RESULTS AND DISCUSSION

STUDYING THE CORROSION BEHAVIOR OF IRON IN ACIDIC SOLUTIONS BY THE CHEMICAL TECHNIQUE

To evaluate the influence of the investigated two groups of hydrazone derivatives on the corrosion of iron in 3.5% phosphoric acid, the weight-loss technique was employed as the chemical testing technique.

3.1- Weight Loss Method

3.1.1- Corrosion inhibition behavior:

The corrosion behavior of a metal in an aqueous environment is characterized by the extent to which it dissolves in the solution. The degree of dissolution, of course, dependent on the surface area of the metal exposed and the time of exposure; hence the amount of corrosion is given with respect to area and time. The resulting quantity, corrosion rate, is thus a fundamental measurement in corrosion science. Corrosion rates can be evaluated by measuring either the concentration of the dissolved metal in solution by chemical analysis or by measuring weight of a specimen before and after exposure and applying equation (2.1). The late is most common method. The weight-loss method is usually preferred because the quantity measured is directly related to the extent of corrosion and does not rely on any assumptions about reactions occurring during corrosion.

Figures (3.1-3.7) show the weight loss-time curves for iron in 3.5% phosphoric acid in absence and presence of different concentrations of investigated hydrazone derivatives. As shown from these figures, by increasing the concentration of these derivatives, the weight loss of iron samples are decreased. This means that the presence of these derivatives retards the corrosion of iron in 3.5% phosphoric acid or in other words, these compounds act as an inhibitors. The linear variation of weight loss with time in uninhibited and inhibited 3.5% H_3PO_4 indicates the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitors are first adsorbed on to the metal surface and there after impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes. The inhibition efficiencies (%In) of hydrazone derivatives were determined by using the equation(2.2).

From the calculated values of %In given in Table (3.1) the order of the inhibition efficiencies of the investigated hydrazone derivatives (first group) is as follow:

First group:

(1)> (2)> (3)

From the calculated values of %In given in Table (3.2) the order of the inhibition efficiencies of the investigated hydrazone derivatives (second group) is as follow:

Second group:

(I)>(II)>(III)>(IV)

These behavior of first and second groups will be discussed later in inhibition mechanism.

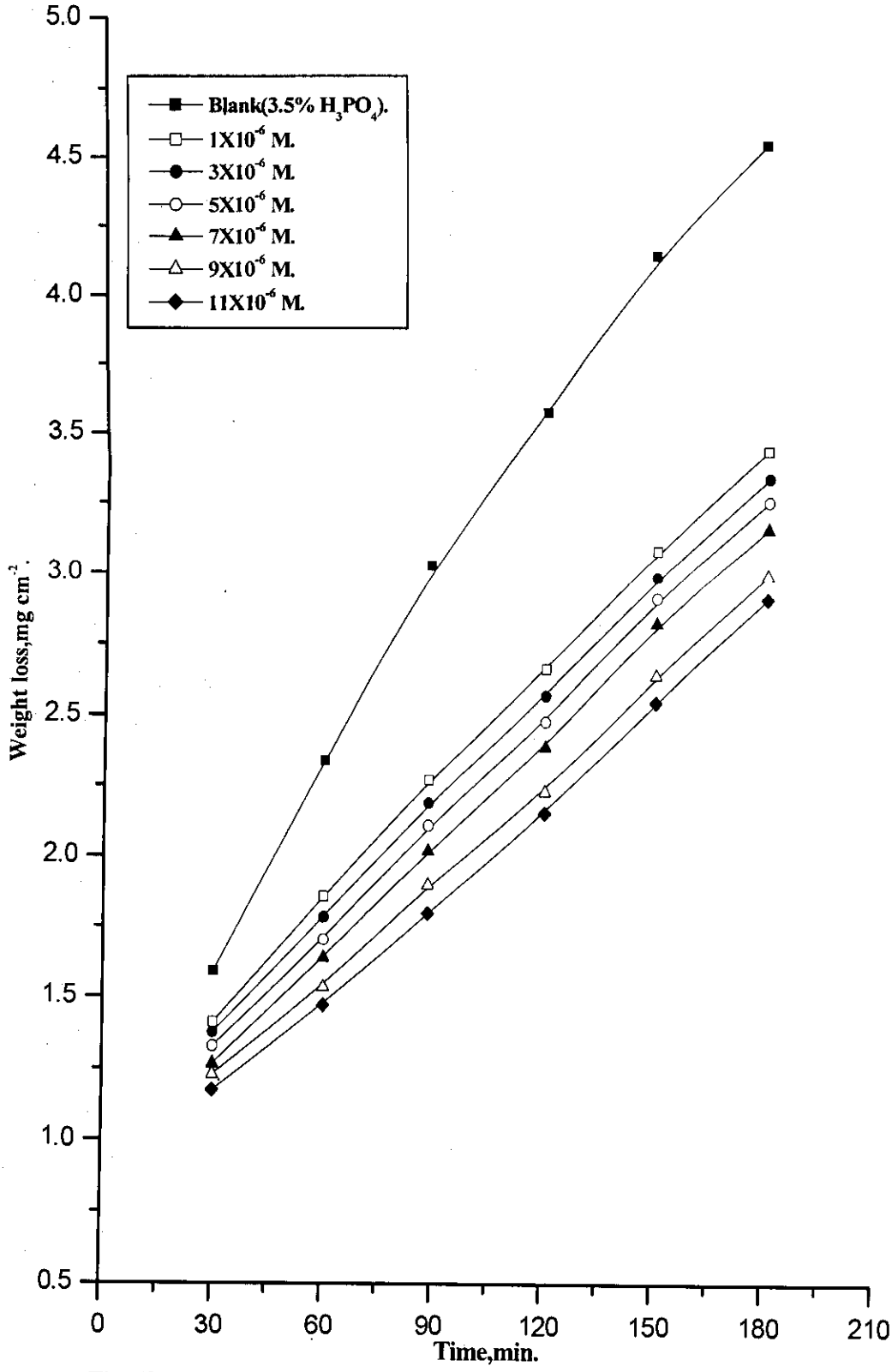


Fig: (3.1) .Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (1) at 30^{O}C.

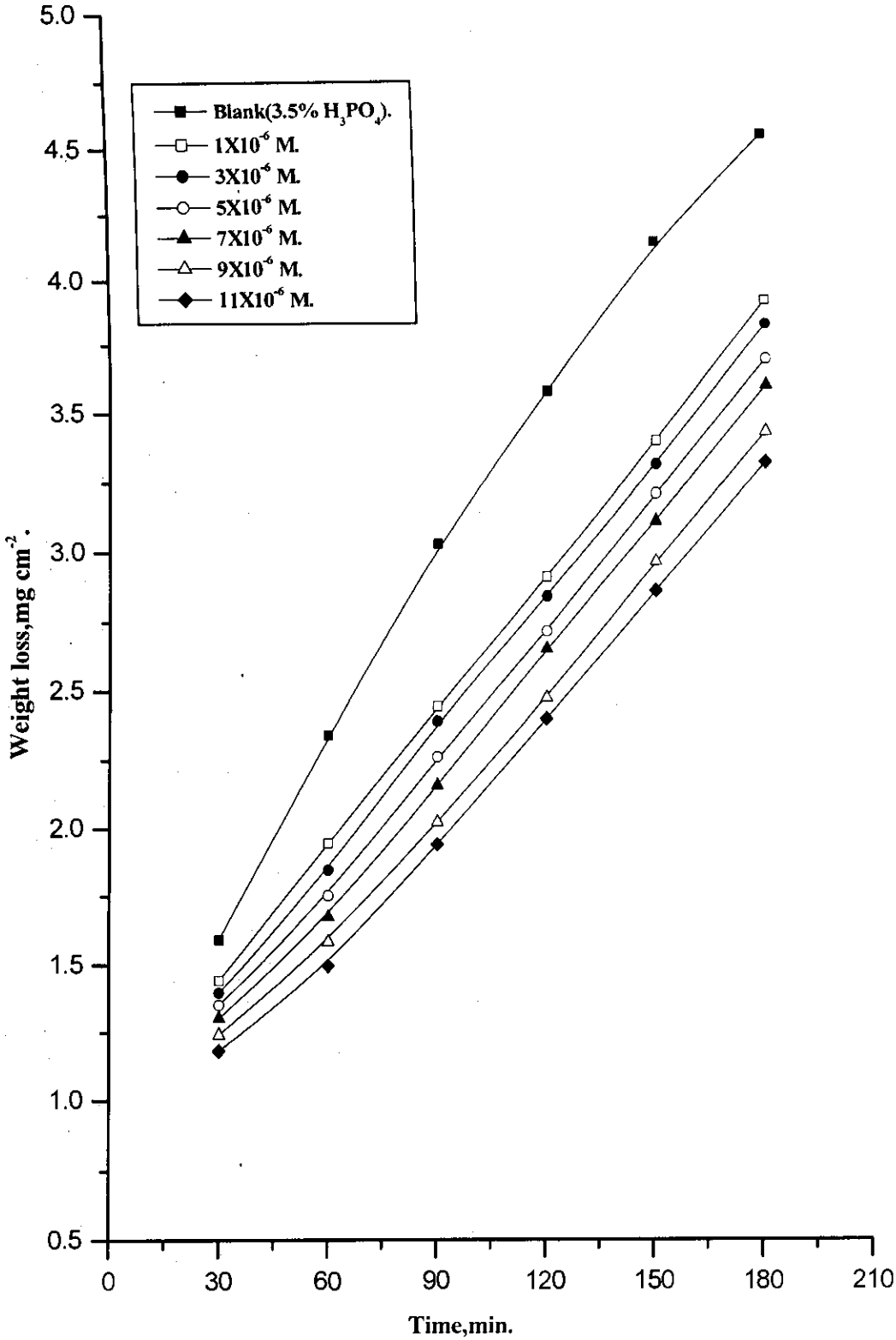


Fig: (3.2).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (2) at 30^{O}C.

