (I) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

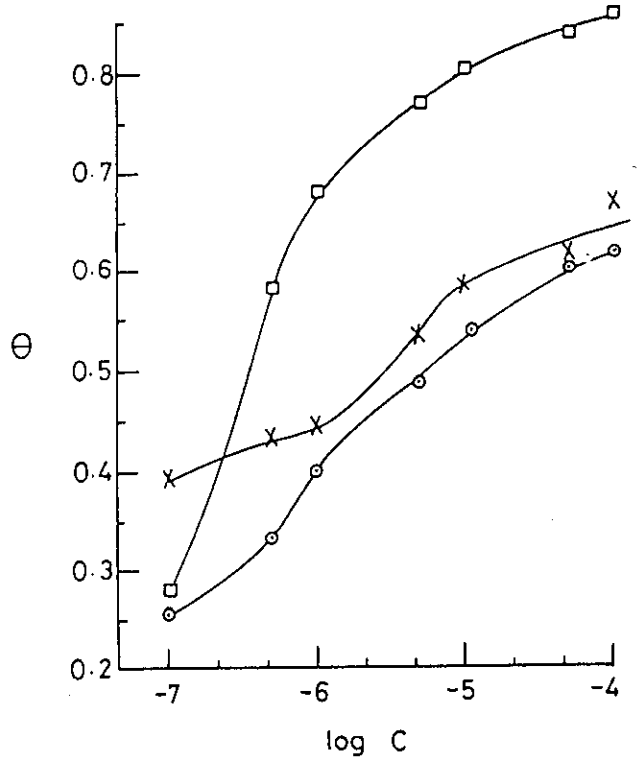


Fig.(3.136): Effect of compound (II) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

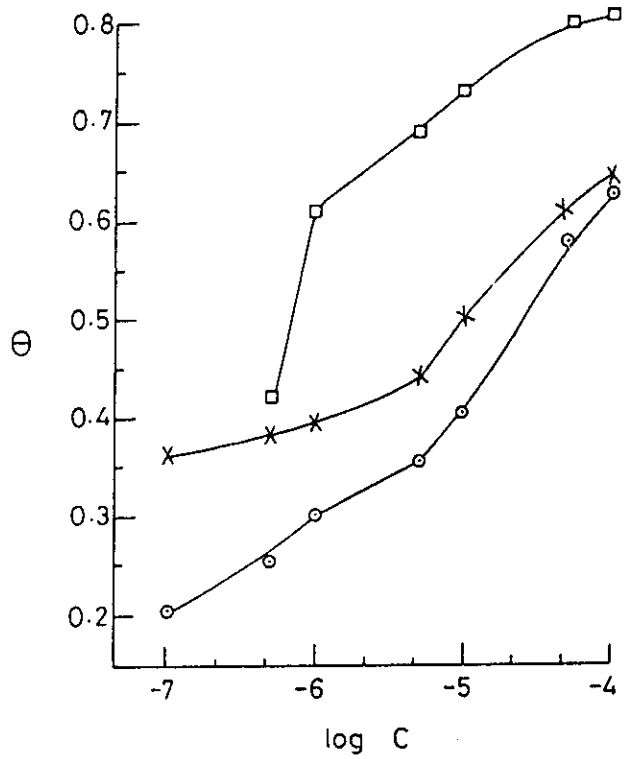


Fig.(3.137): Effect of compound (III) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

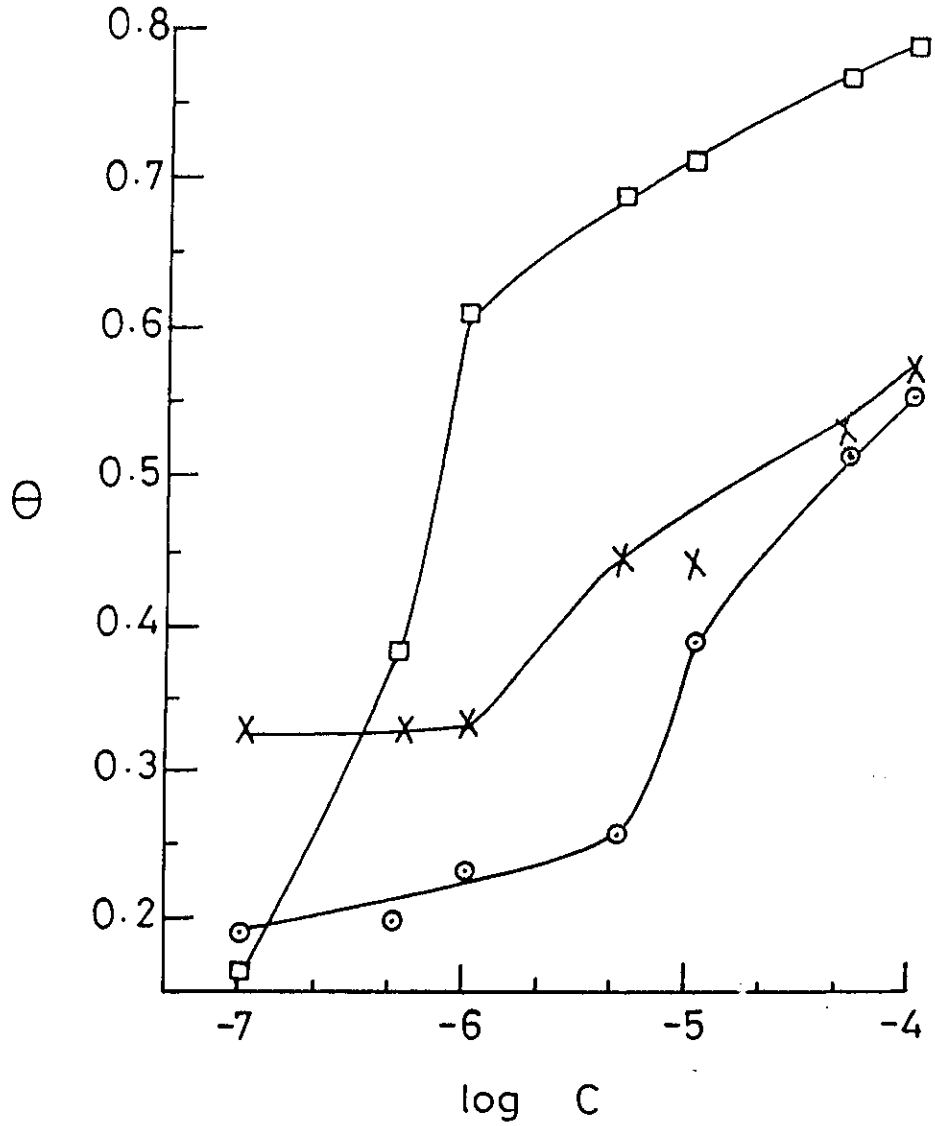


Fig. (3.138): Effect of compound (IV) concentration on the degree of surface coverage for copper in 0.1 M HCl from different techniques (□) polarization, (X) linear polarization and (⊙) weight loss.

Chemical Structure and Corrosion Inhibition:

Inhibition of corrosion of copper in 0.1M HCl by the investigated quinazoline phenylhydrazone derivatives (three serieses) as measured by potentiostatic polarization, linear polarization and weight loss measurements was found to depend on the concentration and nature of the inhibitor.

The observed corrosion data in the presence of the inhibitors showed the following: (I) the decrease of corrosion rate with increase of concentration of the inhibitor, (II) the linear variation of the weight loss with time, (III) the parallel shift in Tafel lines to higher potential regions and (IV) the decrease in the corrosion inhibition with increasing temperature, indicate that the corrosion inhibition occures by adsorption of the inhibitors at the electrode-solution interface [175]. The nature of inhibitor interaction on the metal surface during corrosion inhibition has been known from its adsorption characteristics [176]. However, inhibition efficiency of additive compounds depends [177] on many factors which include the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption and formation of metallic complexes.

It was obvious that the loss in weight and the decrease in the corrosion current density (i_{corr}) in the presence of each of the investigated quinazoline phenylhydrazone derivatives and halide ions is lower than in its absence, and mostly decrease as the concentration of quinazoline phenylhdrazone derivatives is increased, whereas the inhibition efficiency (In) and the degree of surface coverage (θ) increase. This inhibitive effect may be explained by considering the adsorption of quinazoline phenylhydrazone molecules (with higher negative density at the N-hetero atom, and other atoms e.g. O, Br, I,...) on the copper surface [178, 179] which have incomplete d shells [180], and /or the complex formation of the

inhibitor molecules on the corroding copper surface [181] (surface chelation). The inhibition efficiency of quinazoline phenylhyrazone derivatives was found to increase in the following order:

Fist series: 2 > 3 > 1.

Second series: a > b > C > d.

Third series: I > II > III > IV.

It seems that the ring-hetero atom is responsible for this behaviour, A lone pair of electrons of the hetero atom could be used in the conjugation resonance of the molecule, while the second lone pair in the case of the other N-hetero atoms facilitates the protonation in the acidic medium [182] which slightly catalyze the hydrogen evolution reaction [183] which in turn is reflected in a slight increase in the corrosion process. According to Antropov [182], the protonation of heterocyclic compounds may take place as the following reaction sequence:

$$B+H^{+} = BH^{+}_{ads}.$$

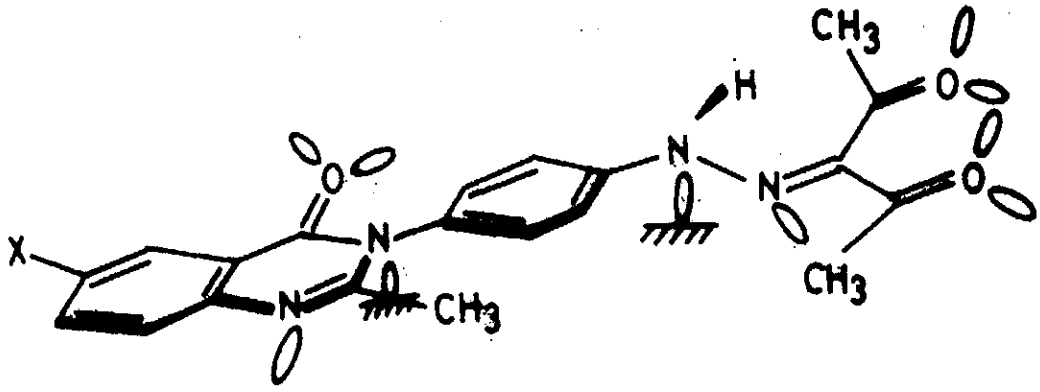
$$BH^{+}_{ads} + e = BH_{ads}.$$

$$BH_{ads} = B_{ads} + H_{ads}.$$

$$2H_{ads}=H_2$$

Skeletal representation of the mode of adsorption of the studied quinazoline phenylehydrazone derivatives (1, 2, 3 – a, b, c, d – I, II, III, IV) is shown in Fig. 3.139 and clearly indicates the active adsorption sites.

First series



2 > 3 > 1

(1) X = H

(2) X = —Br

(3) X = —I

Fig. (3.139): Skeletal representation of the mode of adsorption of inhibitors.

Second series

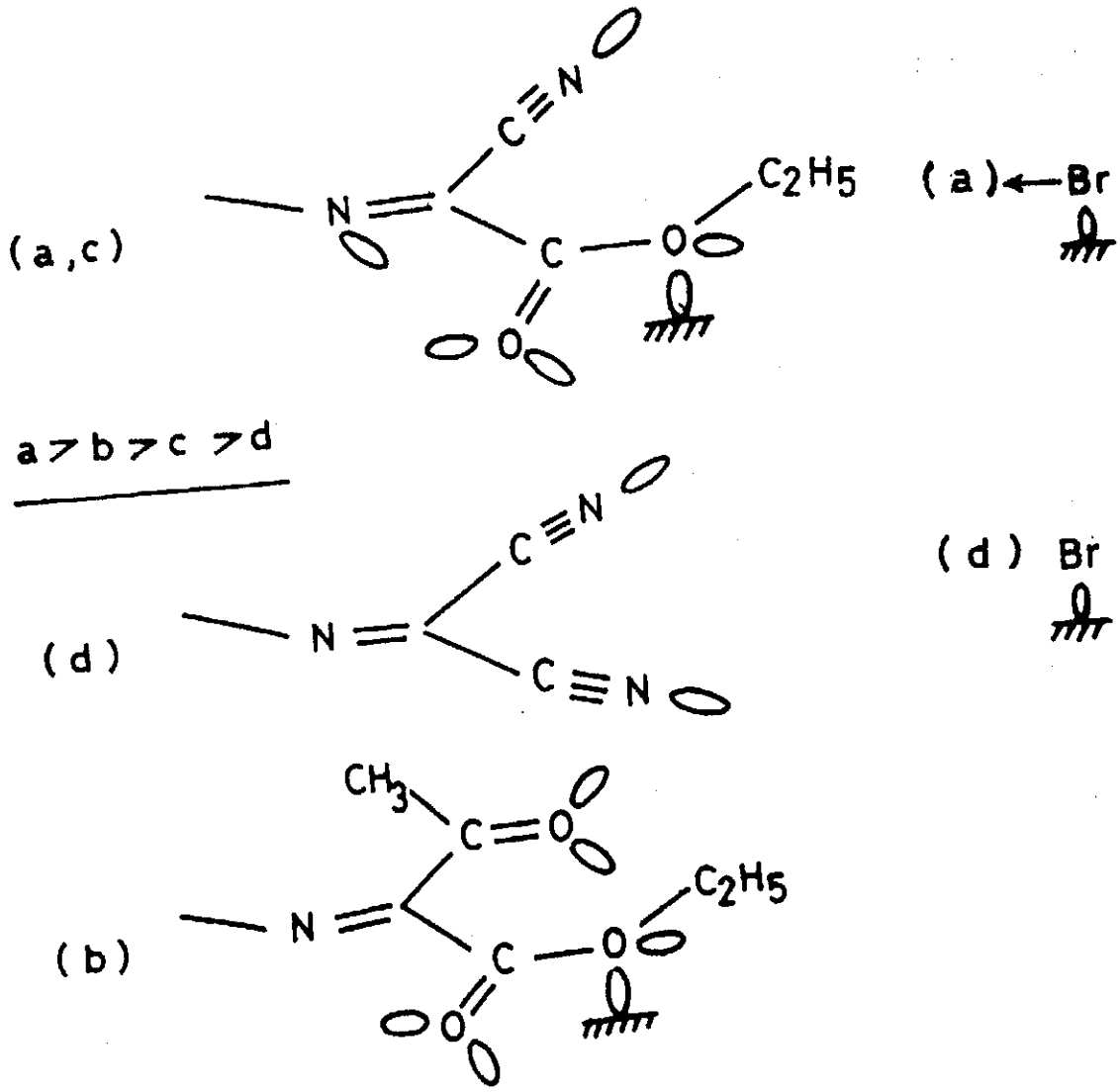
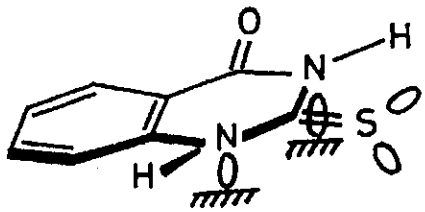
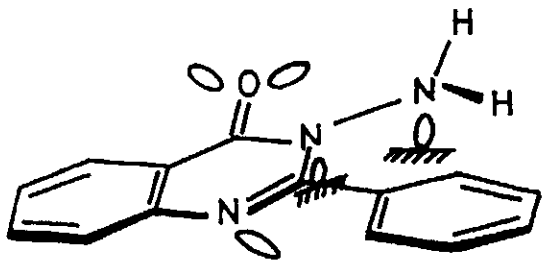


Fig. (3.139): Continued.

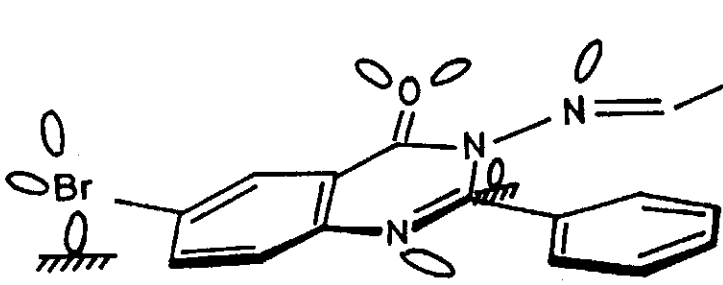
Third series



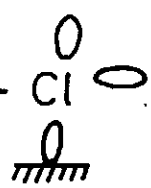
(IV)



(III)



(I-II)

(II) R = 

I > II > III > IV

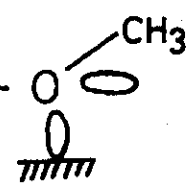
(I) R = 

Fig. (3.139): Continued.

The obtained results of the first series compounds (Tables 3.1a, 3.19a, 3.34a) indicate that compound (1) gave a lower corrosion inhibition than that of compound (2) and (3), this may be ascribed to its lower molecular size and to its lesser number of active sites (two active centers). On the other hand compound (2) gave the highest inhibition efficiency this may be due to its higher molecular size and the larger number of adsorption sites (three active centers). Compound (3) comes after compound (2) in the succession of increased protection efficiency in spite of its higher molecular size than compound (2), this may be explained on the basis of the basically of halide ions (Br atom more basic than I atom, so Br atom is more strongly adsorbed on the metal surface than I atom).