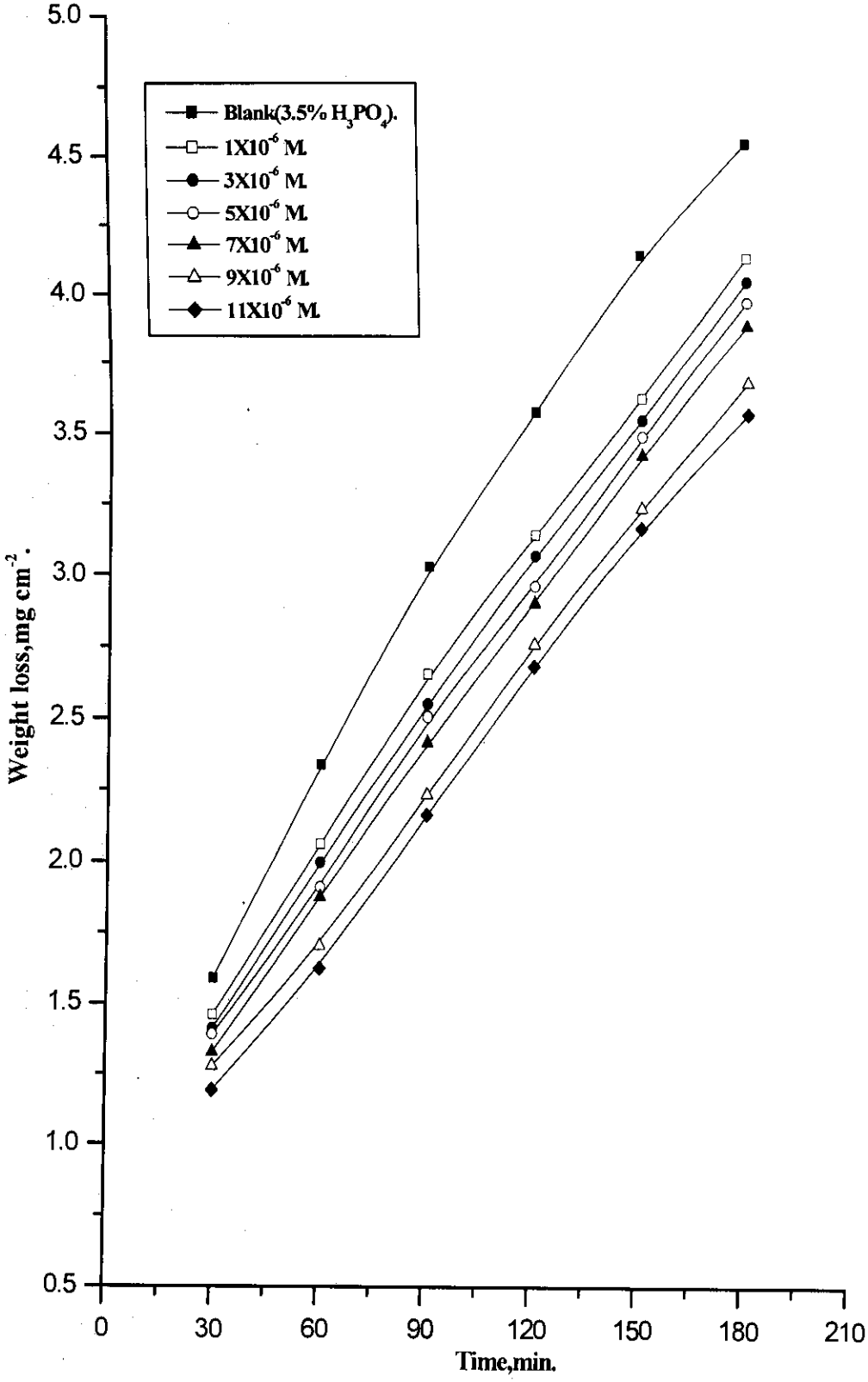


Fig: (3.3) .Weight loss time curves for the dissolution of iron in absence and presence of different concentrations of compound (3) at 30^{O}C.

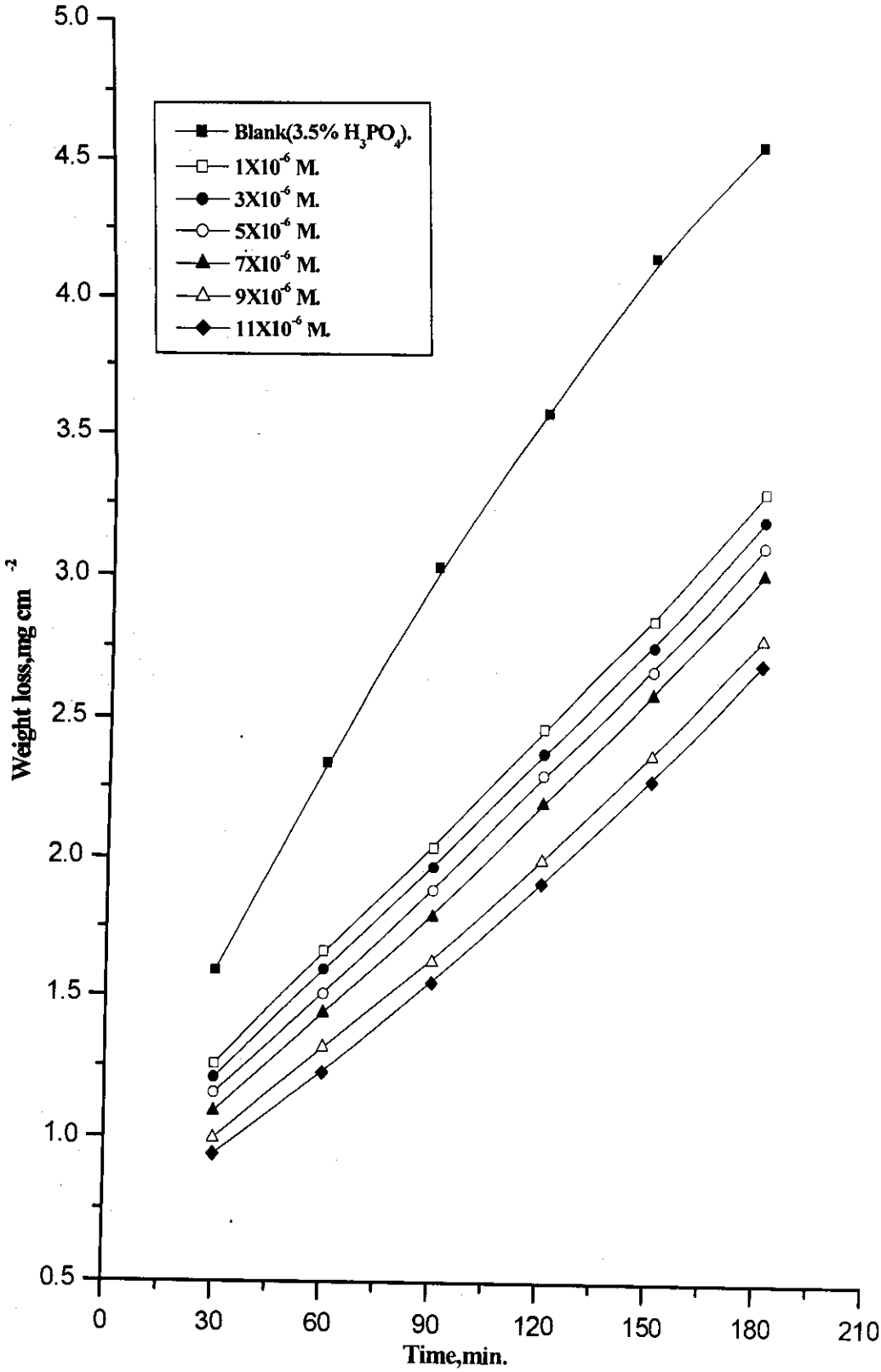


Fig: (3.4) .Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (I) at 30°C.

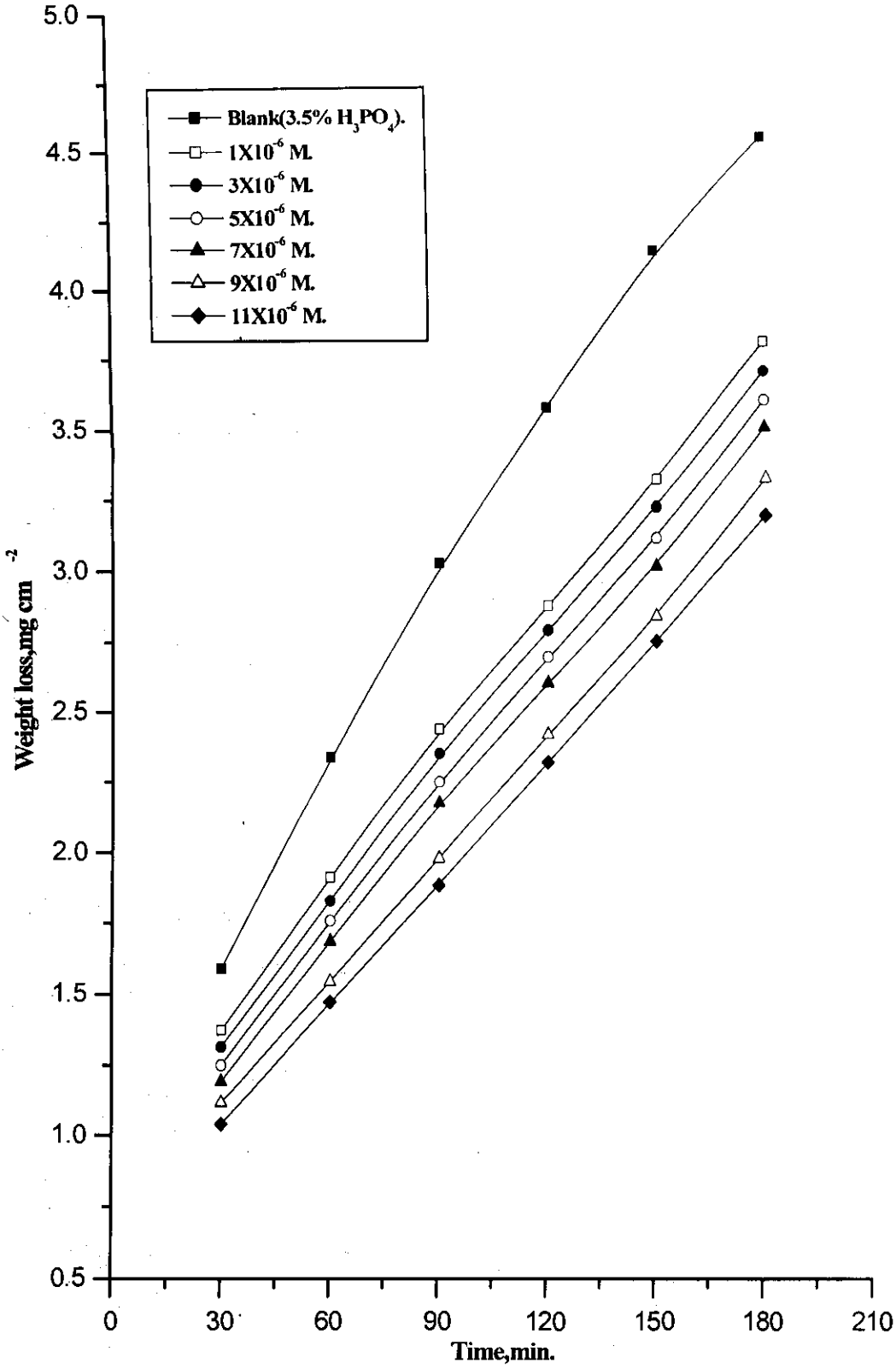


Fig: (3.5) .Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (II) at 30°C.

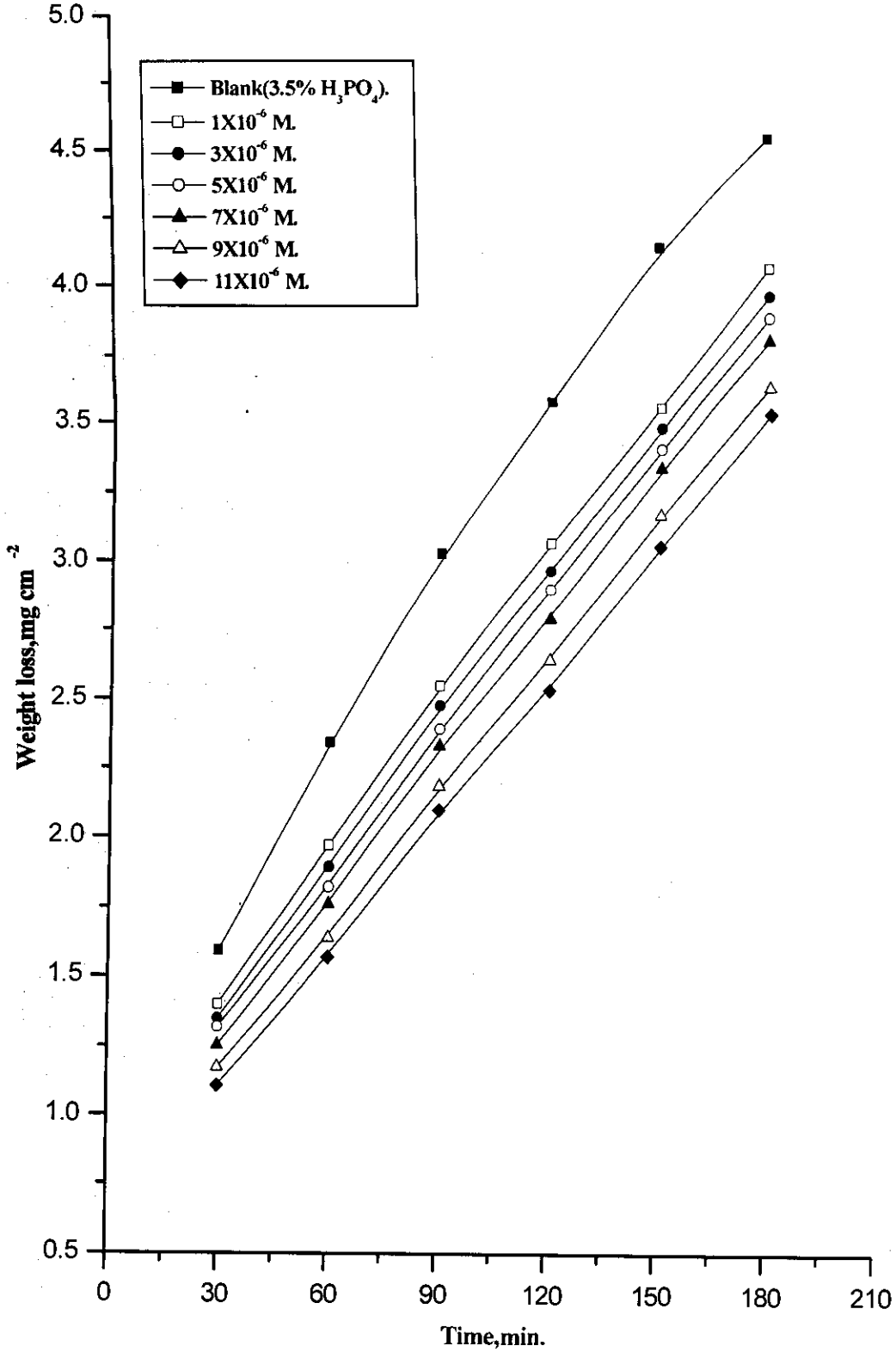


Fig: (3.6) .Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (III) at 30°C.

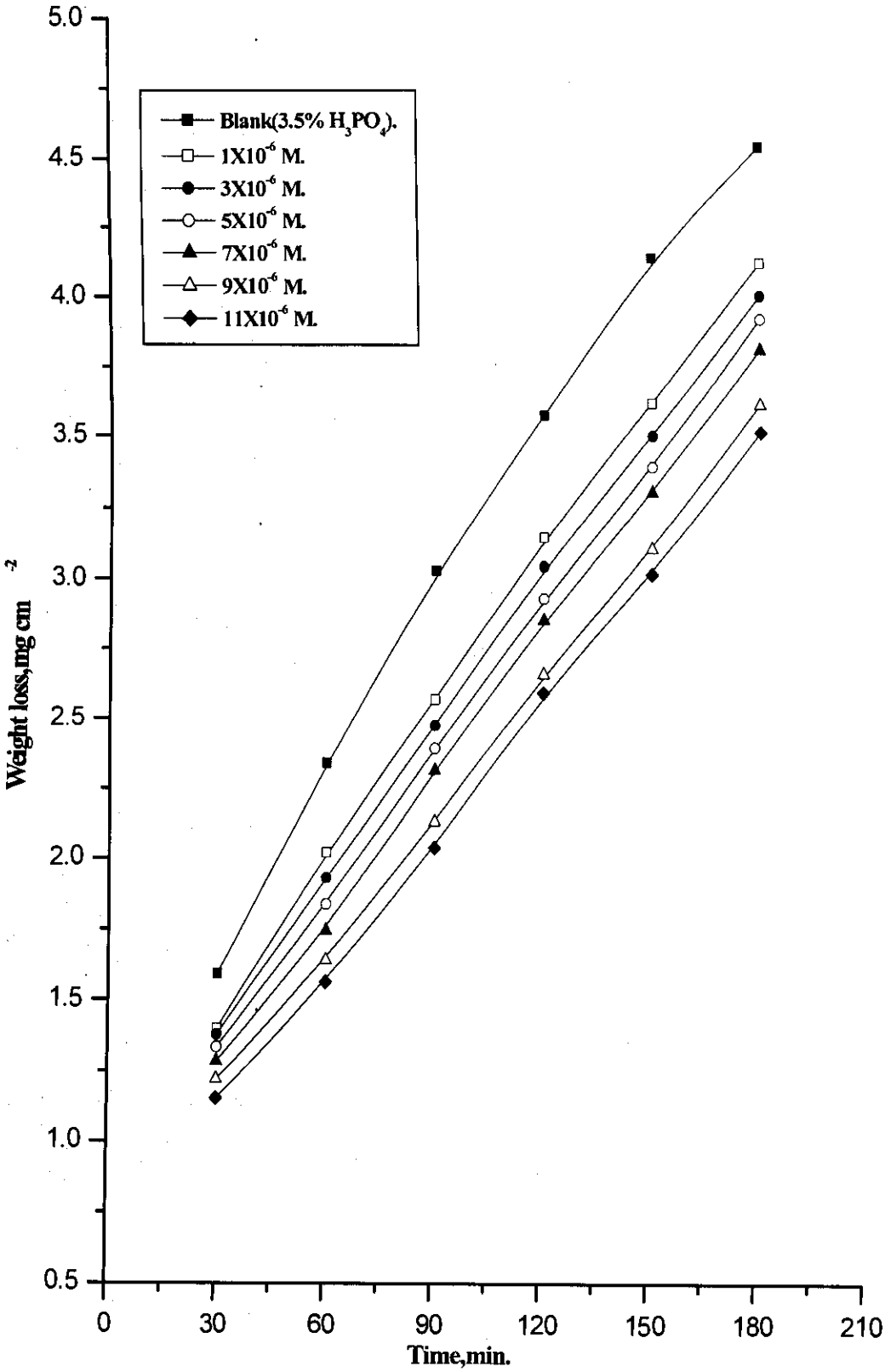


Fig: (3.7) .Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (IV) at 30°C.

Table(3.1): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of first group compounds at 30°C.

Concentration M	%Inhibition		
	1	2	3
$1X10^{-6}$	25.6	18.7	12.1
$3X10^{-6}$	28.1	20.7	14.2
$5X10^{-6}$	30.7	24.1	17.2
$7X10^{-6}$	33.2	25.9	18.9
$9X10^{-6}$	37.7	30.9	22.9
$11X10^{-6}$	39.8	33	25

Table(3.2): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5 % H_3PO_4 in presence of different concentrations of second group compounds at 30°C .

Concentration M	%Inhibition			
	I	II	III	IV
$1X10^{-6}$	31.1	19.5	14.3	12
$3X10^{-6}$	33.5	21.9	17	14.9
$5X10^{-6}$	35.8	24.6	19	18.1
$7X10^{-6}$	38.6	27.2	22	20.2
$9X10^{-6}$	44.2	32.3	26.1	25.6
$11X10^{-6}$	46.6	35.1	29.2	27.5

3.1.2- Role of anions in corrosion-inhibition of iron in acidic solutions and their synergistic effect.

The effect of I^-,Br^- and Cl^- ions on the corrosion inhibition of iron in 3.5% H_3PO_4 solution in presence and absence of the investigated hydrazone derivatives was studied by the weight loss method.

Figs.(3.8-3.28) represent the weight loss-time curves for iron dissolution in 3.5% H_3PO_4 in presence of 10^{-2},10^{-3},10^{-4},10^{-5}M of I^-, Br^-, Cl^- and also in presence of $7x10^{-6}$M of hydrazone derivatives.

Figs.(3.29-3.49) represent the weight loss time curves for iron dissolution in 3.5% H_3PO_4 in presence of 10^{-2}M of I^-, Br^-, Cl^- and also in presence of different concentrations of the investigated hydrazone derivatives.

The values of inhibition efficiency (% In) for various concentrations of inhibitors in the presence of specific concentration of these anions are given in Tables (3.3-3.8)

It is observed that %In of the inhibitors increases on addition of these different anions due to synergistic effects [109]. The strong chemisorption of these anions on the metal surface is responsible for the synergistic effect of these ions in combination with cation of the inhibitor. The cation is then adsorbed by coulombic attraction on the metal surface where these anions are already adsorbed by chemisorption. Stabilization of these adsorbed anions with cations leads to greater surface coverage and therefore greater inhibition.