In the second series compounds (Tables 3.2a, 3.20a, 3.35a) the order of increasing inhibition efficiency is as follows: d < C < b <a. the inhibition efficiency of this series depends on two factors, the number of adsorption active centers in the molecule and their charge density and the molecular size, compound (a) comes on top of the series as the efficient inhibitor. This due to its higher molecular size and also it has four probable sites of adsorption. (two nitrogen, one oxgen and one bromide atom). Compound (b) comes after compound (a) in the percentage inhibition, this is due to its lower molecular size and it has only three probable sites of adsorption (two nitrogen atoms and one oxgen atom). Compound (c) comes after compounds (a) and (b) in inhibition efficiency, this may be due to its lower molecular size and the presence of one cyanide group which is electron withdrawing group, so the electron density on the molecule will be lower than that on the compound (b). On the compound (d) there are two cyanide groups, which are electron withdrawing groups, so the electron density on compound (d) is less than

The order of inhibition efficiency of the additives revealed by the weight loss method, further supported by polarization and polarization resistance methods. The observed agreement among these independent techniques prove the validity of the results obtained and supports the explanation given for the effect of chemical structure on the inhibition action of the compounds investigated.

on compound (c), this lowers the inhibition efficiency of compound (d) from compound (c).

In the third series compounds (Tables 3.3a, 3.21a, 3.36a) the order of decreased inhibition efficiency for quinazoline phenylhydrazone derivatives is:

I > II > III > IV. Differences in the inhibition efficiency for copper corrosion in 0.1M HCl as indicated by the above orders probably orginate from the electrophilic character of the substituents in the molecule, its molecular size and the number of adsorption active centers in the molecule.

It is not surprising that compound (I) comes on top of the series as the most efficient inhibitor. This due to the presence of three adsorption active centers in the molecule and the presence of the electron releasing methoxy group in the para position to the hydrazone group increases its charge density and consequently enhances its adsorption on the copper electrode surface.

The p-chloro derivative (II) follows next despite the electrophilic character of the Cl substituent obviously due in part to increased molecular size, and the molecule has three adsorption active centers. Here also a mesomeric effect (+M) involving electron pairs on Cl can operate in opposite direction to the – I effect and the overall mechanism constitutes electron release which maintains sufficient electron charge density on the hydrazone group. A similar effect was noted in other cases[184, 185]. Compounds (III) and (IV) each has two adsorption active centers but compound (III) has a higher molecular size and as known, the large sized molecules can provide better surface coverage and as a result better inhibition. So we observe that compound III is more efficient than compound (IV) and the two compounds come after compounds (I) and (II) in the succession of increased inhibition efficiency.

B- Electrical Conductance Measurements

The specific conductance values of $CuSO_4$ in methanol – water in presence of quinazoline phenylhydrazone derivatives were measured experimentally and from which the value of molar equivalent conductance (Λ) was calculated according to:

$$\Lambda = (K_S \cdot K_{cell} \cdot 1000) / C \qquad (3.9)$$

where K_S is the difference between conductance of solution and that of solvent, K_{cell} is the cell constant and C is the molar concentration.

Limiting molar conductance ($\Lambda_\circ$) values were obtained by extrapolating the relation between Λ and $(C)^{1/2}$ to zero concentration, Figs. (3.140 – 3.148). The figures show straight lines with one break (two straight lines) in presence of the quinazoline phenyl hydrazone derivatives indicating the formation of stoichiometric complexes between $CuSO_4$ and all quinazoline phenyl hydrazone derivatives used with ratios (1:1), (2:1) (L:M).

The values of $\Lambda_\circ$ for each stoichiometric complex are obtained by extrapolating Λ versus $(C)^{1/2}$ to zero concentration for each line separately.

The association constants of K_A all salts in presence of the quinazoline hydrazone derivatives in methanol-water mixtures can be calculated using Fuoss and Shedlovesky equation (3.9)[186,187,188]

$$1/\Lambda = [(K_A C \Lambda \gamma_{\pm} S(Z)) / \Lambda_\circ^2] + (1/ \Lambda_\circ) \qquad \text{.....(3.10)}$$

where $\gamma_\pm$ is the mean activity coefficient and S(Z) is Fuoss – Shedlovsky function. The mean activity coefficient ($\gamma\pm$) is estimated from the Debye Hückel limiting law as modified by Robinson and Stokes equation [186,189]. S(Z), Fuoss-Shedlovsky function can be determined by using the following equations:

$$S(Z) = [Z/2 + [1+(Z/2)^2]^{1/2}]^2 \qquad \text{.....(3.11)}$$

Where $Z = S\,\Lambda_o^{-3/2}\,(C\,\Lambda)^{1/2}$ ..... .(3.12)

$S = n\,\Lambda_o + m$ .....(3.13)

where $n = 0.8204 \times 10^6/(\varepsilon.T)^{3/2}$, $m = 0.825/\mu(\varepsilon.T)^{1/2}$ and η is the viscosity of solvents [190]. The dissociation constants K_D can be also calculated for the salts used from the reciprocal values of the association constants. The values obtained in our system indicate that the dissociation constants decrease with increasing the organic solvent percentage. The values of C, Λ, Λ_o, $\gamma_\pm$, S, Z, S(Z), K_A and dissociation constants (K_D) are recorded in Tables(3.37a – 3.64b).

The ion-pair association constant (K_A) for symmetrical electrolytes calculated from the previous Fuoss and Shedlovesky equation refers to the equilibrium:

$M^{2+} + A^{2-} = MA$

where one cation associates with an anion yielding a non-conducting species; if α is the degree of dissociation, we have $K_A = (1-\alpha)/(\alpha^2 C\,\gamma_\pm)$

$\alpha = 1 - \alpha^2\,CK_A\,\gamma^2_\pm$ .....(3.14)

The degree of dissociation (α) was also calculated on applying the relation:

$\alpha = \Lambda\,S(Z)\,/\,\Lambda_o$ [188].

Tables (3.37a – 3.64b) show the following results that:

i) The increase in concentration of $CuSO_4$ solution was followed by decrease in the molar conductance values. This is exactly explained as increase of dilution is followed by increase of conductance due to the free mobility of the ions under consideration.

ii) Two straight lines are obtained on drawing the relations between Λ and $(C)^{1/2}$, Fig. (3.140 – 3.148), these two lines indicate that two different stoichiometric complexes in

solutions are formed, because $CuSO_4$ alone as strong electrolyte , give one straight line for this relation.

iii) The molar conductance values decreased with more adding alcohol to the mixtures. This may due to hindering of the mobility and increase of the ion - solvent interactions by the increase of volume percentages of methanol.

iv) S factors are constant for each percentage of alcohol, this is because S factor depend only on the dielectric constant, which is constant at the specific alcohol concentration. This last value decrease by more adding alcohol due also the decrease in the dielectric constant on more increase of methanol portions.

v) S(Z) and $\gamma_{\pm}$ values are almost constant for each group of measurements due to the higher activity values of the ions under consideration which is mainly the chief factor affecting them (i.e higher $\gamma_{\pm}$ values).

vi) The K_A values are increased by increasing both the concentration of $CuSO_4$ and alcohol percentage for each type of complexes. This is due to the increase of ion– ion interaction for the former and increase of the ion – solvent interaction of the later.

Naturally the dissociation constant values K_D showed the opposite trend of the association constants K_A, because of there opposite values.

The free energy values ΔG_A are increased by more increasing of concentration of $CuSO_4$ and also by more increasing of the alcohol percentage at constant ligand concentration. These two behaviours can also be discussed in the base of two different interactions, which are ion – ion and ion – solvent interaction which are increased by more adding of both electrolyte and solvent, respectively.

The main effect of temperature on the experimented conductivity results are increasing of association constants K_A and free energy of solvation (ΔG_A) due mainly to the decrease in the dissociation constants .

On discussing the effect of ligands on the conductometric data , the ligands used are classified into three different groups depending upon their structure.

In case of 1:1 (metal : ligand ratio) stoichiometric complexes formed, it was found that group 3 gave the most association (K_A) alues than the first and the second group. This shows that following their abilities for forming complexes.

But in the case of 2:1 (metal: lagand ratio) stoichiometric complexes, it was found that the first group having more association than the second and the third ones, this is because the first group is less able to do electrostatic complexes with two transition metal ions than the other two groups. This may due to electron density which is smaller on the first group than the others.

According to the results of the first series it was observed that: The association constant of $CuSO_4$ in MeOH-H_2O in presence this series followed the order 1 > 3 > 2. This may be due to the electronegativity, which is greater in Br than that of I. This effect increase the electro-density for the compound tending to more complexation with copper.

So the free ions of copper which were found in solution in presence of compound (3) are more than that of compound (2) favouring more association of Cu^{++} with the former ligand than the latter.

In case of compound (1), it favours to make less complexation with copper than that with the compound 2 and 3, so more free ions of copper are available in solution and give higher association constant than compound 2 and 3.

According to the results of the second series it was observed that:

i) If we take compounds (a,d) the association constant of $CuSO_4$ in MeOH-H_2O in presence compounds (a,d) follow the order a>d this may be due to the more electronegativity of cyanide group than ethyl acetate. So compound (d) show more complexation with Cu^{2+} than compound (a), so the free ions of copper which is found in solution in presence of compound (a) are more than compound (d) so the association of Cu^{2+} with solvent is higher in presence of compound (a) than (d).

Also we found that in case of compounds (c) and (b) where the association constants of (b) are greater than (c) because of elctronegativity of cyanide group which is more than methyl ketone group.

ii) The association constant of compounds (c) and (b) are more than that of compounds (a) and (d) because of presence Br^- in compounds (a), (d) which tends more complexation than (b) and (c).

In the third series the association constant of $CuSO_4$ in MeOH-H_2O was found to follow the order III> IV. This may be due to the electronegativity which is greater in S than that of phenyl group. So compound IV give more complexation with copper than compound III.

Table (3.37a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (1) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	1.500	2.135	598.0	8.2	100.08	0.999	5.00	2.00	26.8
	1.60	1.280	2.135	598.0	8.7	100.09	0.999	7.10	1.40	27.7
	2.03	1.065	2.135	598.0	8.9	100.09	0.999	9.70	1.00	28.4
40	1.23	1.315	1.920	672.0	10.2	100.10	0.999	5.50	1.80	27.0
	1.60	1.110	1.920	672.0	10.6	100.11	0.999	7.80	1.30	27.9
	2.03	0.910	1.920	672.0	10.9	100.11	0.999	11.80	0.85	28.9
60	1.23	1.105	1.590	716.0	13.2	100.13	0.999	4.96	2.00	26.8
	1.60	0.940	1.590	716.0	13.8	100.14	0.999	7.30	1.40	27.7
	2.03	0.770	1.590	716.0	14.0	100.14	0.999	10.60	0.94	28.7

Table (3.37b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (1) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.450	0.715	207.4	11.5	100.100	0.999	3.80	2.63	26.1
	1.60	0.405	0.715	207.4	12.0	100.120	0.999	4.50	2.22	26.5
	2.03	0.315	0.715	207.4	12.5	100.130	0.999	7.00	1.43	27.6
40	1.23	0.410	0.670	237.2	13.85	100.138	0.999	4.20	2.40	26.4
	1.60	0.365	0.670	237.2	14.4	100.140	0.999	5.10	1.96	26.9
	2.03	0.280	0.670	237.2	14.9	100.150	0.999	7.75	1.30	27.9
60	1.23	0.335	0.540	248.4	18.1	100.180	0.999	3.90	2.56	26.2
	1.60	0.305	0.540	248.4	19.0	100.190	0.999	4.60	2.17	26.6
	2.03	0.235	0.540	248.4	19.7	100.200	0.999	7.70	1.30	27.9

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.38a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (2) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.825	1.120	313.6	8.4	100.08	0.999	4.0	2.50	26.3
	1.60	0.725	1.120	313.6	9.0	100.09	0.999	5.1	1.96	26.9
	2.03	0.625	1.120	313.6	9.4	100.09	0.999	6.8	1.50	27.6
40	1.23	0.740	1.020	357.0	10.5	100.11	0.999	4.3	2.30	26.4
	1.60	0.640	1.020	357.0	10.5	100.11	0.999	6.0	1.70	27.3
	2.03	0.540	1.020	403.0	11.5	100.12	0.999	8.2	1.20	28.0
60	1.23	0.665	0.895	403.0	13.6	100.14	0.999	3.8	2.60	26.1
	1.60	0.580	0.895	403.0	14.5	100.15	0.999	5.4	1.90	27.0
	2.03	0.500	0.895	403.0	15.2	100.15	0.999	7.0	1.40	27.6

Table (3.38b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (2) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	ΛoX 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.275	0.375	101.3	11.60	100.110	0.999	1.90	5.30	24.4
	3.03	0.255	0.375	101.3	12.30	100.120	0.999	2.20	4.50	24.8
	4.23	0.220	0.375	101.3	13.50	100.130	0.999	2.29	3.42	25.5
40	2.50	0.235	0.330	112.2	14.34	100.140	0.999	2.20	4.50	24.8
	3.03	0.220	0.330	112.2	15.30	100.150	0.999	2.30	4.35	24.9
	4.23	0.185	0.330	121.2	16.60	100.170	0.999	3.22	3.10	25.7
60	2.50	0.220	0.315	135.5	17.97	100.180	0.999	2.30	4.35	24.9
	3.03	0.205	0.315	135.5	19.10	100.185	0.999	2.80	3.60	25.4
	4.23	0.170	0.315	135.5	20.60	100.200	0.999	3.80	2.63	26.1

C in (mol/ l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.39a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (3) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.750	1.065	298.0	8.2	100.08	0.999	4.96	2.00	26.8
	1.60	0.640	1.065	298.0	8.7	100.09	0.999	6.4	1.60	27.4
	2.03	0.530	1.065	298.0	8.9	100.09	0.999	9.8	1.00	28.5
40	1.23	0.675	0.960	336.0	10.3	100.10	0.999	4.9	2.00	26.8
	1.60	0.575	0.960	336.0	10.8	100.11	0.999	7.1	1.40	27.7
	2.03	0.480	0.960	336.0	11.2	100.11	0.999	9.6	1.00	28.4
60	1.23	0.570	0.820	369.0	13.2	100.13	0.999	5.1	1.96	26.9
	1.60	0.480	0.820	369.0	13.8	100.14	0.999	7.2	1.40	27.7
	2.03	0.390	0.820	369.0	14.0	100.14	0.999	11.3	0.90	28.8

Table (3.39b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (3) for 2 : 1 association at 25°C in MeOH–H_2O mixture usirg Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.910	1.460	423.8	11.4	100.11	0.999	3.8	2.6	26.1
	3.03	0.815	1.460	423.8	11.9	100.12	0.999	4.6	2.2	26.6
	4.23	0.620	1.460	423.8	12.3	100.12	0.999	7.6	1.3	27.8
40	2.50	0.590	0.945	334.5	14.0	100.14	0.999	3.8	2.6	26.1
	3.03	0.535	0.945	334.5	14.7	100.15	0.999	4.5	2.2	26.5
	4.23	0.420	0.945	334.5	15.3	100.15	0.999	6.5	1.5	27.5
60	2.50	0.580	0.935	430.0	18.1	100.18	0.999	4.1	2.4	26.3
	3.03	0.525	0.935	430.0	19.0	100.19	0.999	4.5	2.2	26.5
	4.23	0.405	0.935	430.0	19.7	100.20	0.999	7.2	1.4	27.7

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.40a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (a) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.745	1.060	286.2	7.94	100.080	0.999	4.85	2.10	26.7
	1.60	0.625	1.060	286.2	8.30	100.083	0.999	7.40	1.40	27.8
	2.03	0.505	1.060	286.2	8.40	100.840	0.999	11.63	0.86	28.9
40	1.23	0.495	0.705	239.7	10.00	100.100	0.999	4.96	2.00	26.8
	1.60	0.420	0.705	239.7	10.50	100.110	0.999	7.10	1.40	27.7
	2.03	0.350	0.705	239.7	10.80	100.110	0.999	10.00	1.00	28.5
60	1.23	0.330	0.470	202.1	12.64	100.130	0.999	4.96	2.00	26.8
	1.60	0.285	0.470	202.1	13.40	100.134	0.999	6.60	1.52	27.5
	2.03	0.240	0.470	202.1	13.84	100.140	0.999	9.20	1.10	28.3

Table (3.40 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (a) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.680	1.055	306.0	11.6	100.12	0.999	3.4	2.9	25.9
	3.03	0.620	1.055	306.0	12.2	100.12	0.999	3.9	2.6	26.3
	4.23	0.495	1.055	306.0	12.9	100.13	0.999	5.7	1.8	27.2
40	1.23	0.645	0.970	343.4	11.4	100.11	0.999	3.0	3.3	25.5
	1.60	0.585	0.970	343.4	15.0	100.15	0.999	3.5	2.9	25.9
	2.03	0.475	0.970	343.4	16.0	100.16	0.999	5.0	2.0	26.8
60	1.23	0.565	0.830	381.8	19.0	100.19	0.999	2.8	3.6	25.4
	1.60	0.520	0.830	381.8	20.0	100.20	0.999	3.1	3.2	25.7
	2.03	0.425	0.830	381.8	21.4	100.21	0.999	4.4	2.3	26.6

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.41 a): The values of C, Λ , Λ◦ , $\gamma_{\pm}$,S , S(Z), K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (b) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.660	0.950	256.5	7.90	100.08	0.999	5.2	1.90	26.9
	1.60	0.550	0.950	256.5	8.20	100.08	0.999	7.7	1.30	27.9
	2.03	0.450	0.950	256.5	8.40	100.08	0.999	11.7	0.85	28.9
40	1.23	0.470	0.700	238.0	9.80	100.10	0.999	5.7	1.80	27.1
	1.60	0.390	0.700	238.0	10.20	100.10	0.999	9.3	1.10	28.3
	2.03	0.310	0.700	238.0	10.20	100.10	0.999	14.7	0.68	29.5
60	1.23	0.395	0.600	258.0	12.20	100.12	0.999	6.2	1.60	27.3
	1.60	0.325	0.600	258.0	12.65	100.13	0.999	10.1	1.00	28.5
	2.03	0.255	0.600	258.0	12.63	100.13	0.999	16.2	0.62	29.7