The synergistic inhibition effect was evaluated using a parameter, S_θ, obtained from the surface coverage values (θ) of the anion, cation and both. Aramaki and Hackerman [110] calculated the synergism parameter S_θ using the following equation:

$$S_\theta = 1-\theta_{1+2} / 1-\theta'_{1+2} \qquad (3.9)$$

where:

$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$;

θ_1 = surface coverage by anion;

θ_2 = surface coverage by cation;

θ'_{1+2} = measured surface coverage by both the anion and cation.

We calculate synergism parameters from the above equation. The plot of the synergism parameter (S_θ) against various concentrations of investigated hydrazone derivatives given in Figs.(3.50-3.55) and the corresponding values are shown in Tables (3.9-3.14). As can be seen from these Tables, values are nearly equal to unity, which suggests that the enhanced inhibition efficiencies caused by the addition of these anions to hydrazone derivatives is due mainly to the synergistic effect.

Synergistic adsorption is classified into two types plus a mixture of the two:

(i) specific co-adsorption of anions and cations.

(ii) ionic or physical overlap adsorption of cations over the anion covered iron surface.

- From previous results it is known that KI would be considered as one of the effective anions for synergistic action within the investigated salt. The net increment of inhibition efficiency shows a synergistic effect of KI, KBr, KCl with hydrazone derivatives. The synergistic effect depends on the type and concentration of anions. The adsorption ability on the iron surfaces was in the order KI> KBr >KCl[111].

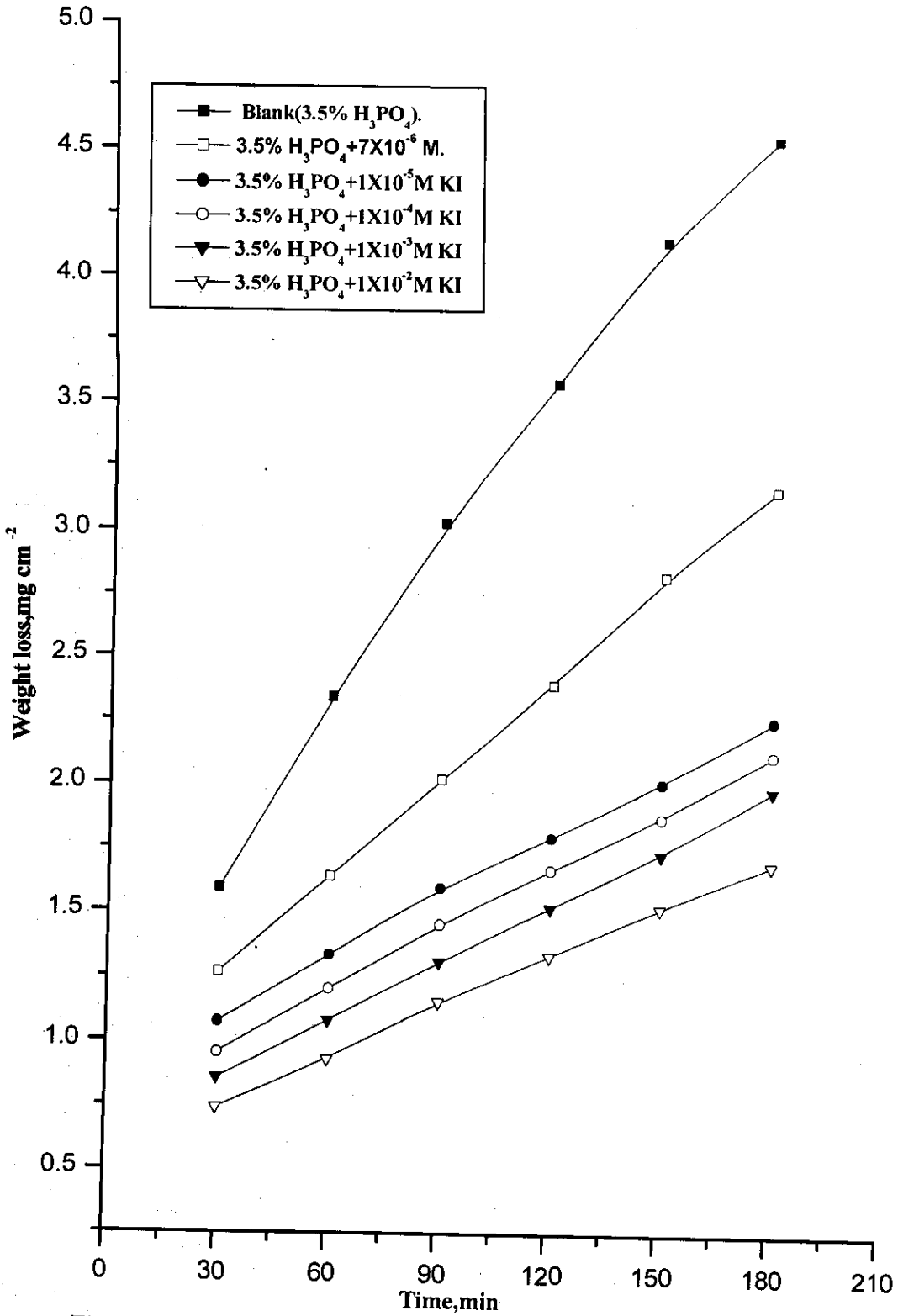


Fig.(3.8): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KI and at 7x10^{-6}M of compound(1) at 30°C.

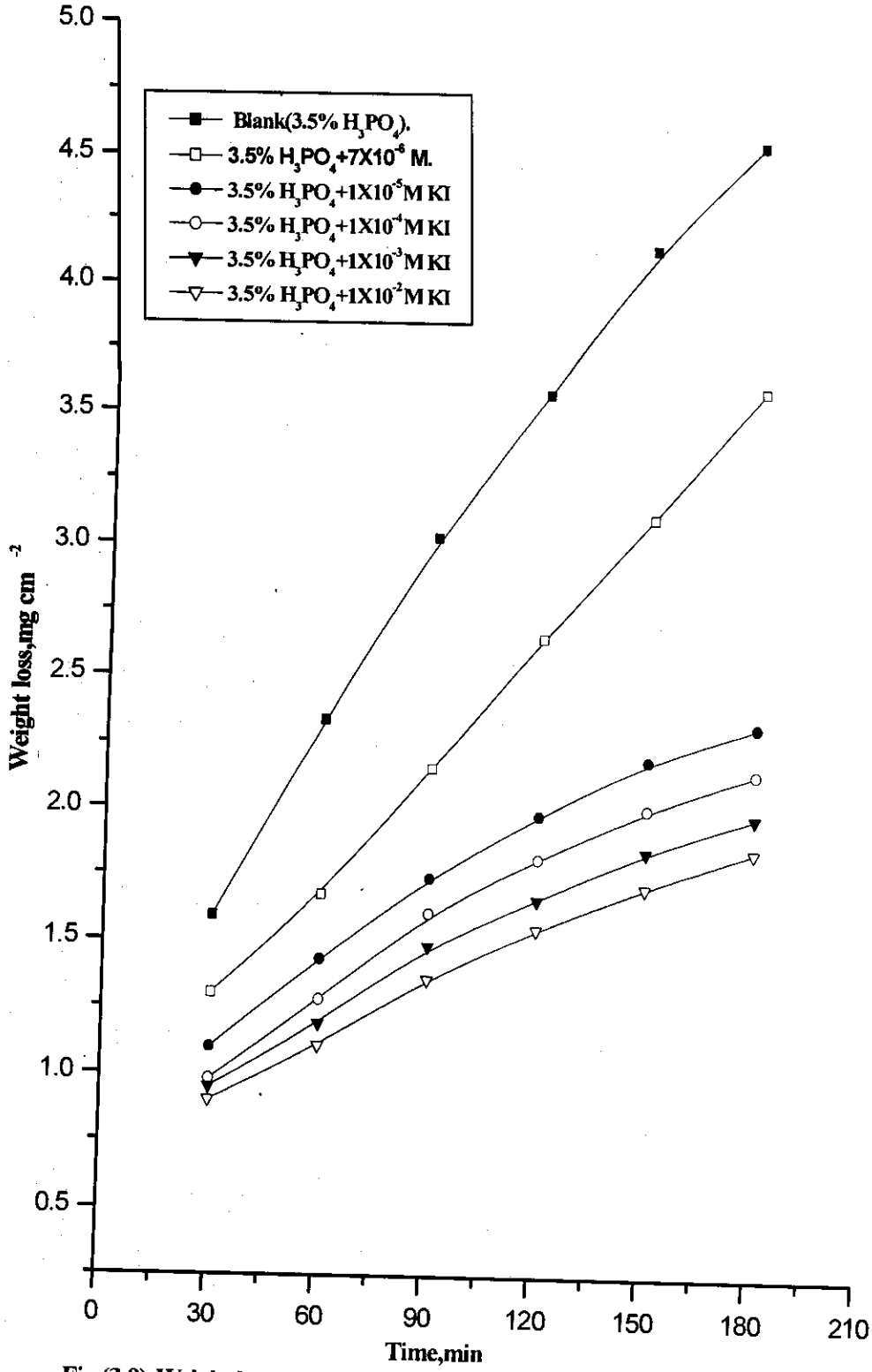


Fig.(3.9): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KI and at 7x10^{-6}M of compound(2) at 30°C.

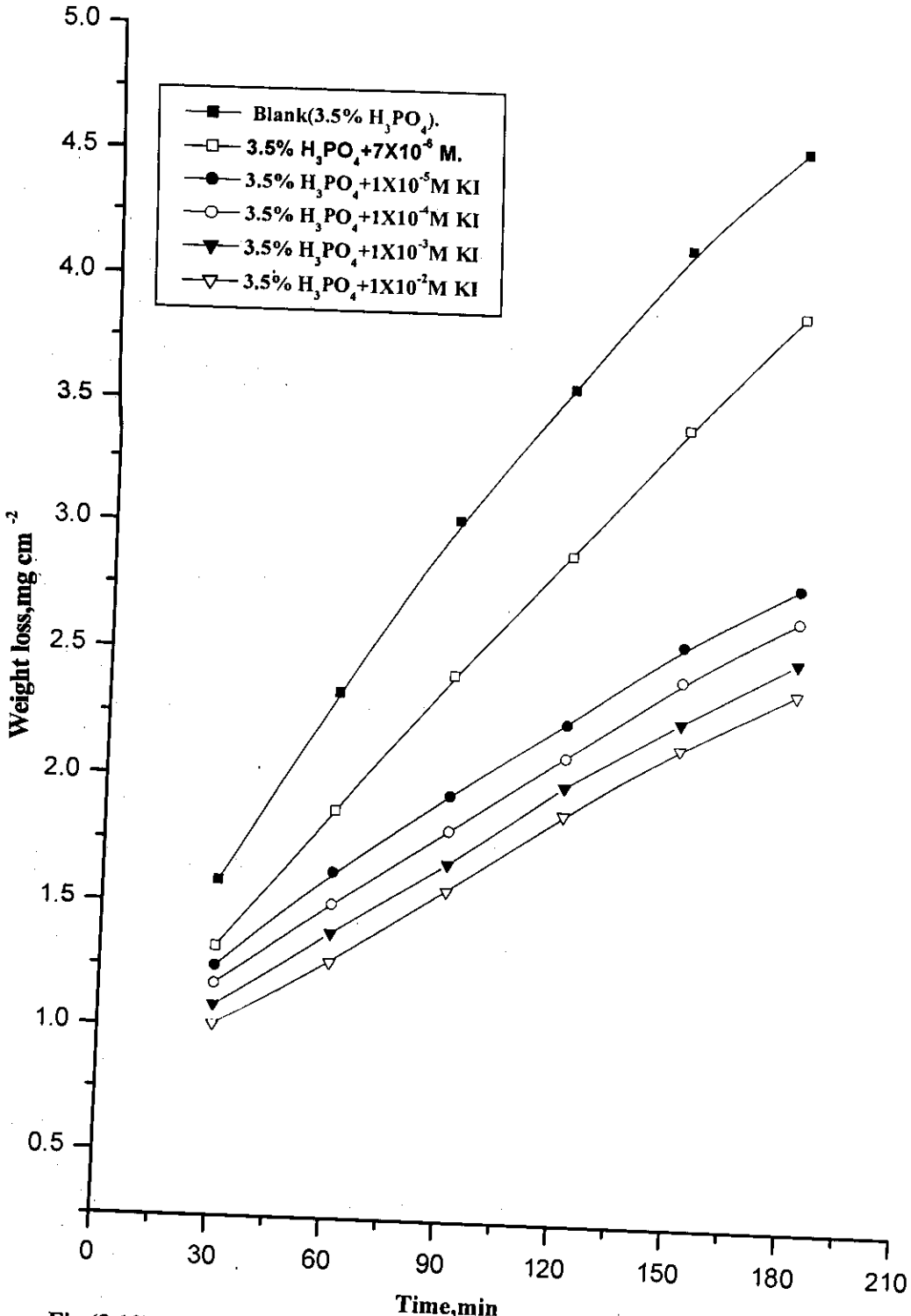


Fig.(3.10):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KI and at 7x10^{-6}M of compound(3) at 30°C.

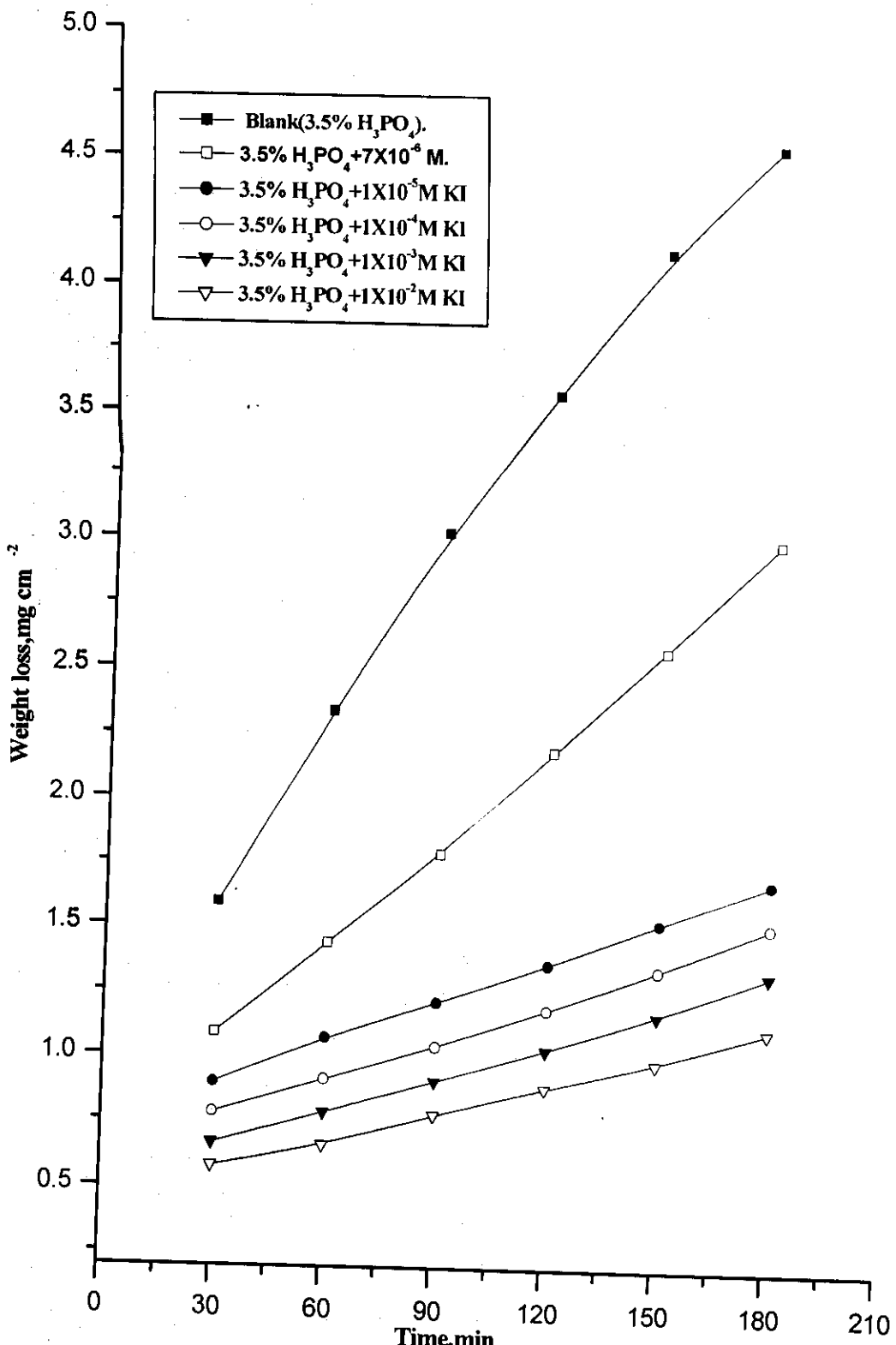


Fig.(3.11):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KI and at 7x10^{-6}M of compound(I) at 30°C.

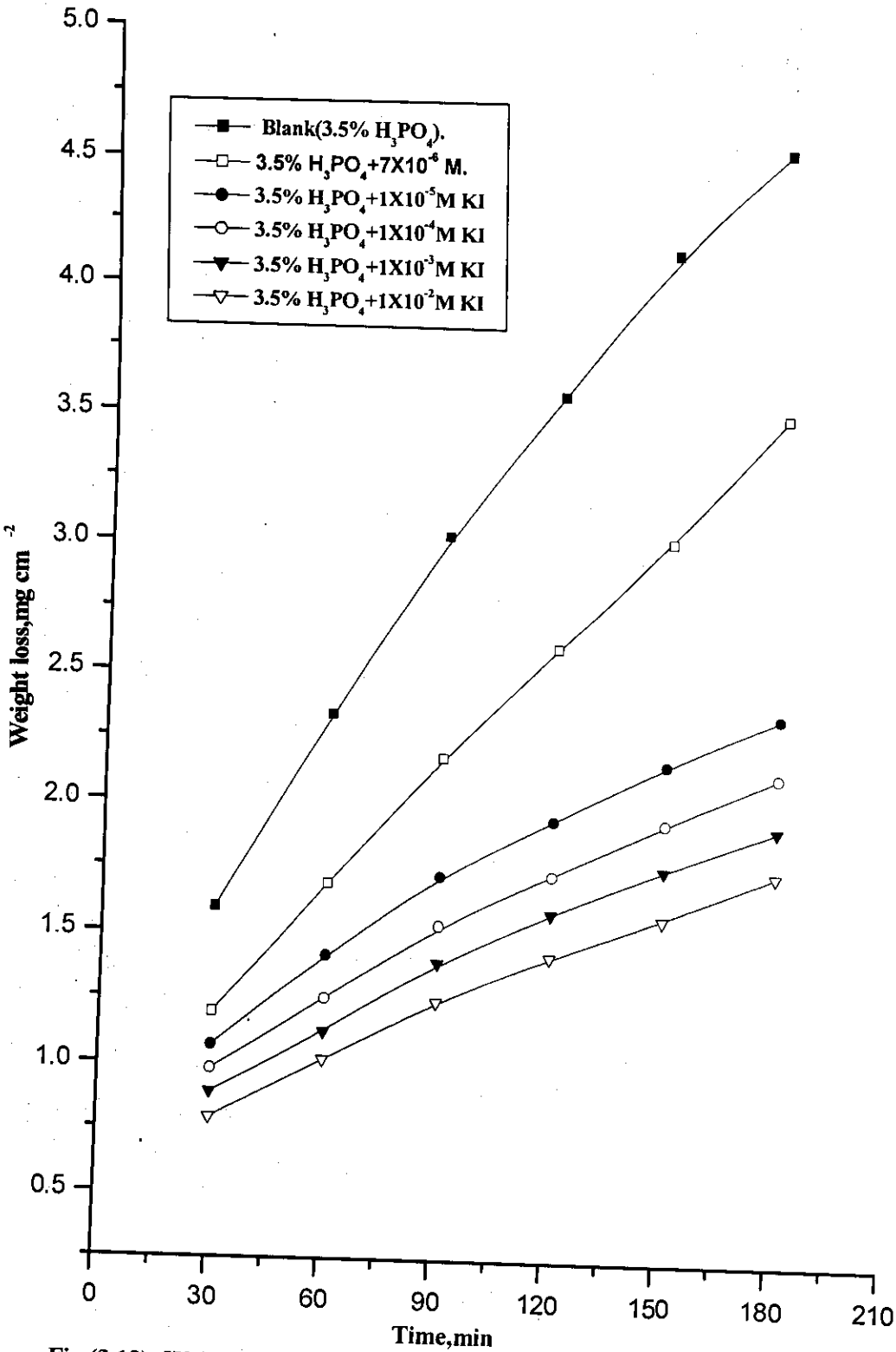


Fig.(3.12): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KI and at 7x10^{-6}M of compound(II) at 30°C.