Table (3.41 b): The values of C, Λ, Λ◦ , $\gamma_{\pm}$, S , S(Z), K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (b) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.460	0.765	214.2	10.2	100.10	0.999	4.6	2.2	26.6
	3.03	0.410	0.765	214.2	11.3	100.11	0.999	5.5	1.8	27.1
	4.23	0.310	0.765	214.2	11.6	100.12	0.999	8.6	1.2	28.2
40	2.50	0.370	0.560	196.0	14.2	100.14	0.999	3.2	3.1	25.7
	3.03	0.340	0.560	196.0	15.0	100.15	0.999	3.6	2.8	26.0
	4.23	0.280	0.560	196.0	16.0	100.16	0.999	4.7	2.1	26.6
60	2.50	0.340	0.540	243.0	17.9	100.18	0.999	3.7	2.7	26.1
	3.03	0.305	0.540	243.0	18.6	100.19	0.999	4.6	2.2	26.6
	4.23	0.235	0.540	243.0	19.2	100.19	0.999	7.0	1.4	27.6

C in (mol / l), Λ and Λ◦ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.42 a): The values of C, Λ , Λ∘ , $\gamma_{\pm}$, S, S(Z), K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (c) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	2.360	3.375	945.0	8.20	100.08	0.999	5.2	1.92	26.9
	1.60	1.970	3.375	945.0	8.60	100.09	0.999	8.0	1.25	27.9
	2.03	1.575	3.375	945.0	8.60	100.09	0.999	12.0	0.83	29.0
40	1.23	1.730	2.650	928.0	9.90	100.10	0.999	6.7	1.50	27.5
	1.60	1.425	2.650	928.0	10.30	100.10	0.999	9.9	1.00	28.5
	2.03	1.125	2.650	928.0	10.30	100.10	0.999	15.5	0.65	29.6
60	1.23	1.390	2.030	914.0	13.10	100.13	0.999	5.5	1.80	27.0
	1.60	1.170	2.030	914.0	13.70	100.14	0.999	7.8	1.30	27.9
	2.03	0.960	2.030	914.0	13.95	100.14	0.999	11.9	0.84	28.9

Table (3.42 b): The values of C, Λ , Λ∘ , $\gamma_{\pm}$, S, S(Z), K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (c) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	1.190	1.960	549.0	10.9	100.11	0.999	4.20	2.40	26.4
	3.03	1.060	1.960	549.0	11.3	100.11	0.999	5.20	1.92	27.0
	4.23	0.800	1.960	549.0	11.6	100.12	0.999	8.30	1.20	28.1
40	2.50	0.850	1.405	492.0	13.6	100.14	0.999	4.40	2.30	26.5
	3.03	0.765	0.1405	492.0	14.2	100.14	0.999	5.11	196.00	26.9
	4.23	0.585	1.405	492.0	14.7	100.15	0.999	7.90	1.30	28.0
60	2.50	0.750	1.145	515.0	18.2	100.18	0.999	3.20	3.12	25.7
	3.03	0.685	1.145	515.0	19.1	100.19	0.999	3.60	2.80	26.0
	4.23	0.555	1.145	515.0	20.4	100.20	0.999	5.30	1.90	27.0

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.43 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (d) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	1.115	1.570	440.0	8.3	100.08	0.999	4.6	2.2	26.6
	1.60	0.970	1.570	440.0	8.8	100.09	0.999	6.0	1.7	27.3
	2.03	0.820	1.570	440.0	9.1	100.09	0.999	8.4	1.2	28.0
40	1.23	1.060	1.490	521.5	10.4	100.10	0.999	4.6	2.2	26.6
	1.60	0.915	1.490	521.5	11.0	100.11	0.999	6.2	1.6	27.3
	2.03	0.760	1.490	521.5	11.3	100.11	0.999	9.5	1.0	28.4
60	1.23	0.970	1.415	637.0	13.1	100.13	0.999	5.0	2.0	26.8
	1.60	0.815	1.415	637.0	13.7	100.14	0.999	8.0	1.3	28.0
	2.03	0.675	1.415	637.0	14.0	100.14	0.999	11.0	0.9	28.8

Table (3.43 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (d) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.345	0.470	132.0	12.0	100.12	0.999	1.9	5.00	24.4
	3.03	0.325	0.470	132.0	12.9	100.13	0.999	2.1	4.80	24.7
	4.23	0.280	0.470	132.0	14.1	100.14	0.999	2.6	3.80	25.2
40	2.50	0.305	0.420	147.0	14.9	100.15	0.999	2.1	4.80	24.7
	3.03	0.285	0.420	147.0	15.9	100.16	0.999	2.3	4.30	24.9
	4.23	0.235	0.420	147.0	17.0	100.17	0.999	3.3	3.00	25.8
60	2.50	0.250	0.310	139.5	16.0	100.16	0.999	1.2	0.83	23.3
	3.03	0.240	0.310	139.5	21.8	100.22	0.999	1.3	0.77	23.5
	4.23	0.225	0.310	139.5	24.9	100.25	0.999	1.2	0.83	23.3

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.44 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (III) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	2.060	2.950	855.50	8.5	100.09	0.999	5.10	1.96	26.9
	1.60	1.775	2.950	855.50	9.0	100.09	0.999	6.96	1.44	27.7
	2.03	1.500	2.950	855.50	9.3	100.09	0.999	9.50	1.10	28.4
40	1.23	1.870	2.725	964.65	10.0	100.10	0.999	5.40	1.90	24.9
	1.60	1.575	2.725	964.65	10.8	100.11	0.999	7.90	1.30	25.9
	2.03	1.275	2.725	964.65	10.9	100.11	0.999	11.90	0.84	27.0
60	1.23	1.650	2.460	1131.60	13.2	100.13	0.999	6.00	1.70	27.3
	1.60	1.375	2.460	1131.60	13.8	100.14	0.999	8.80	1.14	28.3
	2.03	1.100	2.460	1131.60	13.9	100.14	0.999	13.80	0.72	29.4

Table (3.44 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (III) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.290	0.460	124.2	10.7	100.11	0.999	3.80	2.63	26.1
	3.03	0.260	0.460	124.2	11.2	100.11	0.999	4.40	2.30	26.5
	4.23	0.220	0.460	124.2	12.1	100.12	0.999	5.60	1.80	27.1
40	2.50	0.230	0.350	119.0	13.8	100.14	0.999	3.00	3.30	25.5
	3.03	0.215	0.350	119.0	15.0	100.15	0.999	3.13	3.20	25.6
	4.23	0.185	0.350	119.0	16.0	100.16	0.999	3.90	2.60	26.2
60	2.50	0.210	0.310	133.3	17.7	100.18	0.999	2.93	3.40	25.5
	3.03	0.195	0.310	133.3	18.8	100.19	0.999	3.00	3.30	25.5
	4.23	0.170	0.310	133.3	20.7	100.20	0.999	3.63	2.75	26.0

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.45 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (IV) for 1 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.475	0.665	179.6	8.00	100.080	0.999	4.40	2.30	26.50
	1.60	0.415	0.665	179.6	8.50	100.080	0.999	5.70	1.75	27.10
	2.03	0.355	0.665	179.6	8.90	100.090	0.999	8.30	1.20	28.10
40	1.23	0.435	0.645	219.3	9.80	100.098	0.999	6.20	1.60	27.30
	1.60	0.370	0.645	219.3	10.30	100.100	0.999	8.00	1.25	28.00
	2.03	0.300	0.645	219.3	10.40	100.100	0.999	12.30	0.81	29.00
60	1.23	0.325	0.440	189.2	12.96	100.130	0.999	3.90	2.60	26.20
	1.60	0.290	0.440	189.2	13.96	100.140	0.999	4.53	2.20	26.66
	2.03	0.250	0.440	189.2	14.60	100.150	0.999	6.70	1.50	27.50

Table (3.45 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (IV) for 2 : 1 association at 25°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.610	0.835	234.0	12.0	100.12	0.999	2.0	5.0	24.5
	3.03	0.575	0.835	234.0	12.8	100.13	0.999	2.2	4.5	25.3
	4.23	0.500	0.835	234.0	14.1	100.14	0.999	2.7	3.7	25.8
40	2.50	0.560	0.810	284.0	14.6	100.15	0.999	2.6	3.8	25.2
	3.03	0.520	0.810	284.0	15.5	100.16	0.999	2.8	3.6	25.4
	4.23	0.440	0.810	284.0	16.8	100.17	0.999	3.6	2.8	26.0
60	2.50	0.505	0.750	338.0	18.5	100.19	0.999	2.8	3.6	25.4
	3.03	0.445	0.750	338.0	19.1	100.19	0.999	3.9	2.6	26.2
	4.23	0.380	0.750	338.0	20.9	100.21	0.999	4.7	2.1	26.7

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.46 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (1) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.915	1.375	398.8	8.30	100.080	0.999	6.30	1.60	27.8
	1.60	0.755	1.375	398.8	8.60	100.086	0.999	9.40	1.10	28.8
	2.03	0.600	1.375	398.8	863.00	100.086	0.999	14.80	0.68	30.0
40	1.23	0.825	1.235	437.2	10.10	100.100	0.999	6.10	1.64	27.8
	1.60	0.680	1.235	437.2	10.50	100.110	0.999	9.40	1.06	28.8
	2.03	0.550	1.235	437.2	10.64	100.110	0.999	13.94	0.72	29.8
60	1.23	0.660	0.985	453.1	13.20	100.130	0.999	8.80	1.14	28.7
	1.60	0.550	0.985	453.1	13.75	100.138	0.999	8.80	1.14	28.7
	2.03	0.440	0.985	453.1	13.85	100.139	0.999	13.70	0.73	29.8

Table (3.46 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (1) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.850	1.430	400.0	10.8	100.11	0.999	4.6	2.20	27.0
	3.03	0.750	1.430	400.0	11.1	100.11	0.999	5.6	1.80	27.5
	4.23	0.560	1.430	400.0	11.4	100.11	0.999	9.2	1.00	28.8
40	2.50	0.695	1.165	4.8	13.5	100.14	0.999	4.1	2.40	26.8
	3.03	0.620	1.165	408.0	14.1	100.14	0.999	5.4	1.90	27.5
	4.23	0.465	1.165	408.0	14.4	100.14	0.999	8.7	1.10	28.7
60	2.50	0.600	1.045	470.0	17.0	100.17	0.999	5.1	0.94	29.0
	3.03	0.525	1.045	470.0	17.5	100.18	0.999	6.4	1.96	27.3
	4.23	0.375	1.045	470.0	17.5	100.18	0.999	11.6	1.60	27.9

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.47 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (2) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.905	1.280	371.2	8.55	100.09	0.999	4.80	2.1	27.2
	1.60	0.775	1.280	371.2	8.90	100.09	0.999	6.90	1.4	28.1
	2.03	0.640	1.280	371.2	9.20	100.09	0.999	9.80	1.0	29.0
40	1.23	0.825	1.165	412.4	10.40	100.10	0.999	4.80	2.1	27.2
	1.60	0.700	1.165	412.4	11.00	100.11	0.999	7.00	1.4	28.1
	2.03	0.585	1.165	412.4	11.30	100.11	0.999	9.60	1.0	28.9
60	1.23	0.745	1.060	487.6	13.50	100.14	0.999	4.95	2.0	27.2
	1.60	0.640	1.060	487.6	14.30	100.15	0.999	6.90	1.4	28.1
	2.03	0.530	1.060	487.6	14.70	100.15	0.999	9.60	1.0	28.9

Table (3.47 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (2) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.525	0.206	735.0	11.8	100.12	0.999	2.3	4.3	25.3
	3.03	0.490	0.206	735.0	12.6	100.13	0.999	2.4	4.2	25.4
	4.23	0.420	0.206	735.0	13.8	100.14	0.999	3.1	3.2	26.1
40	2.50	0.445	0.217	620.0	14.8	100.15	0.999	2.2	4.5	25.2
	3.03	0.415	0.217	620.0	15.8	100.16	0.999	2.3	4.3	25.3
	4.23	0.355	0.217	620.0	17.2	100.17	0.999	3.1	3.2	26.0
60	2.50	0.420	0.261	580.0	19.1	100.19	0.999	1.8	5.6	24.7
	3.03	0.390	0.261	580.0	20.3	100.20	0.999	2.3	4.3	25.3
	4.23	0.330	0.261	580.0	22.1	100.22	0.999	3.1	3.2	26.1

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.48 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (3) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	1.715	2.475	717.8	8.50	100.09	0.999	5.2	1.90	27.4
	1.60	1.450	2.475	717.8	8.90	100.09	0.999	7.6	1.30	28.3
	2.03	1.180	2.475	717.8	9.00	100.09	0.999	11.3	0.88	29.3
40	1.23	1.065	1.510	534.5	10.40	100.10	0.999	4.8	2.10	27.2
	1.60	0.905	1.510	534.5	11.00	100.11	0.999	7.2	1.40	28.2
	2.03	0.755	1.510	534.5	11.30	100.11	0.999	10.0	0.10	29.0
60	1.23	1.035	1.475	678.5	13.50	100.14	0.999	4.8	2.10	27.2
	1.60	0.875	1.475	678.5	14.20	100.14	0.999	7.2	1.40	28.2
	2.03	0.785	1.475	14.6	100.15	100.15	0.999	10.0	1.00	29.0

Table (3.48 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (3) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.420	0.700	196.0	10.8	100.11	0.999	4.65	2.20	27.0
	3.03	0.375	0.700	196.0	11.3	100.11	0.999	5.50	1.80	27.5
	4.23	0.285	0.700	196.0	11.6	100.12	0.999	8.50	1.20	28.6
40	2.50	0.385	0.625	222.0	13.9	100.14	0.999	3.90	2.60	26.6
	3.03	0.345	0.625	222.0	14.5	100.15	0.999	5.10	1.96	27.3
	4.23	0.260	0.625	222.0	14.9	100.15	0.999	7.95	1.30	28.4
60	2.50	0.305	0.495	223.0	17.7	100.18	0.999	3.84	2.60	26.6
	3.03	0.275	0.495	223.0	18.5	100.19	0.999	4.93	2.00	27.2
	4.23	0.210	0.495	223.0	19.1	100.19	0.999	7.40	1.40	28.2

C in (mol /l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.49 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (a) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.820	1.170	327.6	8.2	100.08	0.999	5.0	2.00	27.3
	1.60	0.700	1.170	327.6	8.7	100.09	0.999	7.1	1.40	28.0
	2.03	0.580	1.170	327.6	8.9	100.09	0.999	9.9	1.00	29.0
40	1.23	0.760	1.120	392.0	10.1	100.10	0.999	5.7	1.80	27.6
	1.60	0.635	1.120	392.0	10.5	100.11	0.999	8.5	1.20	28.6
	2.03	0.505	1.120	392.0	10.6	100.11	0.999	13.6	0.74	29.8
60	1.23	0.625	0.900	405.0	13.2	100.13	0.999	5.1	2.00	27.3
	1.60	0.530	0.900	405.0	13.8	100.14	0.999	7.4	1.40	28.2
	2.03	0.435	0.900	405.0	14.1	100.14	0.999	10.9	0.90	29.2

Table (3.49 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (a) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.665	1.105	309.0	10.8	100.11	0.999	4.3	2.3	26.9
	3.03	0.600	1.105	309.0	11.3	100.11	0.999	5.2	1.9	27.4
	4.23	0.460	1.105	309.0	11.7	100.12	0.999	8.1	1.2	28.5
40	2.50	0.615	0.945	331.0	14.0	100.14	0.999	3.4	2.9	26.3
	3.03	0.560	0.945	331.0	14.8	100.15	0.999	3.8	2.6	26.6
	4.23	0.450	0.945	331.0	15.7	100.16	0.999	5.5	1.8	24.5
60	2.50	0.535	0.775	349.0	18.7	100.19	0.999	2.7	3.7	25.7
	3.03	0.490	0.775	349.0	19.7	100.20	0.999	3.8	2.6	26.6
	4.23	0.410	0.775	349.0	21.3	100.21	0.999	4.0	2.5	26.7

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.50 a): The values of C , Λ , Λ∘ , $\gamma_{\pm}$, S , S(Z) , K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (b) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.700	1.005	281.4	8.20	100.08	0.999	4.9	2.00	27.2
	1.60	0.575	1.005	281.4	8.50	100.09	0.999	8.3	1.20	28.5
	2.03	0.400	1.005	281.4	8.50	100.09	0.999	13.2	0.76	29.7
40	1.23	0.610	0.910	318.5	10.00	100.10	0.999	5.9	1.70	27.7
	1.60	0.505	0.910	318.5	10.40	100.10	0.999	9.1	1.10	28.8
	2.03	0.405	0.910	318.5	10.50	100.11	0.999	14.2	0.70	29.9
60	1.23	0.565	0.870	391.5	12.70	100.13	0.999	6.7	1.50	28.0
	1.60	0.460	0.870	391.5	12.70	100.13	0.999	11.0	0.90	29.2
	2.03	0.355	0.870	391.5	12.95	100.13	0.999	18.0	0.56	30.4

Table (3.50 b): The values of C, Λ , Λ∘ , $\gamma_{\pm}$, S, S(Z), K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (b) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.600	0.810	234.9	12.5	100.13	0.999	1.9	5.30	24.8
	3.03	0.565	0.810	234.9	13.3	100.13	0.999	2.1	4.80	25.1
	4.23	0.495	0.810	234.9	15.3	100.15	0.999	2.5	4.00	25.5
40	2.50	0.460	0.800	283.2	13.4	100.13	0.999	5.4	1.85	27.5
	3.03	0.395	0.800	283.2	13.7	100.14	0.999	6.8	1.50	28.0
	4.23	0.280	0.800	283.2	14.0	100.14	0.999	12.4	0.80	29.5
60	2.50	0.365	0.620	285.2	17.6	100.18	0.999	4.8	2.10	27.2
	3.03	0.320	0.620	285.2	18.2	100.18	0.999	5.8	1.72	27.6
	4.23	0.240	0.620	285.2	19.0	100.19	0.999	9.8	1.00	29.0