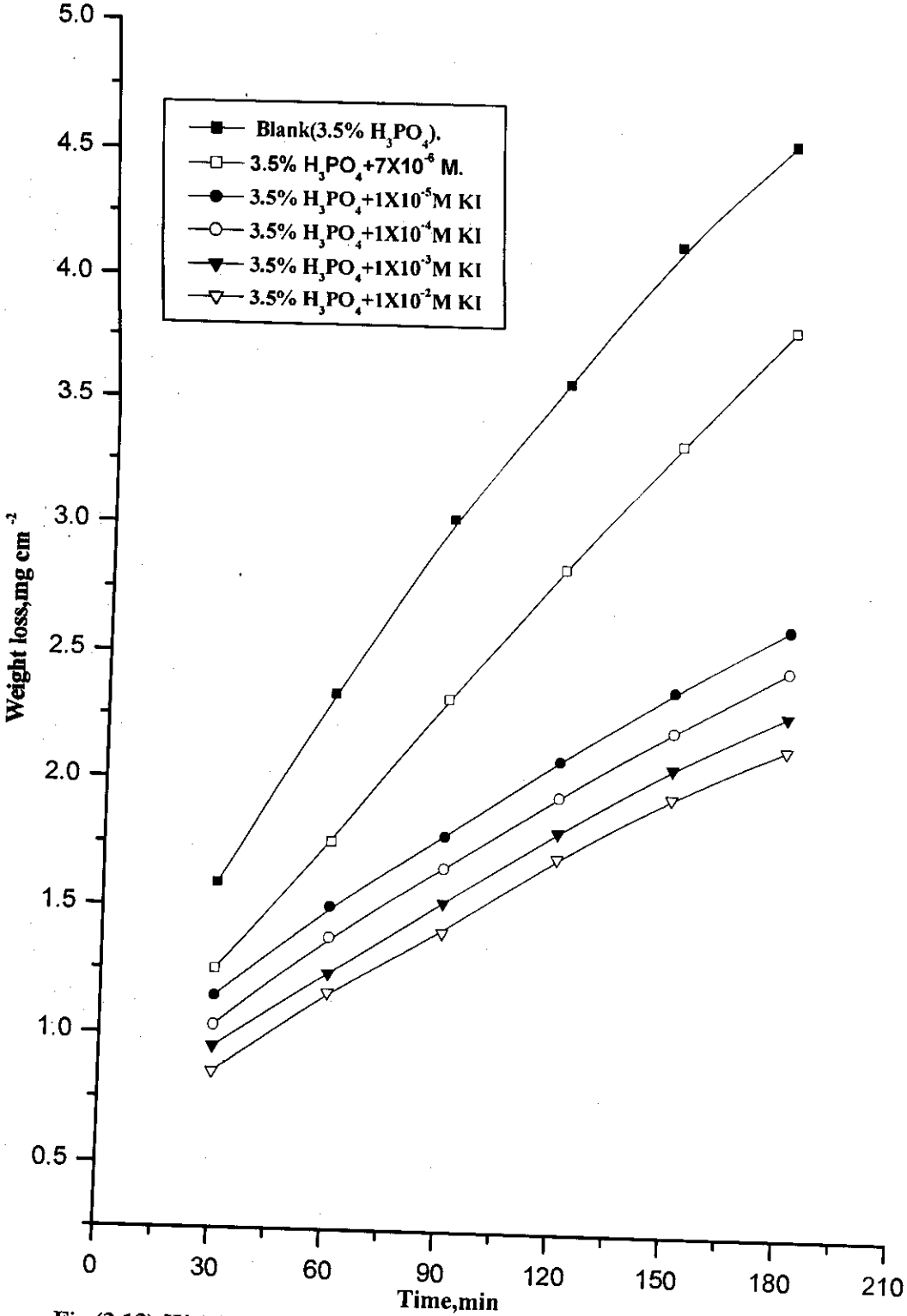


Fig.(3.13): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KI and at 7x10^{-6}M of compound(III) at 30°C.

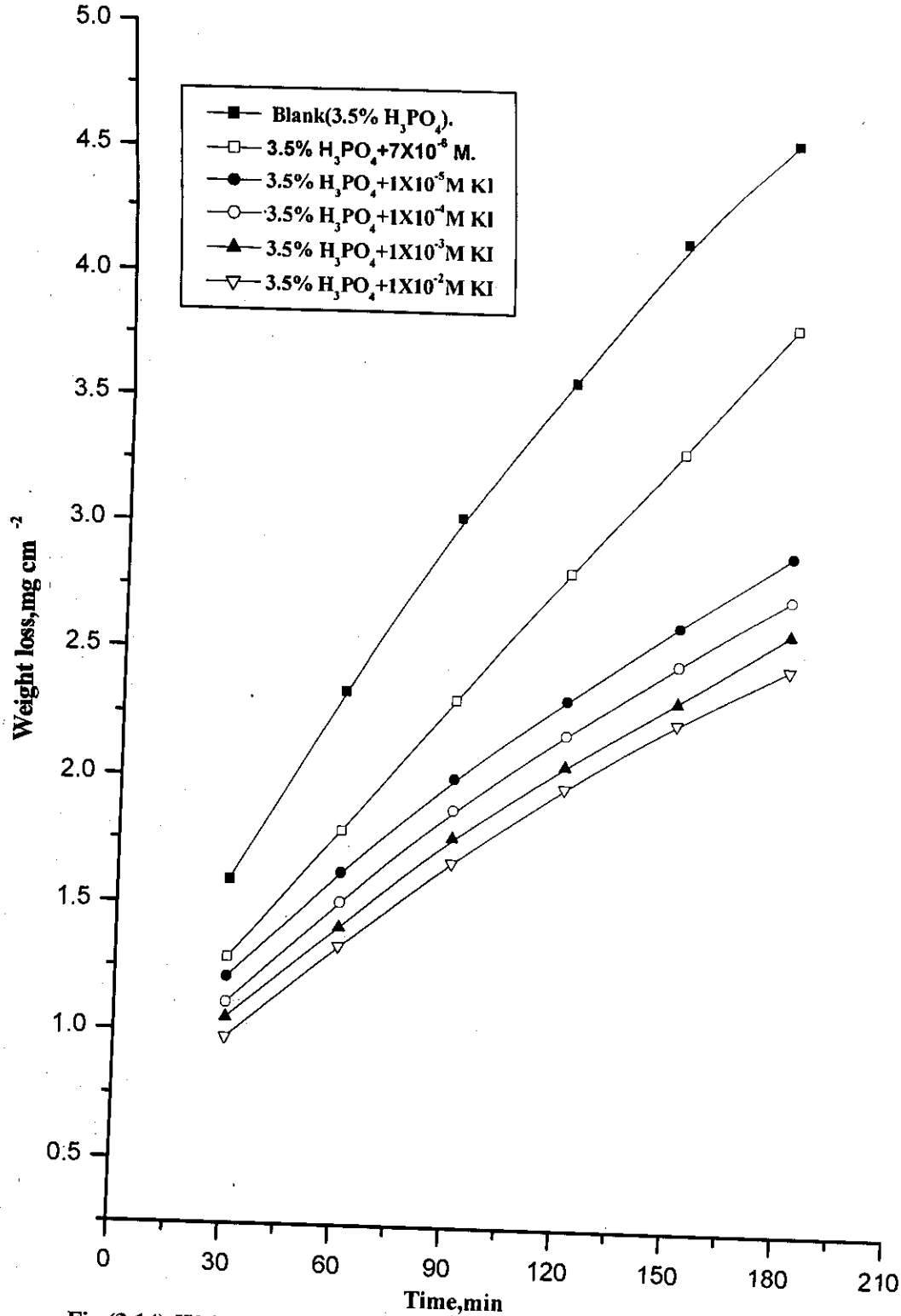


Fig.(3.14):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KI and at 7x10^{-6}M of compound(IV) at 30°C.

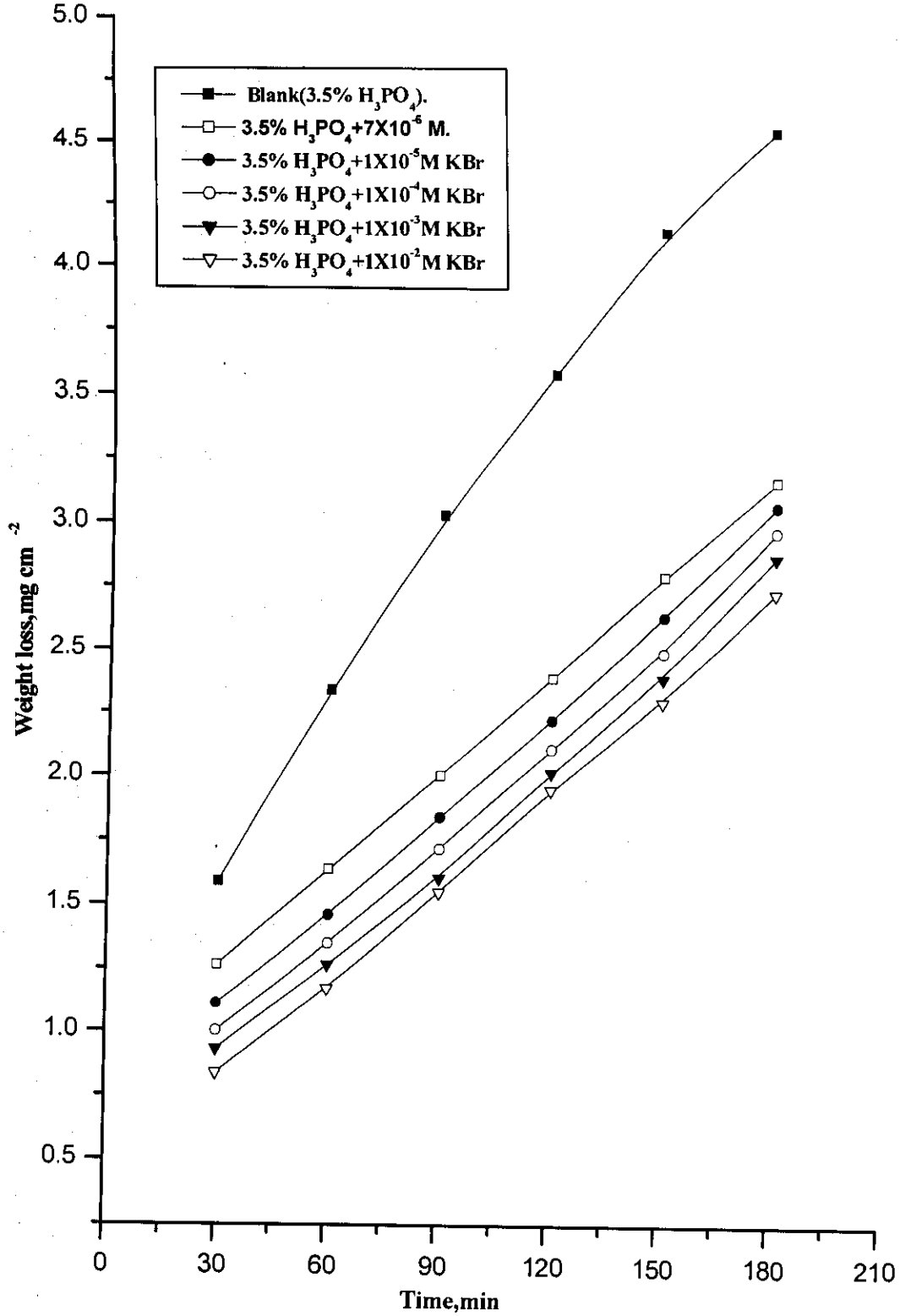


Fig.(3.15): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KBr and at 7x10^{-6}M of compound(1) at 30°C.

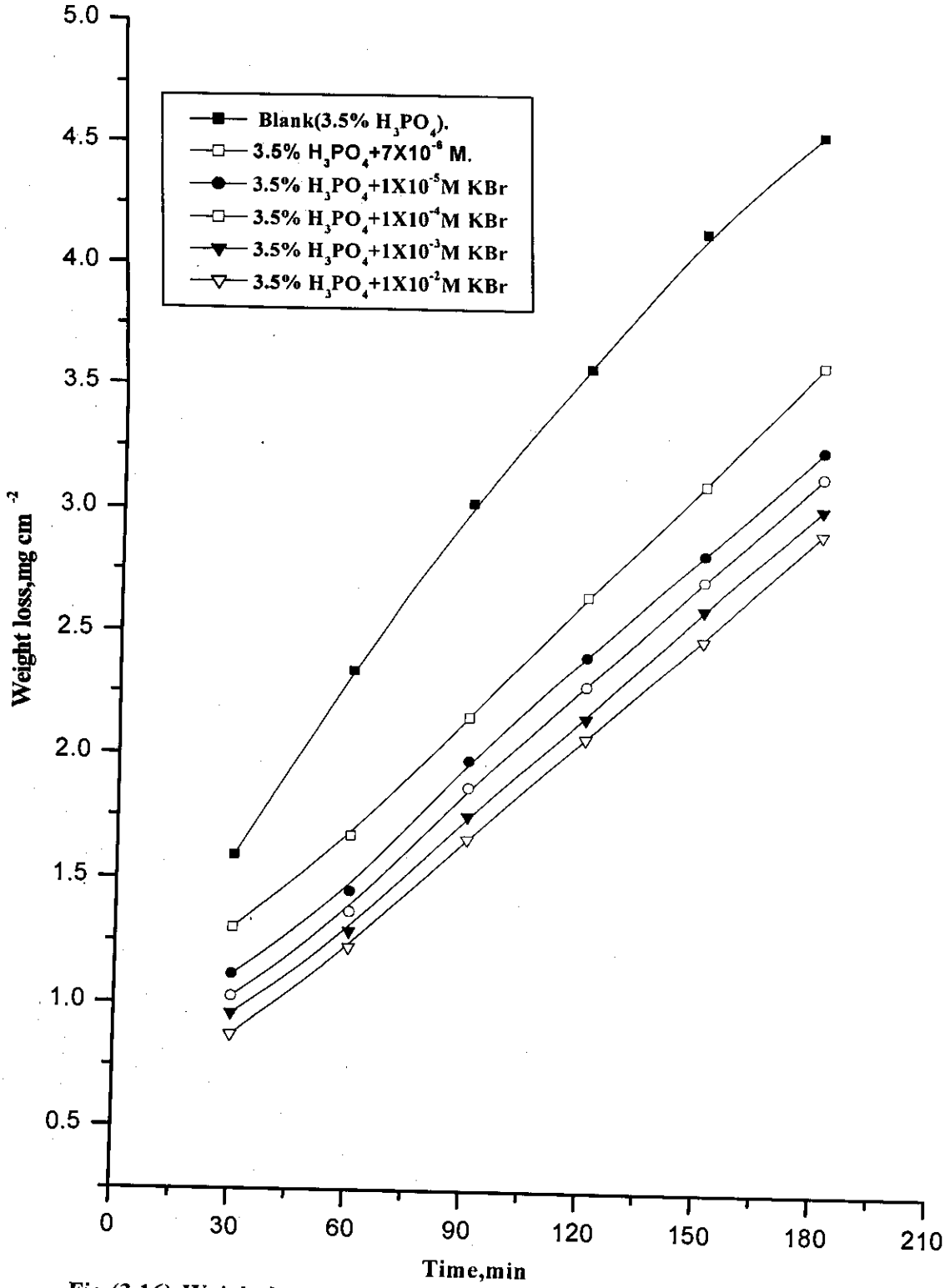


Fig.(3.16):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KBr and at 7x10^{-6}M of compound(2) at 30°C.

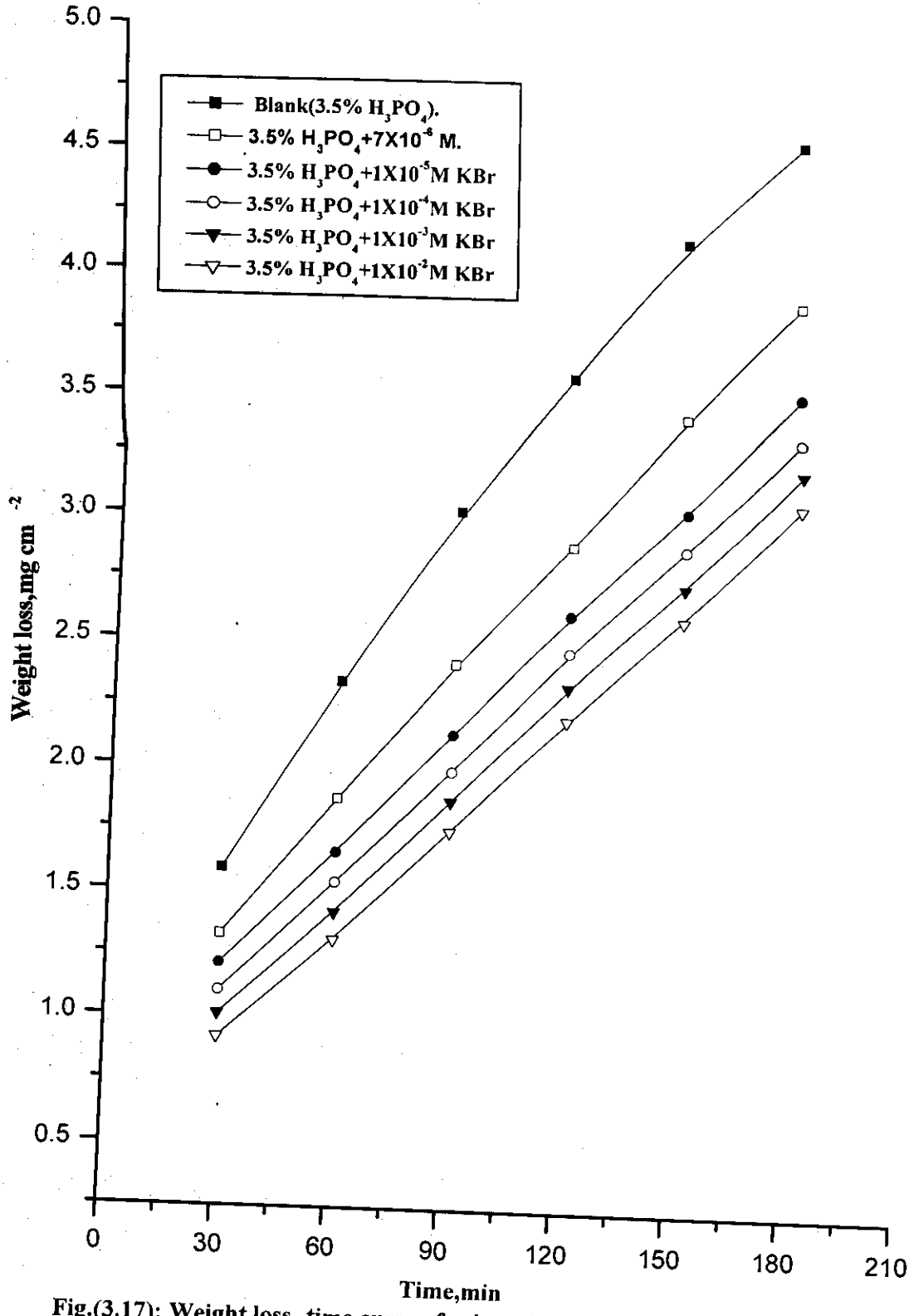


Fig.(3.17): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KBr and at 7x10^{-6}M of compound(3) at 30°C.