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.51 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (c) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.760	1.120	324.8	8.40	0.999	0.0093	5.7	1.80	27.6
	1.60	0.635	1.120	324.8	8.73	0.999	0.0100	8.5	1.20	28.7
	2.03	0.510	1.120	324.8	8.80	0.999	0.0100	13.4	0.75	29.4
40	1.23	0.690	1.040	368.2	10.10	0.999	0.0085	6.2	1.60	27.8
	1.60	0.570	1.040	368.2	10.50	0.999	0.0090	9.5	1.10	28.8
	2.03	0.450	1.040	368.2	10.50	0.999	0.0090	15.1	0.66	30.0
60	1.23	0.600	0.880	404.8	13.30	0.999	0.0074	5.5	1.80	27.5
	1.60	0.500	0.880	404.8	13.19	0.999	0.0080	8.3	1.20	28.5
	2.03	0.400	0.880	404.8	14.00	0.999	0.0080	13.2	0.76	29.7

Table (3.51 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (c) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	1.210	1.975	573.0	11.4	100.11	0.999	4.2	2.40	26.8
	3.03	1.075	1.975	573.0	11.8	100.12	0.999	5.0	2.00	27.2
	4.23	0.820	1.975	573.0	12.2	100.12	0.999	7.9	1.30	28.4
40	2.50	0.800	1.325	469.0	13.8	100.14	0.999	4.3	2.30	26.9
	3.03	0.710	1.325	469.0	14.3	100.14	0.999	5.2	1.92	27.5
	4.23	0.560	1.325	469.0	15.0	100.15	0.999	7.5	1.33	28.4
60	2.50	0.770	1.190	547.0	18.5	100.19	0.999	3.4	2.90	26.3
	3.03	0.700	1.190	547.0	19.4	100.19	0.999	3.9	2.60	26.6
	4.23	0.540	1.190	547.0	20.1	100.20	0.999	6.2	1.60	27.9

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.52 a): The values of C, Λ , Λ∘ , $\gamma_{\pm}$, S, S(Z), K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (d) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.930	1.260	365.4	8.73	100.09	0.999	4.1	2.40	26.7
	1.60	0.820	1.260	365.4	9.40	100.09	0.999	5.2	1.90	27.4
	2.03	0.710	1.260	3654.0	9.80	100 10	0.999	7.0	1.40	28.1
40	1.23	0.820	1.160	410.6	10.40	100.1	0.999	4.8	2.10	27.2
	1.60	0.700	1.160	410.6	11.00	100.11	0.999	6.9	1.40	28.1
	2.03	0.580	1.160	410.6	11.30	100.11	0.999	9.6	1.00	29.0
60	1.23	0.680	0.990	455.4	13.40	100.13	0.999	5.4	1.90	27.5
	1.60	0.575	0.990	455.4	14.00	100.14	0.999	7.9	1.30	28.5
	2.03	0.470	0.990	455.4	14.30	100.14	0.999	10.9	0.92	29.3

Table (3.52 b): The values of C, Λ , Λ∘ , $\gamma_{\pm}$, S, S(Z), K_A , K_D , and ΔG_A of CuSO4 in presence of compound (d) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.390	0.595	160.7	10.9	100.10	0.999	3.20	3.13	26.1
	3.03	0.345	0.595	160.7	11.3	100.11	0.999	4.40	2.30	26.9
	4.23	0.285	0.595	160.7	12.2	100.12	0.999	5.40	1.85	27.4
40	2.50	0.330	0.440	149.6	14.7	100.15	0.999	1.80	5.60	24.7
	3.03	0.310	0.440	149.6	15.7	100.16	0.999	1.95	5.13	24.9
	4.23	0.275	0.440	149.6	17.5	100.18	0.999	2.20	4.55	25.2
60	2.50	0.190	0.255	110.0	18.6	100.19	0.999	1.84	5.40	24.7
	3.03	0.180	0.255	110.0	19.9	100.20	0.999	1.92	5.20	25.0
	4.23	0.160	0.255	110.0	22.2	100.22	0.999	2.20	4.50	25.4

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l)

Table (3.53 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (III) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	1.145	1.730	501.7	8.3	100.08	0.999	6.3	1.60	27.8
	1.60	0.945	1.730	501.7	8.6	100.09	0.999	9.6	1.00	28.9
	2.03	0.745	1.730	501.7	8.6	100.09	0.999	15.2	0.66	30.1
40	1.23	0.820	1.175	416.0	10.4	100.10	0.999	5.1	1.96	27.3
	1.60	0.695	1.175	416.0	10.9	100.11	0.999	7.4	1.35	28.2
	2.03	0.570	1.175	416.0	11.1	100.11	0.999	10.4	0.96	29.1
60	1.23	0.610	0.900	414.0	13.3	100.13	0.999	5.7	1.80	27.6
	1.60	0.510	0.900	414.0	13.9	100.14	0.999	8.6	1.20	28.6
	2.03	0.410	0.900	414.0	13.9	100.14	0.999	8.6	1.20	28.6

Table (3.53 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (III) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	1.220	1.960	568.4	11.4	100.11	0.999	3.95	2.50	26.7
	3.03	1.090	1.960	568.4	11.9	100.12	0.999	4.70	2.10	27.1
	4.23	0.840	1.960	568.4	12.3	100.12	0.999	7.90	1.27	28.5
40	2.50	0.975	1.590	562.9	13.9	100.14	0.999	4.20	2.40	26.8
	3.03	0.870	1.590	562.9	14.4	100.14	0.999	5.10	1.96	27.3
	4.23	0.670	1.590	562.9	14.9	100.15	0.999	7.80	1.30	28.3
60	2.50	0.825	1.240	570.4	18.8	100.19	0.999	3.00	3.30	26.0
	3.03	0.745	1.240	570.4	19.6	100.20	0.999	3.60	2.80	26.5
	4.23	0.590	1.240	570.4	20.6	100.21	0.999	5.40	1.90	27.5

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.54 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (IV) for 1 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	1.055	1.525	411.8	7.90	100.0790	0.999	5.20	1.92	27.4
	1.60	0.890	1.525	411.8	8.30	100.0830	0.999	7.80	1.30	28.4
	2.03	0.715	1.525	411.8	8.33	100.0830	0.999	11.90	0.84	29.4
40	1.23	0.905	1.300	442.0	9.95	100.0995	0.999	5.14	1.95	27.3
	1.60	0.765	1.300	442.0	10.40	100.1000	0.999	7.60	1.32	28.2
	2.03	0.635	1.300	442.0	10.70	100.1070	0.999	10.45	0.96	29.0
60	1.23	0.440	0.660	283.8	12.30	100.1230	0.999	6.10	1.64	27.8
	1.60	0.375	0.660	283.8	12.30	100.1300	0.999	8.33	1.20	28.6
	2.03	0.305	0.660	283.8	13.20	100.1320	0.999	12.40	8.10	29.6

Table (3.54 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (IV) for 2 : 1 association at 30°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.550	0.715	207.4	12.7	100.13	0.999	1.5	6.67	24.2
	3.03	0.525	0.715	207.4	13.7	100.14	0.999	1.6	6.30	24.4
	4.23	0.470	0.715	207.4	15.3	100.15	0.999	1.9	5.30	24.8
40	2.50	0.435	0.695	246.0	14.0	100.14	0.999	3.8	2.60	26.6
	3.03	0.390	0.695	246.0	14.6	100.15	0.999	4.5	2.20	27.0
	4.23	0.300	0.695	246.0	15.1	100.15	0.999	7.0	1.40	28.2
60	2.50	0.310	0.485	223.0	18.4	100.18	0.999	3.5	2.90	26.4
	3.03	0.280	0.485	223.0	19.2	100.19	0.999	4.2	2.40	26.9
	4.23	0.220	0.485	223.0	20.1	100.20	0.999	6.5	1.50	28.0

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.55 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (1) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.765	0.1125	303.8	7.80	100.078	0.999	5.6	1.80	28.0
	1.60	0.640	0.1125	303.8	8.23	100.082	0.999	12.7	0.79	30.1
	2.03	0.515	0.1125	303.8	8.23	100.082	0.999	12.7	0.79	30.1
40	1.23	0.610	0.915	311.1	9.74	100.097	0.999	6.1	6.10	28.2
	1.60	0.510	0.915	311.1	9.74	100.097	0.999	8.4	1.20	29.0
	2.03	0.410	0.915	311.1	10.25	100.100	0.999	13.6	0.74	30.3
60	1.23	0.470	0.715	307.5	12.23	100.120	0.999	6.4	1.56	28.3
	1.60	0.380	0.715	307.5	12.54	100.125	0.999	10.3	0.97	29.6
	2.03	0.300	0.715	307.5	12.55	100.126	0.999	16.2	0.62	30.7

Table (3.55 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (1) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.395	0.745	201.2	9.80	100.098	0.999	6.65	1.50	28.4
	3.03	0.340	0.745	201.2	10.00	100.100	0.999	8.60	1.20	29.1
	4.23	0.225	0.745	201.2	9.70	100.097	0.999	18.0	0.56	31.0
40	2.50	0.305	0.530	180.2	12.90	100.130	0.999	5.10	1.96	27.8
	3.03	0.270	0.530	180.2	13.35	100.134	0.999	6.20	1.61	28.3
	4.23	0.190	0.530	180.2	13.24	100.132	0.999	11.8	0.85	29.9
60	3.50	0.220	0.330	142.0	17.90	100.180	0.999	3.00	3.30	26.4
	3.03	0.200	0.330	142.0	18.44	100.185	0.999	3.50	2.90	26.8
	4.23	0.160	0.330	142.0	19.50	100.200	0.999	5.10	1.96	27.8

C in (mol /l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.56 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (2) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.495	0.725	195.8	7.83	100.078	0.999	5.6	1.79	28.0
	1.60	0.420	0.725	195.8	8.22	100.080	0.999	7.5	1.33	28.7
	2.03	0.345	0.725	195.8	8.40	100.080	0.999	11.4	0.88	29.8
40	1.23	0.415	0.605	205.7	9.90	100.099	0.999	5.5	1.82	28.0
	1.60	0.355	0.605	205.7	10.42	100.104	0.999	7.1	1.40	28.6
	2.03	0.290	0.605	205.7	10.60	100.106	0.999	10.9	0.92	29.7
60	1.23	0.405	0.590	253.7	12.50	100.120	0.999	5.4	1.85	27.9
	1.60	0.345	0.590	253.7	13.15	100.125	0.999	7.0	1.43	28.6
	2.03	0.285	0.590	253.7	13.50	100.126	0.999	10.5	0.95	29.6

Table (3.56 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (2) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.510	0.790	229.1	11.7	100.12	0.999	3.10	3.20	26.5
	3.03	0.460	0.790	229.1	12.2	100.12	0.999	4.00	2.50	27.1
	4.23	0.370	0.790	229.1	13.0	100.13	0.999	5.60	1.80	28.0
40	2.50	0.460	0.690	244.3	14.5	100.15	0.999	3.12	3.20	26.5
	3.03	0.425	0.690	244.3	15.3	100.15	0.999	3.30	3.00	26.6
	4.23	0.345	0.690	244.3	16.3	100.16	0.999	4.60	2.20	27.5
60	2.50	0.425	0.600	276.0	19.4	100.19	0.999	2.23	4.50	25.6
	3.03	0.495	0.600	276.0	20.5	100.21	0.999	2.60	3.80	26.0
	4.23	0.340	0.600	276.0	22.5	100.23	0.999	3.20	3.12	26.6

C in (mol /l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.57 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (3) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.630	0.965	260.6	7.70	100.08	0.999	6.4	1.60	28.3
	1.60	0.520	0.965	260.6	7.90	100.08	0.999	10.3	0.97	29.6
	2.03	0.400	0.965	260.6	7.83	100.08	0.999	17.0	0.60	30.8
40	1.23	0.545	0.820	278.8	9.70	100.10	0.999	5.9	1.70	28.0
	1.60	0.450	0.820	278.8	10.10	100.10	0.999	9.6	1.00	29.4
	2.03	0.355	0.820	278.8	10.10	100.10	0.999	15.3	0.65	30.6
60	1.23	0.460	0.690	296.7	12.30	100.12	0.999	5.7	1.80	28.0
	1.60	0.380	0.690	296.7	12.80	100.13	0.999	9.4	1.10	29.3
	2.03	0.305	0.690	296.7	12.90	100.13	0.999	14.0	0.70	30.3

Table (3.57 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (3) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.285	0.495	133.7	10.2	100.10	0.999	5.2	1.90	27.8
	3.03	0.255	0.495	133.7	10.7	100.11	0.999	5.8	1.70	28.0
	4.23	0.190	0.495	133.7	10.9	100.11	0.999	9.9	1.00	29.5
40	2.50	0.265	0.460	156.4	12.9	100.13	0.999	5.1	1.96	28.1
	3.03	0.230	0.460	156.4	13.2	100.13	0.999	6.6	1.50	28.4
	4.23	0.170	0.460	156.4	13.4	100.13	0.999	10.9	0.92	29.7
60	2.50	0.230	0.415	178.5	16.0	100.16	0.999	5.8	1.70	28.1
	3.03	0.195	0.415	178.5	16.2	100.16	0.999	7.9	1.30	28.9
	4.23	0.140	0.415	178.5	16.2	100.16	0.999	13.8	0.72	30.3

C in (mol /l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l) .

Table (3.58 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (a) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	1.280	1.860	539.4	8.40	100.08	0.999	5.30	1.90	27.9
	1.60	1.075	1.860	539.4	8.80	100.08	0.999	7.97	1.30	28.9
	2.03	0.875	1.860	539.4	8.96	100.09	0.999	11.60	0.86	29.9
40	1.23	1.190	1.055	6124.0	10.30	100.10	0.999	5.20	1.90	27.8
	1.60	1.005	1.055	612.4	10.80	100.11	0.999	7.80	1.30	28.8
	2.03	0.825	1.055	612.4	11.00	100.11	0.999	11.40	0.88	29.8
60	1.23	1.060	1.730	717.6	13.90	100.14	0.999	8.30	1.20	29.0
	1.60	0.895	1.730	717.6	13.90	100.14	0.999	8.30	1.20	29.0
	2.03	0.725	1.730	717.6	14.00	100.14	0.999	11.90	0.84	29.9

Table (3.58 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (a) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.380	0.610	164.7	10.7	100.110	0.999	3.9	2.60	27.1
	3.03	0.345	0.610	164.7	11.2	100.110	0.999	4.7	2.10	27.6
	4.23	0.265	0.610	164.7	11.6	100.120	0.999	7.2	1.40	28.6
40	2.50	0.275	0.485	165.0	12.8	100.130	0.999	5.3	1.90	27.9
	3.03	0.240	0.485	165.0	13.2	100.132	0.999	6.8	1.50	28.5
	4.23	0.175	0.485	165.0	13.3	100.133	0.999	11.6	0.86	29.8
60	2.50	0.190	0.280	120.4	17.7	100.180	0.999	2.8	3.60	26.2
	3.03	0.175	0.280	120.4	18.2	100.182	0.999	3.2	3.10	26.5
	4.23	0.145	0.280	120.4	20.1	100.200	0.999	4.3	2.30	27.2

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.59 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (b) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	2.430	3.540	1026.6	8.7	100.08	0.999	5.40	1.90	27.9
	1.60	2.010	3.540	1026.6	8.7	100.09	0.999	8.96	1.10	29.2
	2.03	1.605	3.540	1026.6	8.8	100.09	0.999	12.90	0.78	30.0
40	1.23	1.750	2.760	977.0	9.9	100.10	0.999	7.20	1.40	28.6
	1.60	1.460	2.760	977.0	10.3	100.10	0.999	10.70	0.93	29.7
	2.03	1.120	2.760	977.0	10.2	100.10	0.999	17.50	0.57	30.9
60	1.23	1.510	2.225	1023.5	13.3	100.13	0.999	5.50	1.80	28.0
	1.60	1.260	2.225	1023.5	13.8	100.14	0.999	8.80	1.10	29.1
	2.03	1.120	2.225	1023.5	14.7	100.15	0.999	9.50	1.10	29.3

Table (3.59 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of CuSO4 in presence of compound (b) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.345	0.625	168.8	10.0	100.10	0.999	5.60	1.80	28.0
	3.03	0.295	0.625	168.8	10.2	100.10	0.999	7.80	1.30	28.8
	4.23	0.205	0.625	168.8	10.1	100.10	0.999	14.20	0.70	29.3
40	2.50	0.235	0.450	153.0	12.3	100.12	0.999	6.80	1.50	28.5
	3.03	0.200	0.450	153.0	12.5	100.13	0.999	9.40	1.10	29.3
	4.23	0.130	0.450	153.0	11.9	100.12	0.999	18.40	0.54	31.0
60	2.50	0.190	0.370	159.1	15.4	100.15	0.999	6.98	1.43	28.6
	3.03	0.165	0.370	159.1	15.8	100.16	0.999	9.20	1.10	29.3
	4.23	0.105	0.370	159.1	14.9	100.15	0.999	23.30	0.43	31.6

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.60 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (c) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.745	1.125	303.8	7.70	100.08	0.999	6.40	1.60	28.3
	1.60	0.615	1.125	303.8	8.00	100.08	0.999	9.30	1.10	29.2
	2.03	0.480	1.125	303.8	7.94	100.08	0.999	15.00	0.67	30.4
40	1.23	0.605	0.875	297.5	9.90	100.10	0.999	5.60	1.80	28.0
	1.60	0.510	0.875	297.5	10.40	100.10	0.999	7.80	1.30	28.8
	2.03	0.410	0.875	297.5	10.50	100.11	0.999	12.40	0.80	30.0
60	1.23	0.530	0.790	339.7	12.40	100.12	0.999	5.52	1.80	28.0
	1.60	0.445	0.790	339.7	12.90	100.13	0.999	8.70	1.10	29.1
	2.03	0.350	0.790	339.7	12.90	100.13	0.999	14.20	0.70	30.3

Table (3.60 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (c) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.350	0.635	158.8	9.30	100.09	0.999	5.7	1.80	28.0
	3.03	0.300	0.635	158.8	9.46	100.09	0.999	7.9	1.30	28.8
	4.23	0.205	0.635	158.8	9.24	100.09	0.999	14.8	0.68	30.4
40	2.50	0.315	0.570	193.8	12.60	100.13	0.999	5.8	1.70	28.1
	3.03	0.265	0.570	193.8	12.80	100.13	0.999	8.2	1.20	28.9
	4.23	0.175	0.570	193.8	12.30	100.12	0.999	18.3	0.55	29.0
60	2.50	0.260	0.460	197.8	16.20	100.16	0.999	5.9	1.70	28.1
	3.03	0.230	0.460	197.8	16.70	100.17	0.999	6.5	1.54	28.4
	4.23	0.160	0.460	197.8	16.50	100.17	0.999	12.3	0.80	29.9

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l) .

Table (3.61 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (d) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.680	0.950	256.5	8.0	100.080	0.999	4.50	2.22	27.4
	1.60	0.575	0.950	256.5	8.4	100.084	0.999	6.90	1.45	28.4
	2.03	0.485	0.950	256.5	8.7	100.087	0.999	9.10	1.10	29.1
40	1.23	0.540	0.760	258.4	10.1	100.100	0.999	4.70	2.13	27.5
	1.60	0.470	0.760	258.4	10.7	100.100	0.999	6.20	1.60	28.1
	2.03	0.400	0.760	258.4	11.1	100.110	0.999	8.50	1.18	28.8
60	1.23	0.380	0.565	243.0	12.4	100.120	0.999	5.83	1.72	28.0
	1.60	0.320	0.565	243.0	12.9	100.130	0.999	8.63	1.16	29.0
	2.03	0.255	0.565	243.0	13.0	100.130	0.999	13.20	0.76	30.0

Table (3.61 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (d) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.385	0.585	169.7	11.8	100.12	0.999	3.15	3.2	26.5
	3.03	0.350	0.585	169.7	12.4	100.12	0.999	3.6	2.8	26.9
	4.23	0.280	0.585	169.7	13.1	100.13	0.999	5.3	1.9	27.9
40	2.50	0.330	0.465	164.6	14.9	100.15	0.999	2.4	4.2	25.8
	3.03	0.305	0.465	164.6	15.8	100.16	0.999	2.7	3.7	26.0
	4.23	0.260	0.465	164.6	17.2	100.17	0.999	3.3	3.0	26.6
60	2.50	0.300	0.460	211.6	18.6	100.19	0.999	3.3	3.0	26.6
	3.03	0.275	0.460	211.6	19.6	100.20	0.999	3.8	2.6	27.0
	4.23	0.220	0.460	211.6	20.7	100.21	0.999	5.6	1.8	28.0

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l) .

Table (3.62 a): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (III) for 1 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	0.725	1.095	307.0	8.0	100.08	0.999	6.2	1.6	28.3
	2.03	0.600	1.095	307.0	8.3	100.08	0.999	9.0	1.1	29.2
	2.50	0.460	1.095	307.0	8.2	100.08	0.999	16.8	0.6	30.8
40	1.23	0.675	1.040	364.0	9.9	100.10	0.999	7.0	1.4	28.6
	2.03	0.555	1.040	364.0	10.2	100.10	0.999	10.0	1.0	29.5
	2.50	0.430	1.040	364.0	10.1	100.10	0.999	16.4	0.6	30.7
60	1.23	0.595	0.910	409.5	12.8	100.13	0.999	6.9	1.4	28.5
	1.60	0.490	0.910	409.5	13.2	100.13	0.999	9.7	1.0	29.3
	2.03	0.380	0.910	409.5	13.1	100.13	0.999	5.8	0.6	30.6

Table (3.62 b): The values of C, Λ, Λ∘, $\gamma_{\pm}$, S, S(Z), K_A, K_D, and ΔG_A of $CuSO_4$ in presence of compound (III) for 2 : 1 association at 35°C in MeOH–H_2O mixture using Fuoss – Shedlovsky method.

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.545	1.030	278.0	9.82	100.098	0.999	6.53	1.53	28.4
	3.03	0.470	1.030	278.1	10.00	100.100	0.999	8.63	1.16	29.1
	4.23	0.310	1.030	278.1	9.63	100.096	0.999	18.40	0.54	30.9
40	2.50	0.505	0.920	312.8	12.60	100.126	0.999	6.00	1.67	28.2
	3.03	0.430	0.920	312.8	12.80	100.128	0.999	8.00	1.25	28.9
	4.23	0.290	0.920	312.8	12.40	100.124	0.999	16.63	0.60	30.7
60	2.50	0.235	0.425	182.8	16.00	100.160	0.999	5.80	1.72	28.1
	3.03	0.205	0.425	182.8	16.44	100.164	0.999	7.30	1.37	28.6
	4.23	0.135	0.425	182.8	15.80	100.158	0.999	16.00	0.63	30.6

C in (mol / l), Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}), K_A (mol / l), K_D (mol^{-1} . l).

Table (3.63 a) : The values of C , Λ , Λ∘ , $\gamma_{\pm}$, S , S(Z) , K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (IV) for 1 : 1 association at 35 °C in MeOH–H_2O mixture using Fuoss – Shedlovsky method .

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	1.23	1.320	2.075	581.0	7.8	100.08	0.999	7.4	1.40	28.7
	1.60	1.065	2.075	581.0	8.0	100.08	0.999	11.6	0.86	29.9
	2.03	0.855	2.075	581.0	8.1	100.08	0.999	17.4	0.57	30.9
40	1.23	1.185	1.845	646.0	9.8	100.10	0.999	6.8	1.50	28.5
	1.60	0.965	1.845	646.0	10.0	100.10	0.999	11.2	0.89	29.8
	2.03	0.775	1.845	646.0	10.2	100.10	0.999	15.9	0.63	30.7
60	1.23	0.995	1.520	684.0	12.8	100.13	0.999	6.7	1.50	28.5
	1.60	0.850	1.520	684.0	13.5	100.14	0.999	8.5	1.20	29.1
	2.03	0.675	1.520	684.0	13.5	100.14	0.999	13.6	0.74	30.3

Table (3.63 b) : The values of C , Λ , Λ∘ , $\gamma_{\pm}$, S , S(Z) , K_A , K_D , and ΔG_A of $CuSO_4$ in presence of compound (IV) for 2 : 1 association at 35 °C in MeOH–H_2O mixture using Fuoss – Shedlovsky method .

Vol. % of Me OH	C X 10^5	Λ X 10^{-3}	Λo X 10^{-3}	S	Z X 10^4	S(Z) X 10^2	$\gamma_{\pm}$	K_A X 10^{-4}	K_D X 10^5	$-\Delta G_A$ K.J / Mol.
20	2.50	0.335	0.495	139.0	11.6	100.12	0.999	2.9	3.4	26.3
	3.03	0.305	0.495	139.0	12.1	100.12	0.999	3.4	2.9	26.7
	4.23	0.250	0.495	139.0	13.0	100.13	0.999	4.4	2.3	27.3
40	2.50	0.305	0.460	161.0	14.2	100.14	0.999	2.9	3.4	26.3
	3.03	0.275	0.460	161.0	14.9	100.15	0.999	3.9	2.6	27.0
	4.23	0.220	0.460	161.0	15.7	100.16	0.999	5.6	1.7	28.1
60	2.50	0.270	0.425	191.0	17.9	100.18	0.999	3.5	2.9	26.8
	3.03	0.245	0.425	191.0	18.8	100.19	0.999	4.4	2.3	27.3
	4.23	0.185	0.425	191.0	19.3	100.19	0.999	6.9	1.4	28.5

C in (mol / l) , Λ and Λ∘ in (Ω^{-1} cm^{-2} mol^{-1}) , K_A (mol / l) , K_D (mol^{-1} . l).

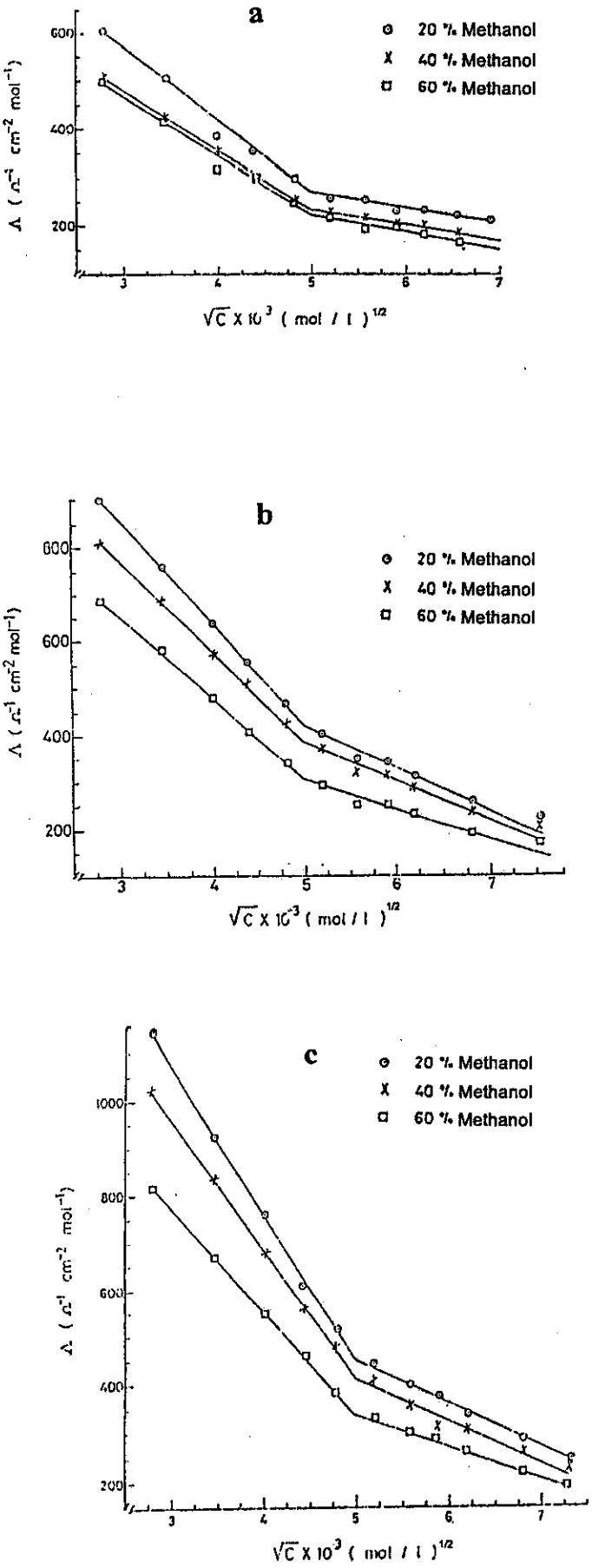
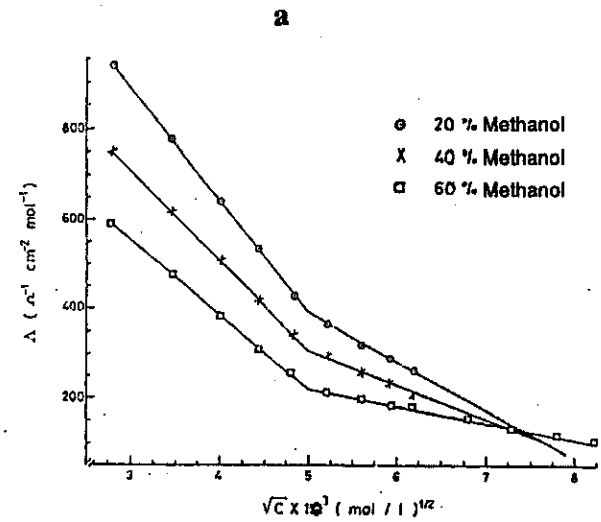
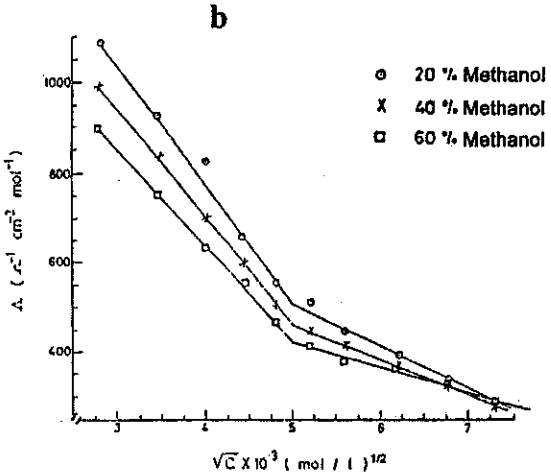


Fig (3.140): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (1) at: (a) 25°C, (b) 30°C and (C) 35°C.





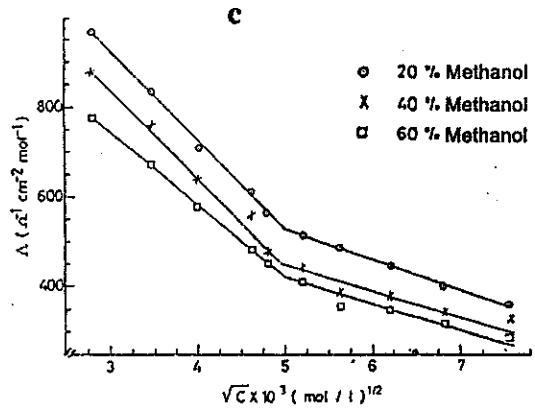


Fig (3.141): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (2) at: (a) 25°C, (b) 30°C and (C) 35°C.

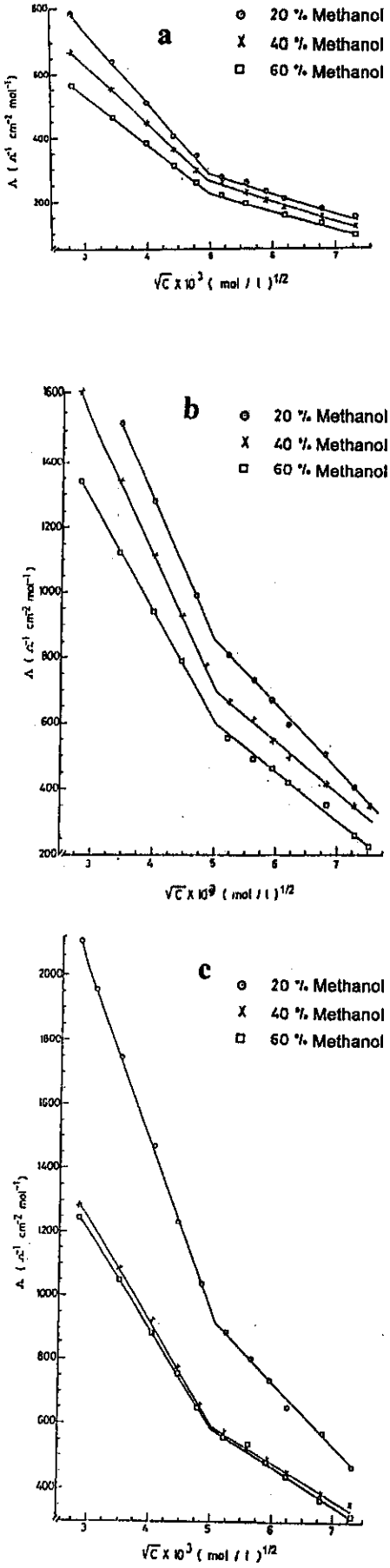


Fig (3.142): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (3) at: (a) 25°C, (b) 30°C and (C) 35°C.

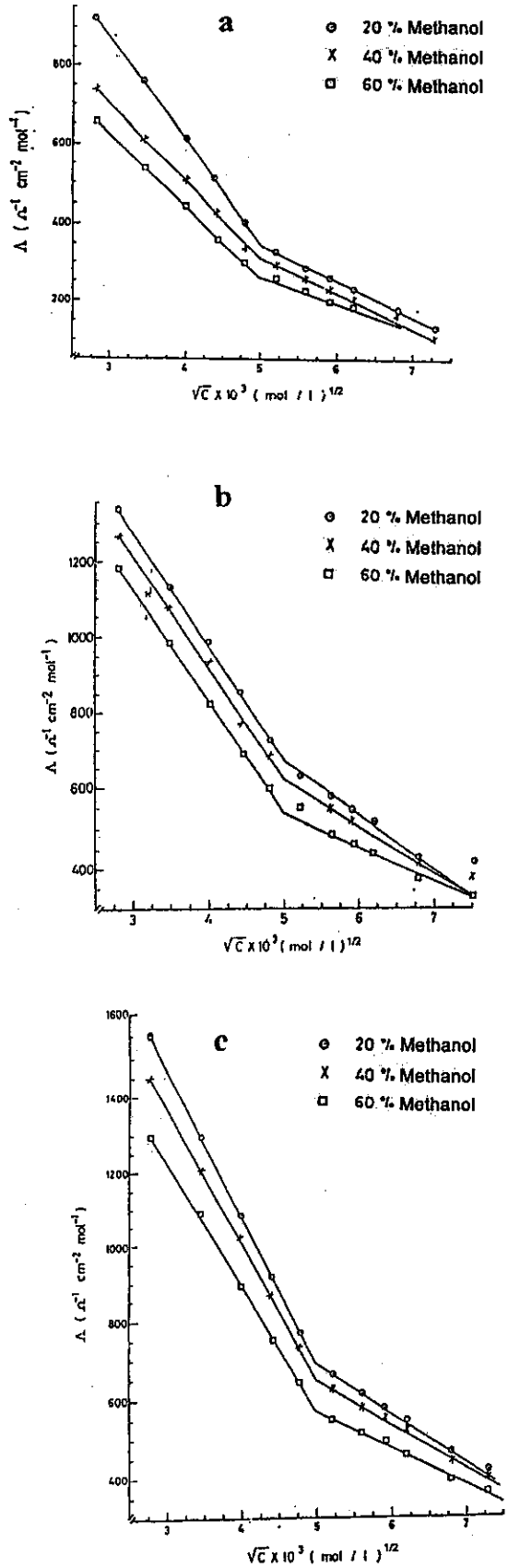


Fig (3.143): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (a) at: (a) 25°C, (b) 30°C and (C) 35°C.

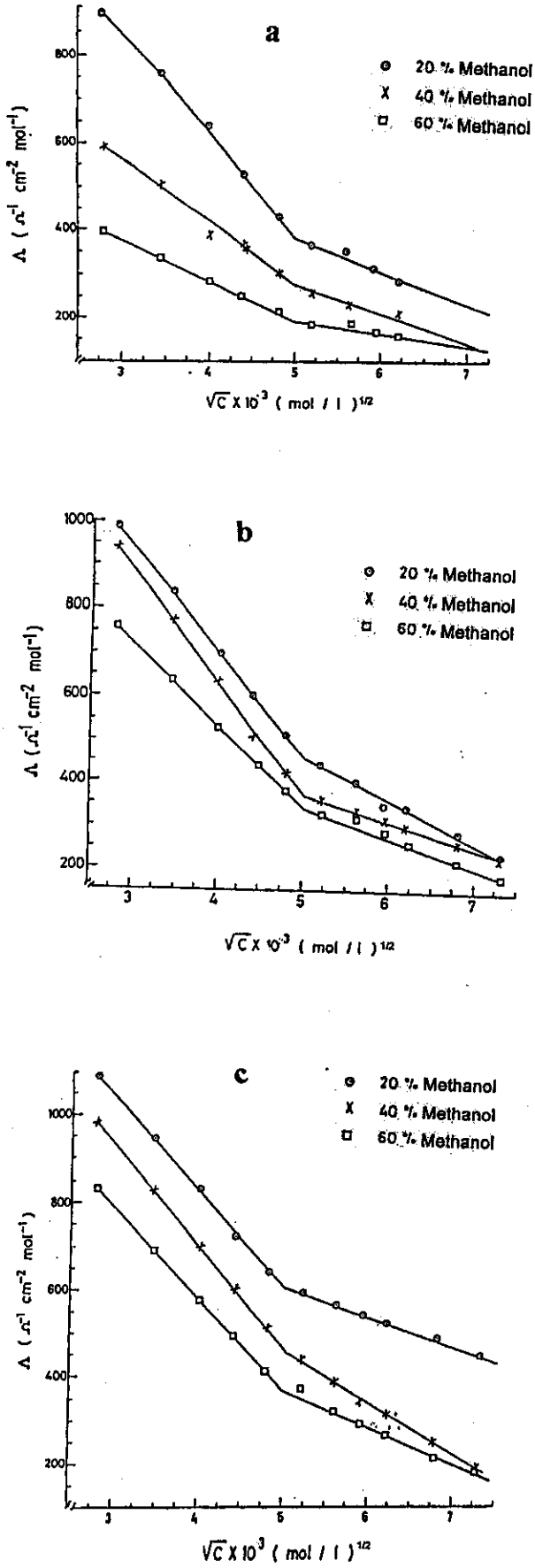


Fig (3.144): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (b) at: (a) 25°C, (b) 30°C and (C) 35°C.

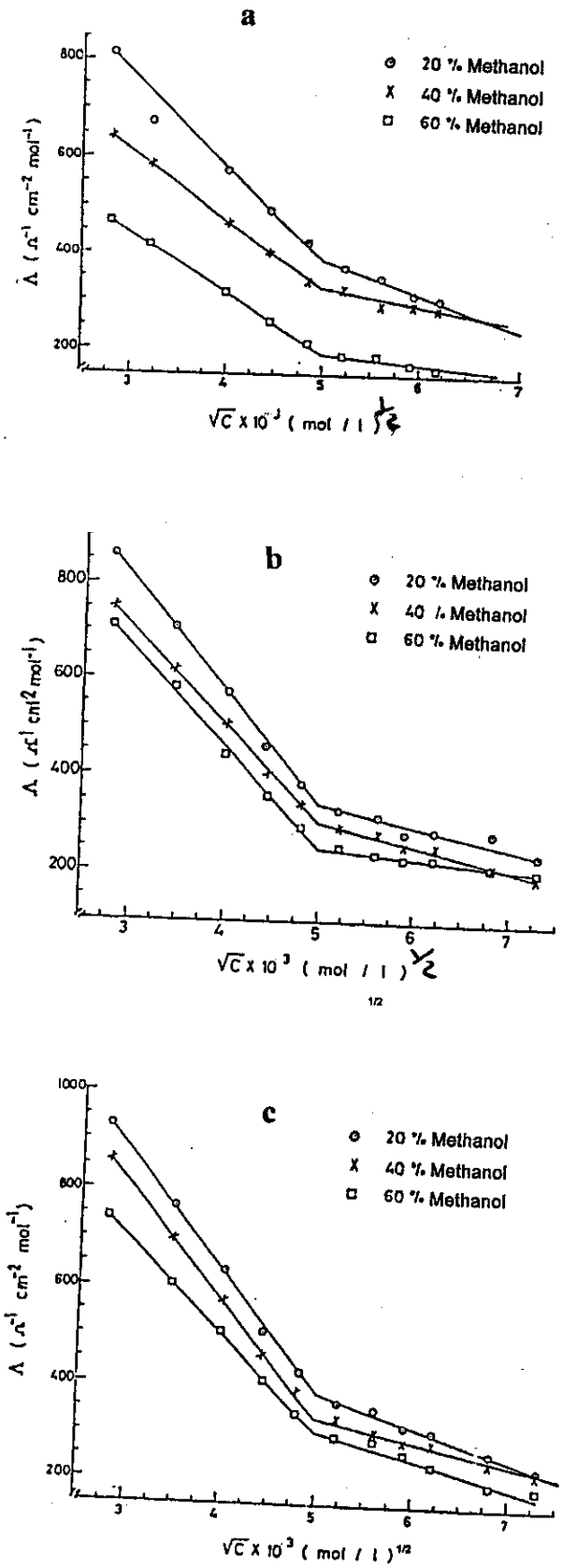


Fig (3.145): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (c) at: (a) 25°C, (b) 30°C and (C) 35°C.

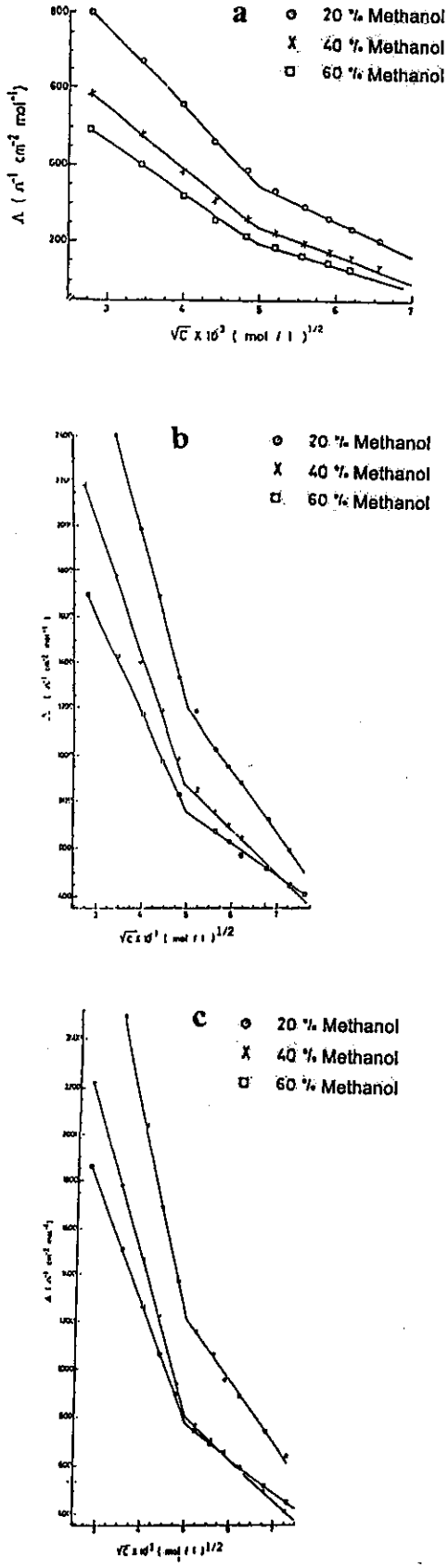


Fig (3.146): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (d) at: (a) 25°C, (b) 30°C and (C) 35°C.

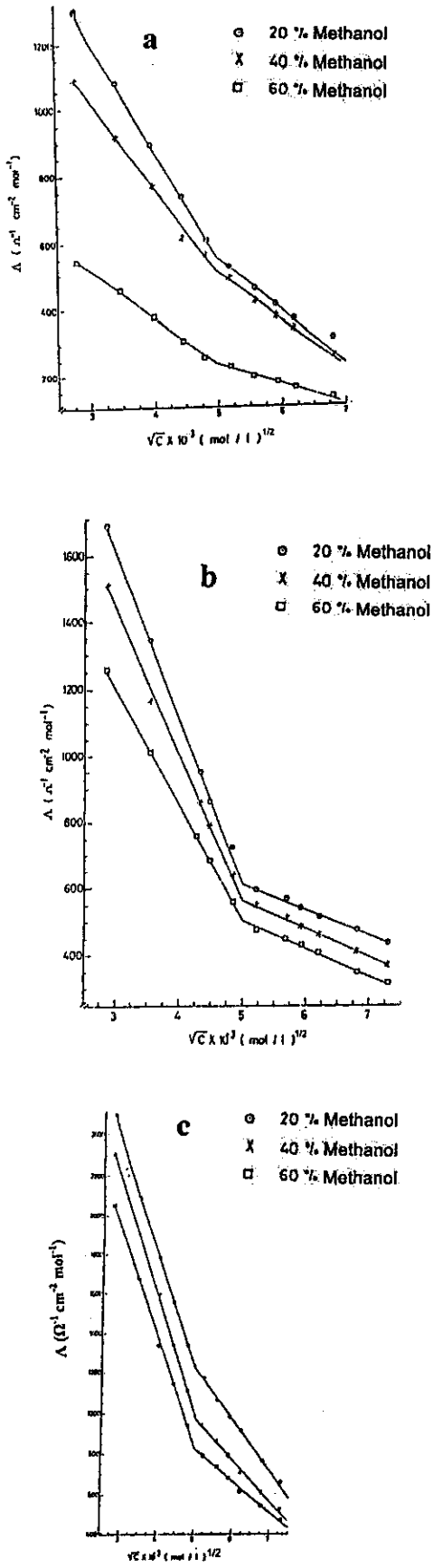


Fig (3.147): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (III) at: (a) 25°C, (b) 30°C and (C) 35°C.

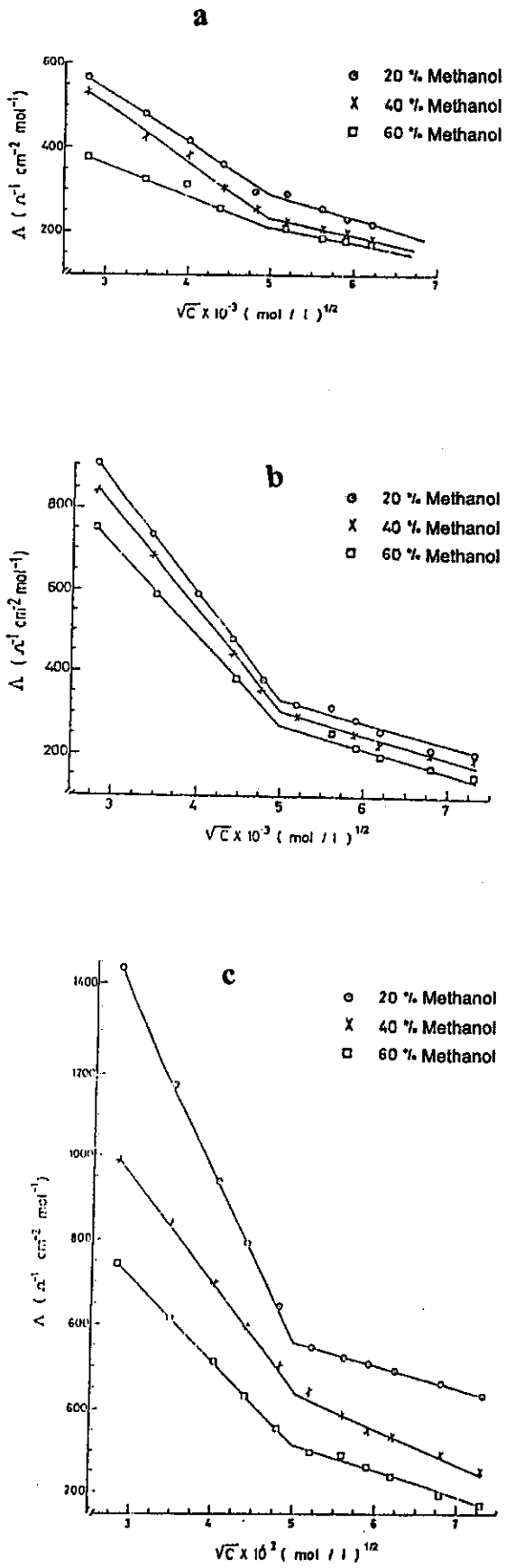


Fig (3.148): Variation of the molar conductance (Λ) with $(C)^{1/2}$ for $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (IV) at: (a) 25°C, (b) 30°C and (C) 35°C.

The free energies of association of stoichionetric complexes are calculated from the association constant values using equation (3.15) [186, 191, 192]

$$\Delta G_A = - R T \ln K_A \qquad (3.15)$$

The heat of association (ΔH) is obtained from the slope of the plot of ln K_A versus 1/T and Gibbes Helmholtz equation, $\Delta G = \Delta H - T\Delta S$.

The free energies of solvation for the 1 : 1 and 2 : 1 stoichiometric complexes are found to increase with increase in the temperature due mainly to the easier spontaneously on increasing temperature. The same trend was also observed in the calculated values of enthalpies.

The free energies for the solvation $CuSO_4$ with quinazoline phenyl hydrazone derivatives are decreased in case of 2: 1 complexes than that of 1:1 stoichiometric complexes. This was mainly due to the increase of entropies of solvation (see Tables 3.64- 3.72). All the entropies values are not affected by temperature because of the balance in values of free energies and enthalpies which are opposite to each other.

The total content of energies (enthalpies) were increased by increasing methanol percentages indicating more solvation of formed complexes in solutions.

The entropies (disorder values) are also increased by more adding alcohol in solutions due mainly to increase in solvent effect (ion-solvent interaction).

In the case of first series, compound 2 show higher ΔH and TΔS values for the stoichiometric complexes than 3 and 1 respectively because of the density factor which is greater in bromide ions than the other groups.

In the case of second series, compound (d) show higher ΔH & TΔS values fir both 1 : 1 and 2 : 1 stoichiometric complexes than (a) , (c) and (b) , due to its higher complexing ability .

In the case of third series, compound III gave more enthalpies and entropies than compound IV because of the more association values.

Table (3.64): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (1) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.7	28.8	30.1	46.0	18.3	17.2	15.9
	2:1	26.5	27.5	29.1	61.3	34.8	33.8	32.2
40	1:1	27.7	27.5	29.1	51.1	23.2	22.3	22.1
	2:1	26.5	28.8	29.0	64.3	37.4	36.8	36.0
60	1:1	27.7	28.7	29.6	61.2	33.5	32.5	31.6
	2:1	26.5	27.3	26.8	76.6	50.0	49.3	49.8

Table (3.65): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (2) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	26.9	28.1	28.7	51.1	24.2	23.0	22.4
	2:1	24.8	25.4	27.1	76.6	51.8	51.2	49.5
40	1:1	27.3	28.1	28.6	73.3	46.0	45.2	44.7
	2:1	24.9	25.3	26.6	117.8	92.9	92.5	91.2
60	1:1	27.0	28.1	28.6	76.6	49.6	48.5	48.0
	2:1	25.4	25.3	26.0	122.5	97.1	97.2	96.5

Table (3.66): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (3) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.7	28.3	29.6	46.0	18.6	17.7	16.4
	2:1	26.6	27.5	28.0	51.1	24.5	23.6	23.1
40	1:1	27.7	28.2	29.4	60.5	32.8	32.3	31.1
	2:1	26.5	27.3	28.4	61.3	34.8	34.0	32.9
60	1:1	27.7	28.2	29.3	61.3	33.6	33.1	32.0
	2:1	26.5	27.2	28.9	91.9	65.4	64.7	63.0

Table (3.67): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (a) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.8	28.0	28.9	38.3	10.5	10.3	9.4
	2:1	26.3	27.4	27.6	60.8	34.5	33.4	33.2
40	1:1	27.7	28.6	28.8	46.0	18.3	17.4	17.2
	2:1	25.9	26.6	28.5	61.3	35.4	34.7	32.8
60	1:1	27.5	28.2	29.0	51.1	23.6	22.9	22.1
	2:1	25.7	26.6	26.8	76.6	50.9	50.0	49.8

Table (3.68): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (b) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.9	28.5	29.2	46.0	18.1	17.5	16.8
	2:1	25.1	27.0	28.8	47.0	21.9	20.0	18.2
40	1:1	28.3	28.8	29.7	61.3	33.0	32.5	31.6
	2:1	26.0	28.0	29.3	76.6	50.6	48.6	47.3
60	1:1	28.5	29.2	29.1	76.6	48.1	47.4	47.5
	2:1	26.6	27.6	29.3	91.9	65.3	64.3	62.6

Table (3.69): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (c) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.9	28.7	29.2	30.6	2.7	1.9	1.4
	2:1	27.0	27.2	28.8	51.0	24.0	23.8	22.2
40	1:1	28.5	28.8	28.8	38.3	9.8	9.5	9.5
	2:1	26.9	27.5	28.9	91.9	65.0	64.4	63.0
60	1:1	27.9	28.5	29.1	46.0	18.1	17.5	16.9
	2:1	26.0	26.6	28.4	122.5	96.5	95.9	94.1

Table (3.70): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (d) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.3	27.4	28.4	38.3	11.0	10.9	9.9
	2:1	24.7	26.9	26.9	46.0	21.3	19.1	19.1
40	1:1	27.3	28.1	28.1	46.0	18.7	17.9	17.9
	2:1	24.9	24.9	26.0	76.6	51.7	51.7	50.6
60	1:1	28.0	28.5	29.0	76.6	48.6	48.1	47.6
	2:1	23.5	25.0	27.0	91.9	68.4	66.9	64.9

Table (3.71): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (III) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.7	28.9	29.2	61.3	33.6	32.4	32.1
	2:1	26.5	27.1	29.1	76.6	50.1	49.5	47.5
40	1:1	25.9	28.2	29.5	76.6	50.7	48.4	47.1
	2:1	25.6	27.3	28.9	137.9	112.3	110.6	109.0
60	1:1	28.3	28.6	29.5	84.2	55.9	55.6	54.7
	2:1	25.5	26.5	28.8	153.2	127.7	126.7	124.6

Table (3.72): Thermodynamic parameters (ΔG, ΔH, TΔS) for the solvation of $CuSO_4$ in MeOH – H_2O mixtures in presence of compound (IV) at different temperature.

Vol.% of MeOH	L:M	$-\Delta G_A$(K.J.mol^{-1})			-ΔH (K.J.mol^{-1})	-TΔS (K.J.mol-1)		
		25°C	30°C	35°C		25°C	30°C	35°C
20	1:1	27.1	28.4	29.9	61.3	33.2	32.9	32.4
	2:1	25.3	24.4	26.7	62.3	37.0	37.9	25.6
40	1:1	28.0	28.2	29.8	76.6	48.6	48.4	46.8
	2:1	25.4	27.0	27.0	84.2	58.8	57.2	57.2
60	1:1	26.7	28.6	29.1	91.9	65.2	63.6	62.8
	2:1	26.2	26.9	27.3	99.6	73.4	72.7	72.3

The association constants (K_A) values were also recalculated by applying another method known as Fuoss – Kraus method of calculations depending on Eq. explained before [186, 187, 188].

$$1/\Lambda S(Z) = 1/\Lambda_\circ + [\, K_A/ \Lambda_\circ^2 \,] [\, C \,.\, \Lambda \,.\, \gamma_\pm^2 \,.\, S(Z) \,] \qquad (3.16)$$

This method was achieved graphically by plotting the relation between ($1/ \Lambda_\circ S(Z)$) vs. ($C. \Lambda. \gamma_\pm^2 . S(Z)$) which gave in all cases straight lines , their slopes equal ($K_A/ \Lambda_\circ^2$) and their intercepts equal ($1/ \Lambda_\circ$), where (K_A) values can be evaluated. Tables (3.74 – 3.76) contain the results of this method.

The calculated K_A and the free energies of solvation values by Fuoss – Kraus method gave results like these values calculated by Fuoss-Shedlovesky method but little greater . The last method depends on the slopes of the curves which are hand to be adjusted.

It also shown in results for Fuoss – Kraus method that only one result is obtained at each solvent percentage due to their graphical presentation.

Finally, by this method it was observed that the association constant increase by increasing alcohol percentages. Also by this method the association constants of the ligands follows the same order of Shedlovsky – Fuoss method.

Table (3.73): Association constants (K_A) and free energies of solvation ($-\Delta G_A$) for $CuSO_4$ in presence of the first series at 25°C calculated by fouss – Kraus method.

Vol. % of Me OH	Compound (1)				Compound (2)				Compound (3)			
	1:1 complex		2:1 complex		1:1 complex		2:1 complex		1:1 complex		2:1 complex	
	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol
20	26.4	36.6	42.1	37.8	5.0	32.5	11.6	34.5	11.6	34.5	20.5	36.0
40	31.2	37.0	41.9	37.8	7.6	33.5	11.6	34.9	11.6	34.9	22.0	36.2
60	36.7	37.5	44.3	37.9	9.4	34.1	14.8	35.0	14.8	35.0	23.7	36.4

Table (3.74): Association constants (K_A) and free energies of solvation ($-\Delta G_A$) for $CuSO_4$ in presence of the second series at 25°C calculated by fouss – Kraus method.

Vol. % of MeOH	Compound (a)				Compound (b)				Compound (c)				Compound (d)			
	1:1 complex		2:1 complex		1:1 complex		2:1 complex		1:1 complex		2:1 complex		1:1 complex		2:1 complex	
	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol	K_AX 10^{-5}	$-\Delta G_A$ K.J./ mol
20	7.1	33.4	12.8	34.8	18.1	35.7	33.1	37.0	6.0	33.0	13.2	34.9	4.4	33.3	6.3	33.3
40	10.0	34.2	16.0	35.4	26.1	36.6	52.0	38.4	13.2	34.9	13.8	35.0	2.2	31.5	12.6	34.8
60	11.8	34.6	7.0	33.3	29.6	36.9	54.0	38.3	30.0	37.2	16.7	35.5	2.8	32.1	15.8	35.4

Table (3.75): Association constants (K_A) and free energies of solvation ($-\Delta G_A$) for $CuSO_4$ in presence of the third series at 25°C calculated by fouss – Kraus method.

Vol. % of Me OH	Compound (III)				Compound (IV)			
	1:1 complex		2:1 complex		1:1 complex		2:1 complex	
	$K_A X 10^{-5}$	$-\Delta G_A$ K.J./ mol	$K_A X 10^{-5}$	$-\Delta G_A$ K.J./ mol	$K_A X 10^{-5}$	$-\Delta G_A$ K.J./ mol	$K_A X 10^{-5}$	$-\Delta G_A$ K.J./ mol
20	44.4	37.9	4.7	32.4	14.2	35.1	6.2	33.0
40	65.3	38.9	13.3	34.9	20.3	36.0	15.4	35.3
60	39.5	37.6	45.0	38.0	12.2	34.7	16.3	35.4

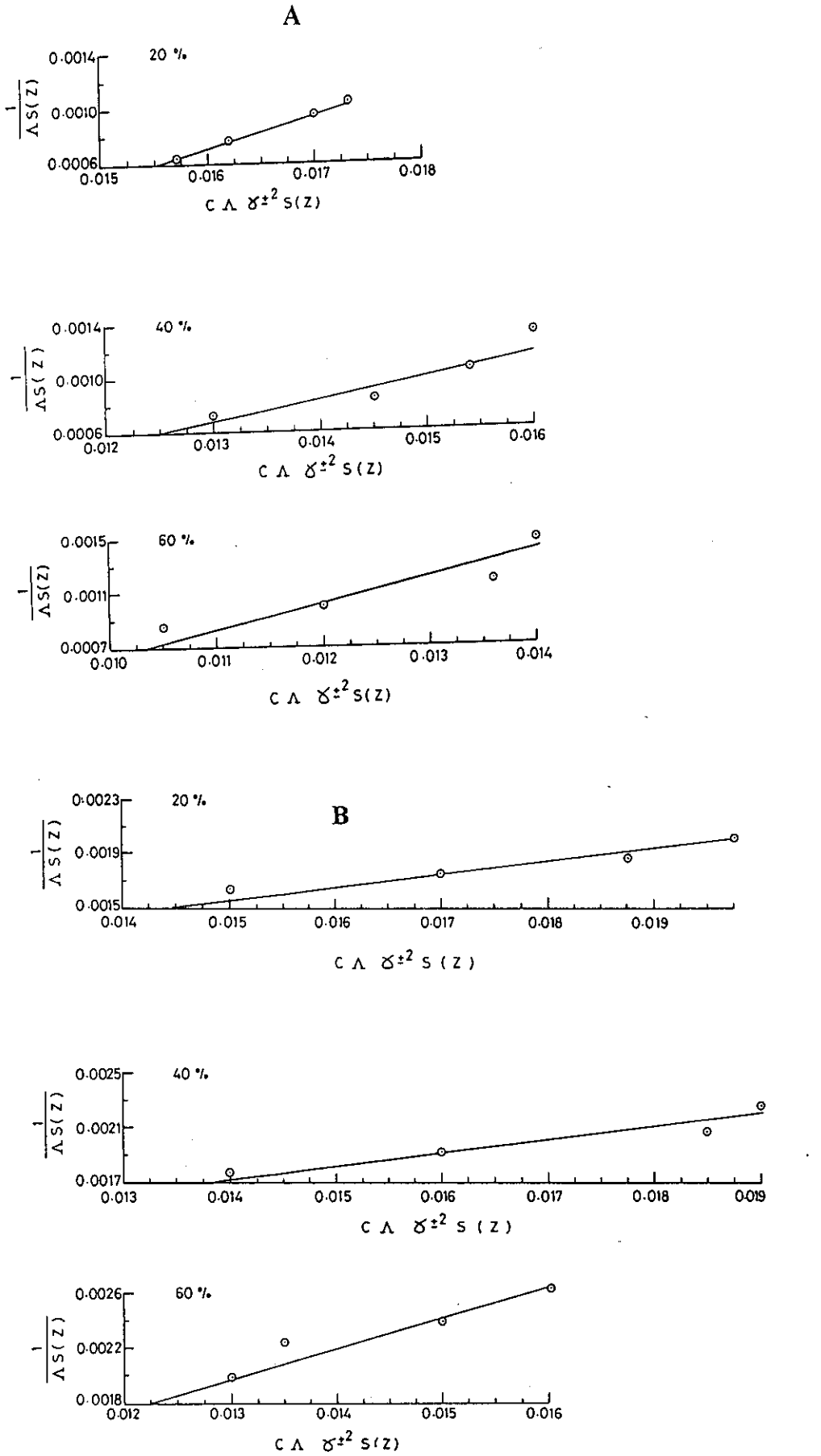


Fig (3.149): Relation between ($1/\Lambda S(Z)$) against ($C\Lambda\gamma_{\pm}^{2}S(Z)$) using fouss – Kraus method for $CuSO_4$ in presence of compound (1) and in MeOH $-H_2O$ mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.

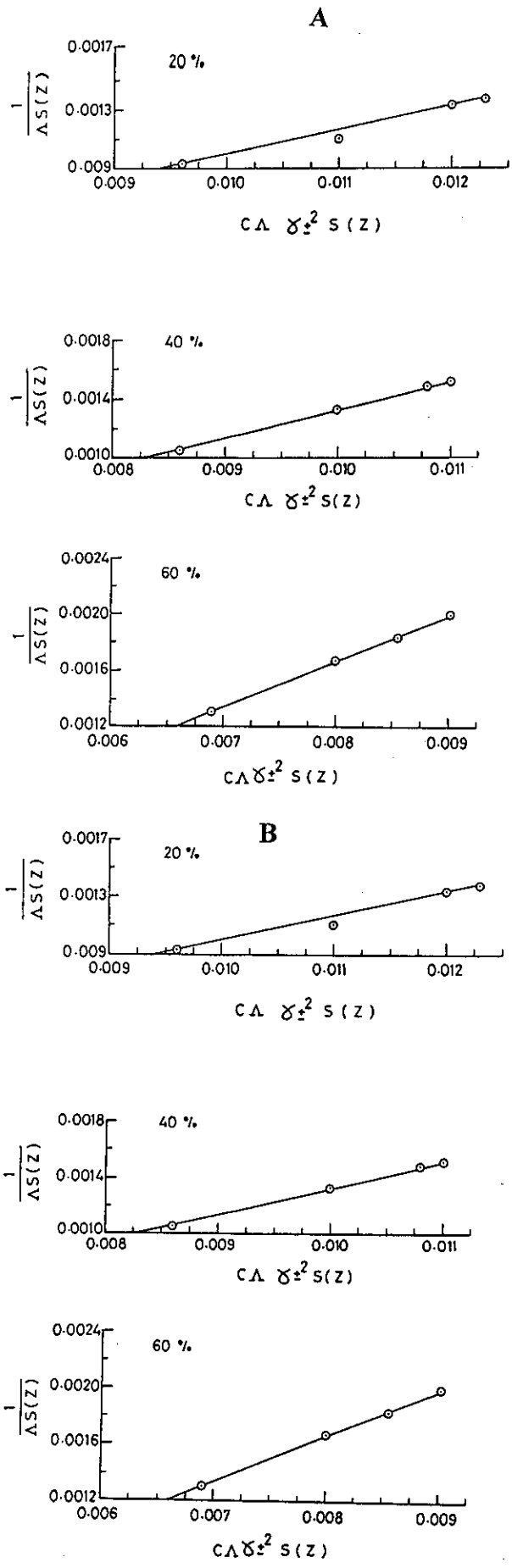


Fig (3.150): Relation between (1/ ΛS(Z)) against (C Λ $\gamma_{\pm}^2$ S(Z)) using fouss – Kraus method for $CuSO_4$ in presence of compound (2) and in MeOH –H_2O mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.

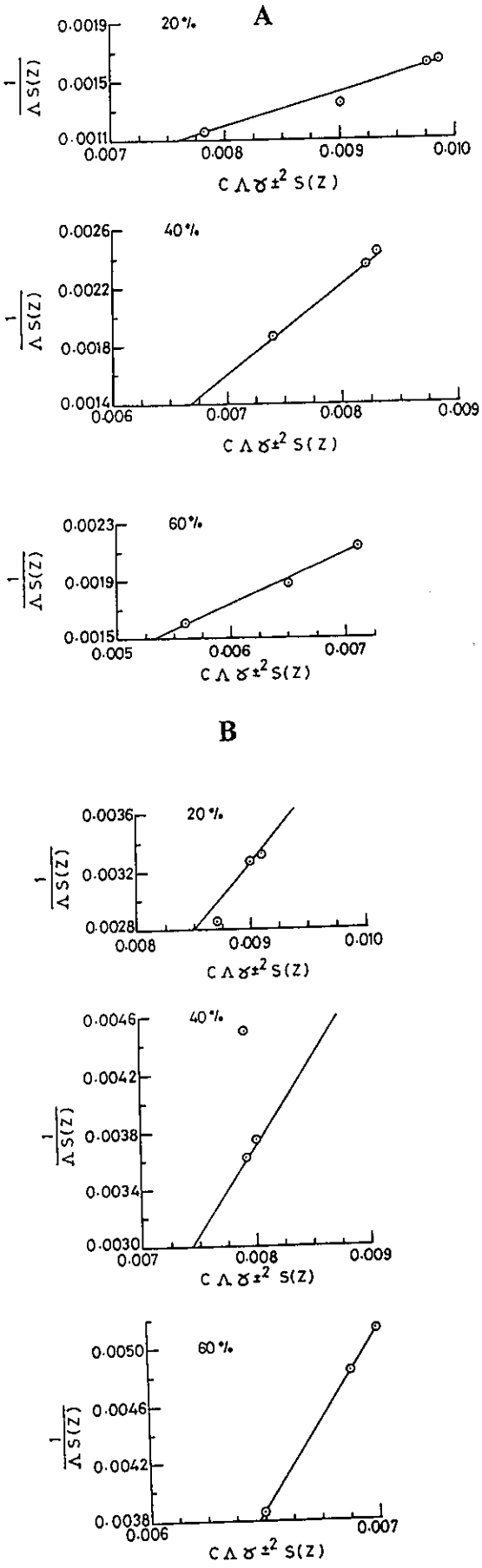


Fig (3.151): Relation between ($1/\Lambda S(Z)$) against ($C\Lambda\gamma_{\pm}^2 S(Z)$) using fouss – Kraus method for $CuSO_4$ in presence of compound (3) and in MeOH –H_2O mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.

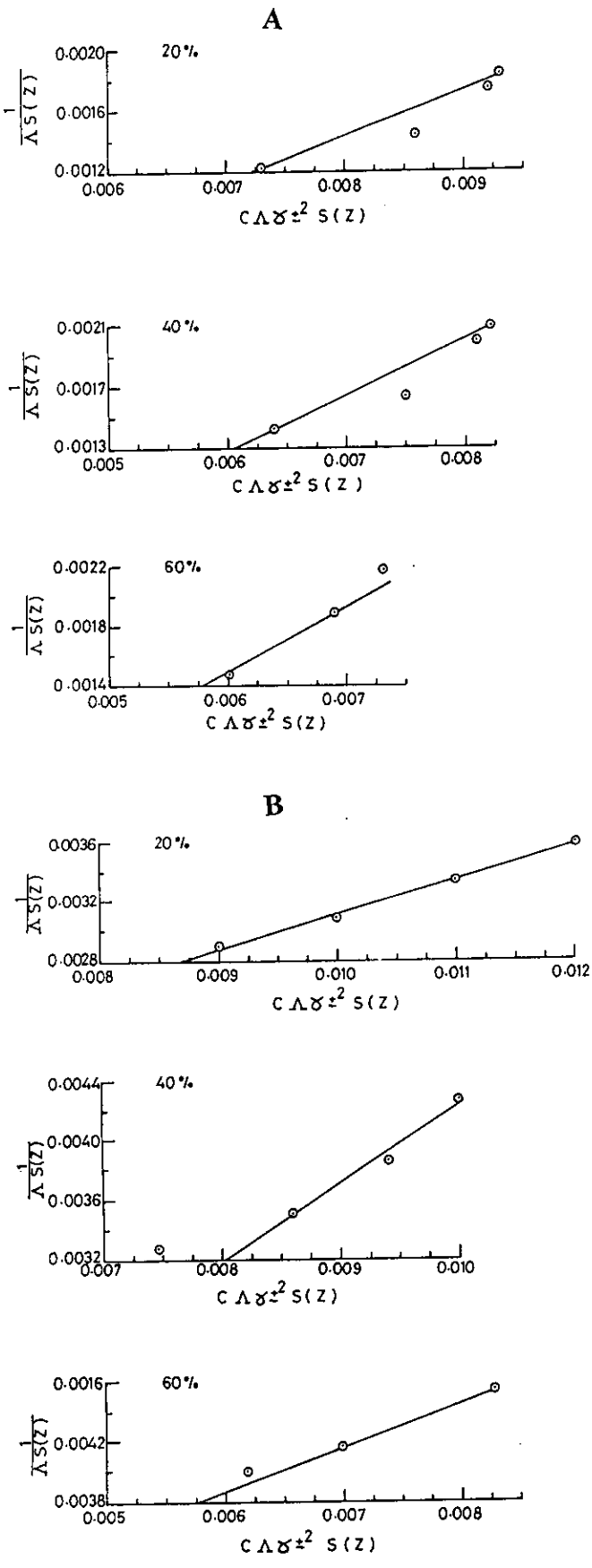


Fig (3.152): Relation between ($1/\Lambda S(Z)$) against ($C\Lambda\gamma_{\pm}^{2} S(Z)$) using fouss – Kraus method for $CuSO_4$ in presence of compound (a) and in MeOH $-H_2O$ mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) compiex.

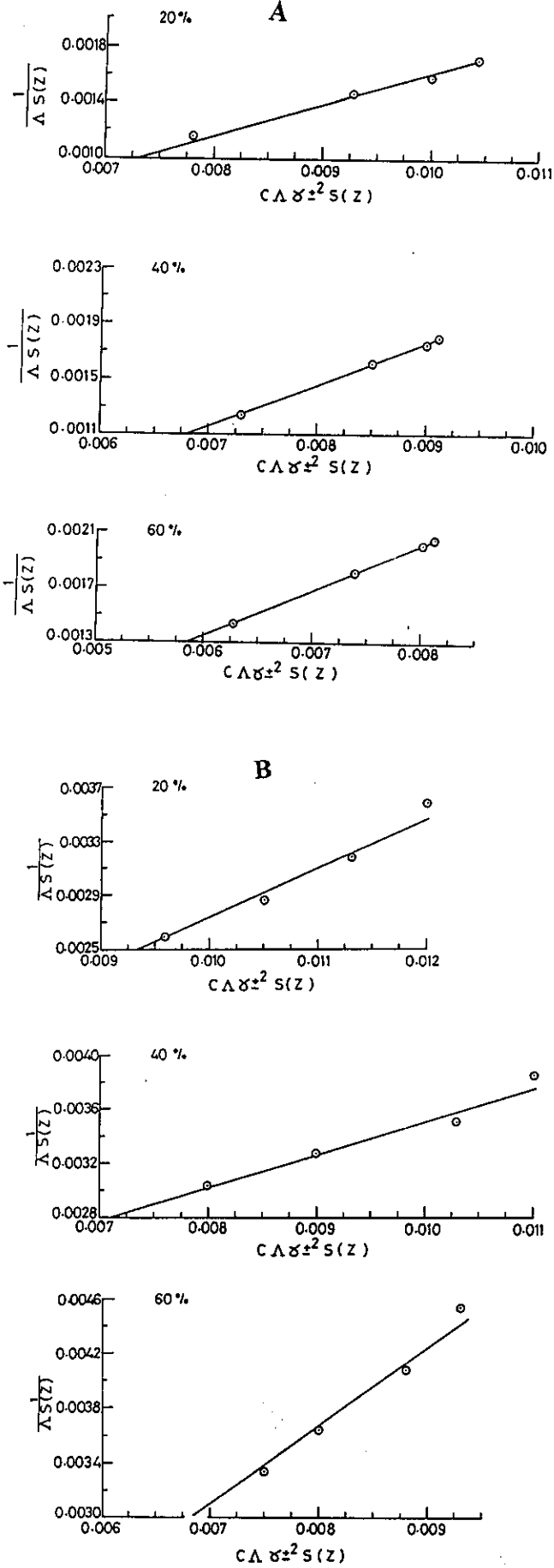
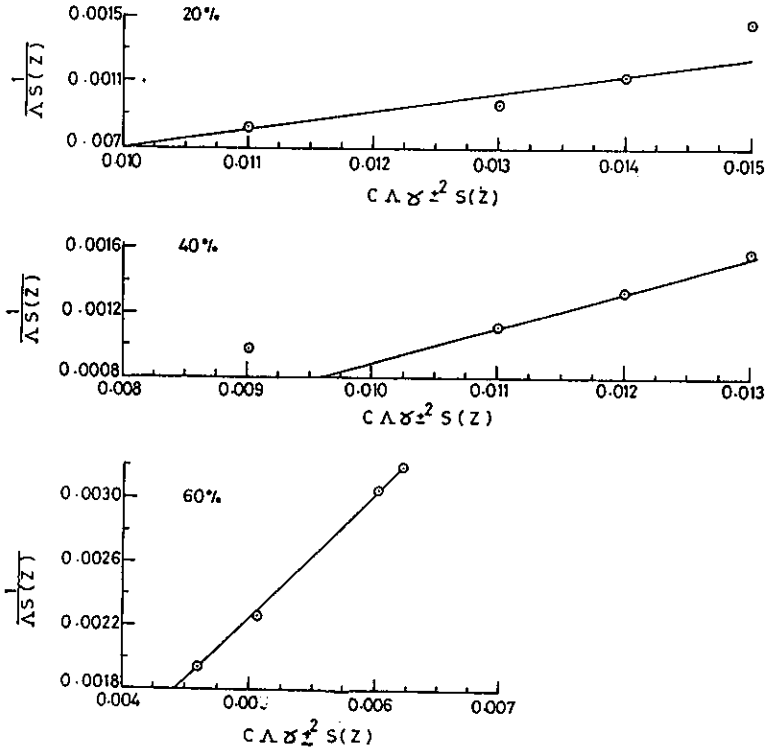


Fig (3.153): Relation between ($1/\Lambda S(Z)$) against ($C\Lambda\gamma_{\pm}^{2} S(Z)$) using fouss – Kraus method for $CuSO_4$ in presence of compound (b) and in MeOH –H_2O mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.

A



B

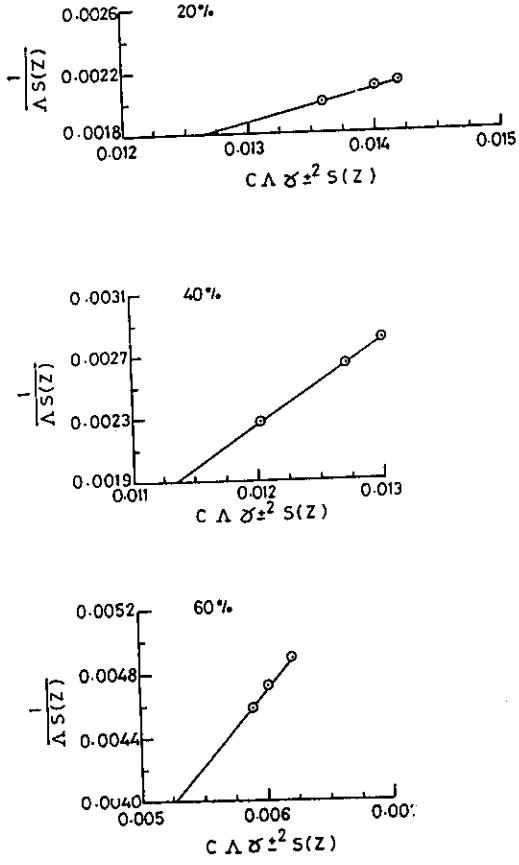


Fig (3.154): Relation between ($1/\Lambda S(Z)$) against ($C\Lambda\gamma_{\pm}^2 S(Z)$) using fouss – Kraus method for $CuSO_4$ in presence of compound (c) and in MeOH –H_2O mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.

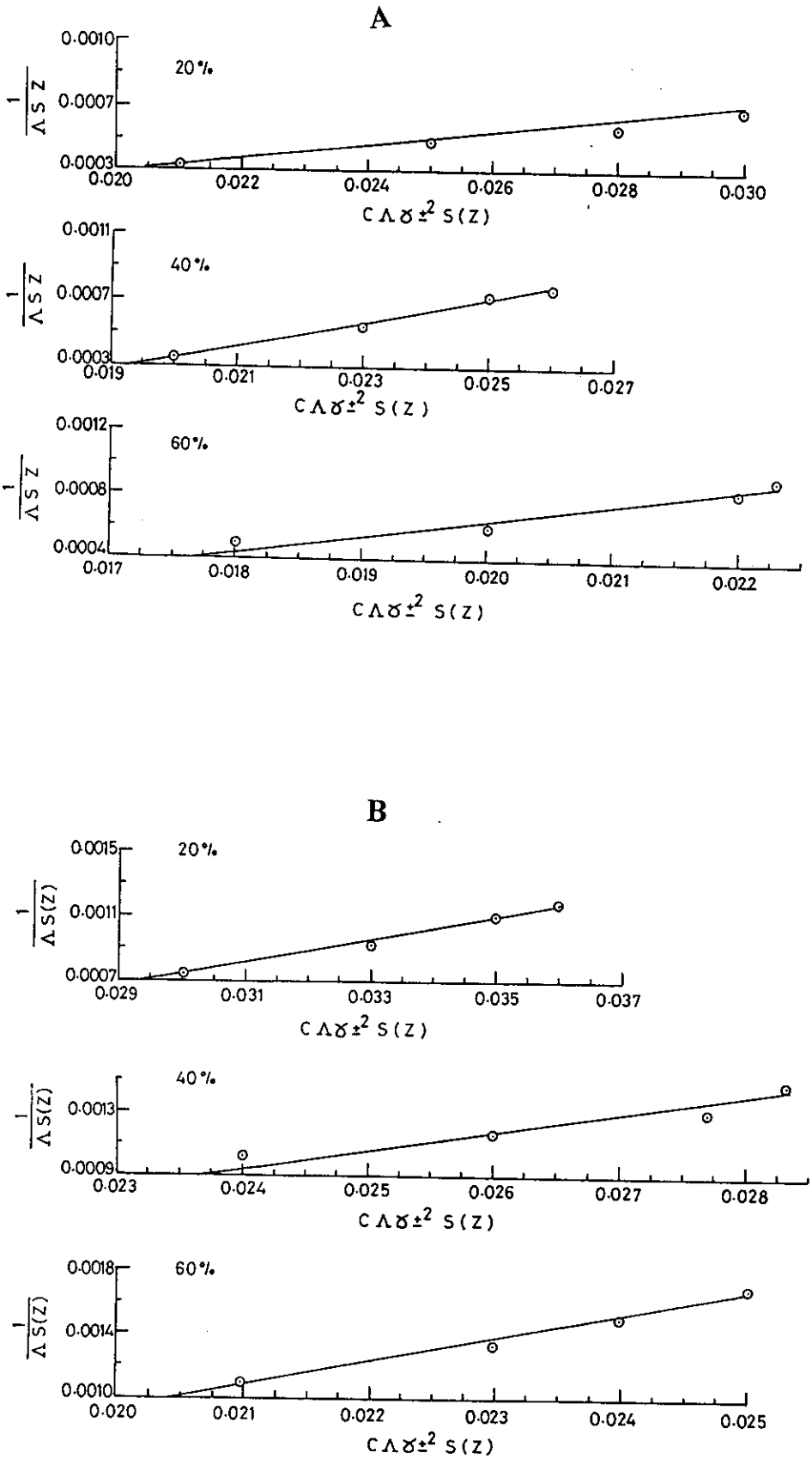
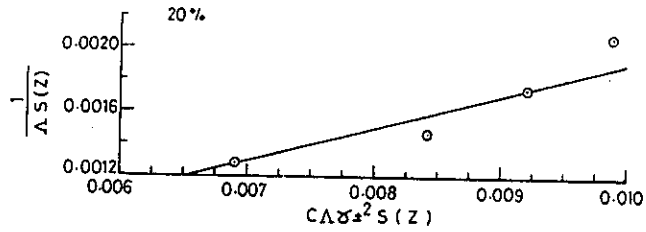
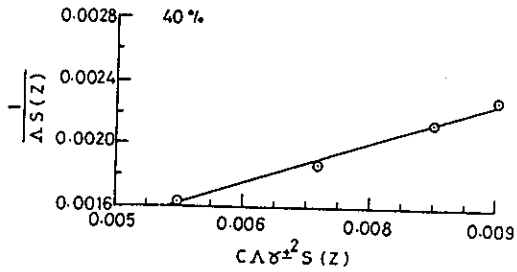
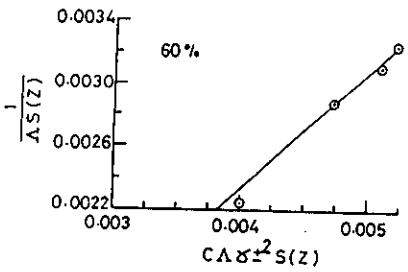


Fig (3.155): Relation between $(1/\Lambda S(Z))$ against $(C\Lambda\gamma_{\pm}^2 S(Z))$ using fouss – Kraus method for $CuSO_4$ in presence of compound (d) and in MeOH $-H_2O$ mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.

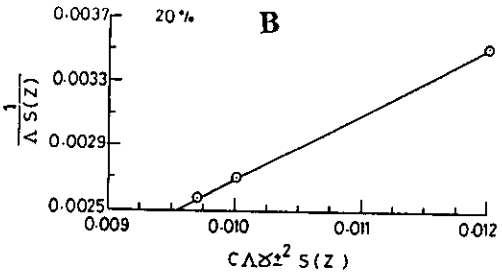
A

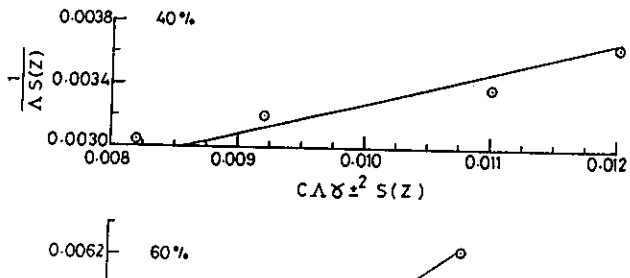






B





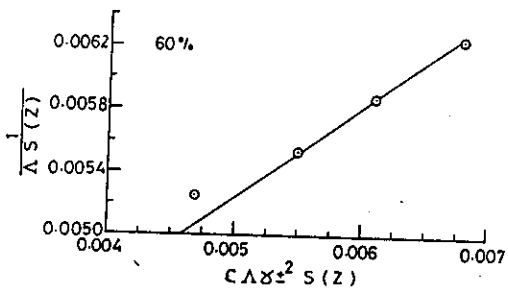


Fig (3.156): Relation between ($1/\Lambda S(Z)$) against ($C\Lambda\gamma_{\pm}^2 S(Z)$) using fouss – Kraus method for $CuSO_4$ in presence of compound (III) and in MeOH –H_2O mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.

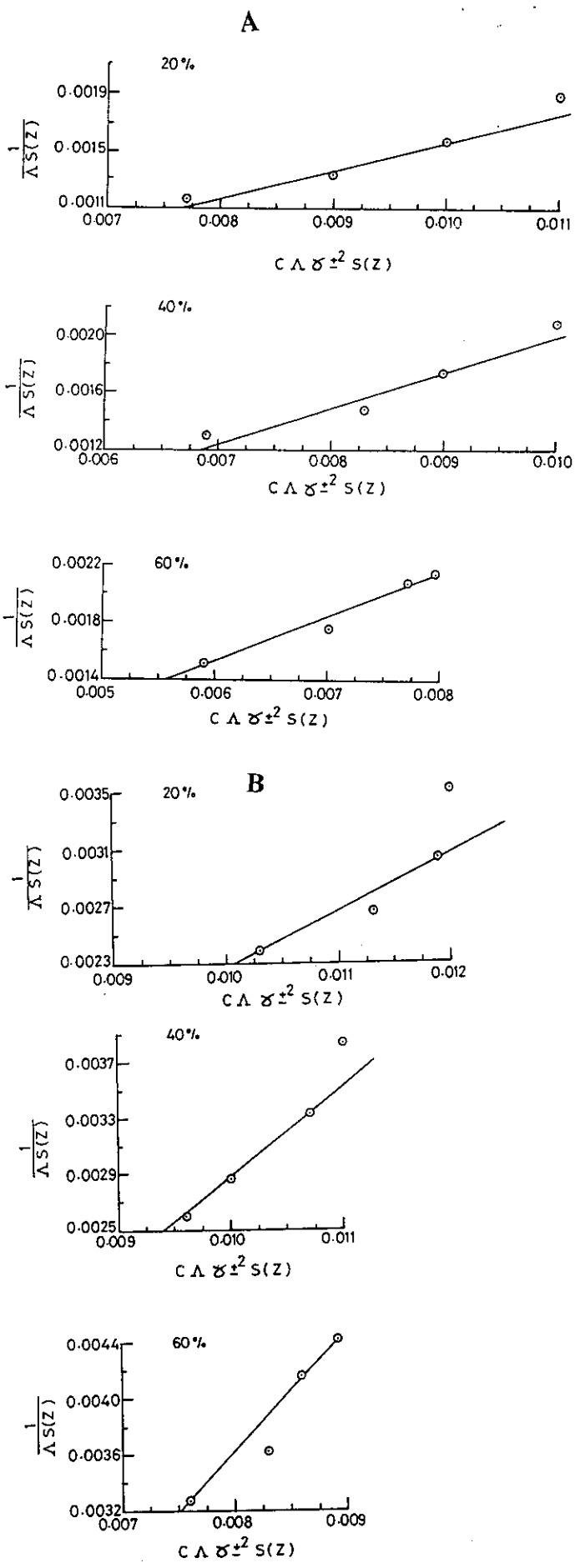


Fig (3.157): Relation between ($1/\Lambda S(Z)$) against ($C\Lambda\gamma_{\pm}^2 S(Z)$) using fouss – Kraus method for $CuSO_4$ in presence of compound (IV) and in MeOH $-H_2O$ mixtures at 25°C, (A) of 1:1 (L:M) complex, (B) of (2:1) (L:M) complex.