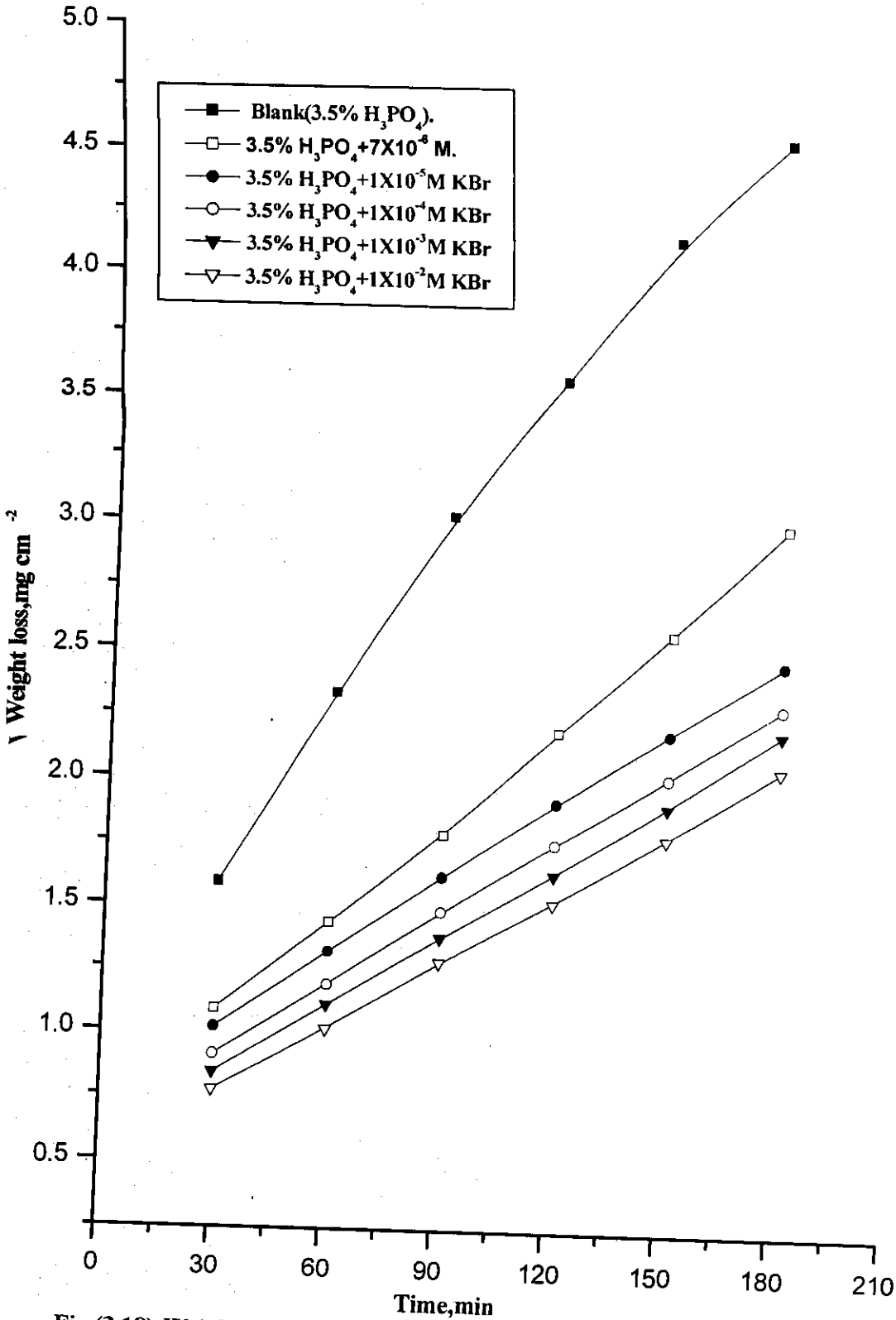


Fig.(3.18): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KBr and at 7x10^{-6}M of compound(I) at 30°C.

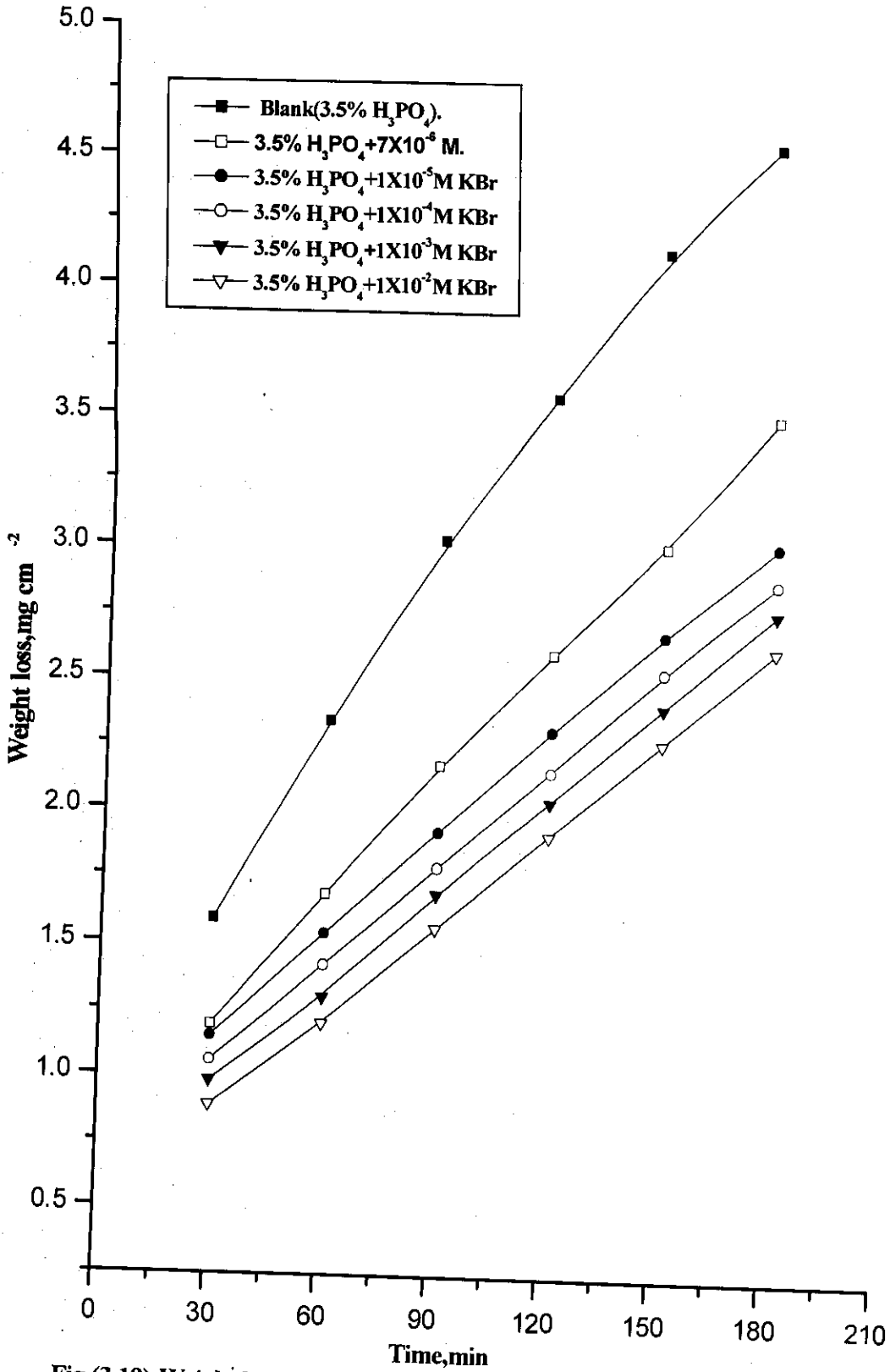


Fig.(3.19):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KBr and at 7x10^{-6}M of compound(II) at 30°C.

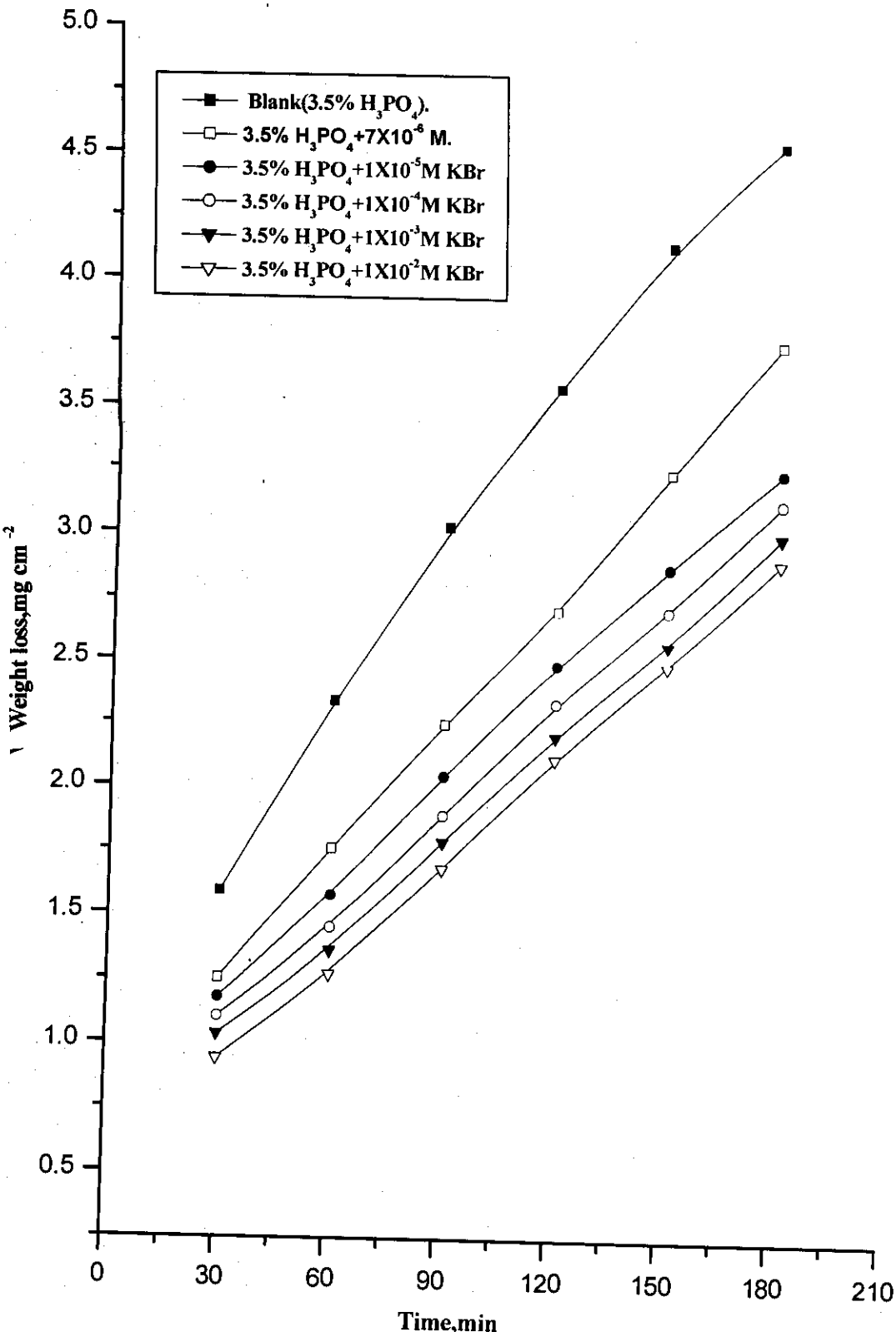


Fig.(3.20): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KBr and at 7x10^{-6}M of compound(III) at 30°C.

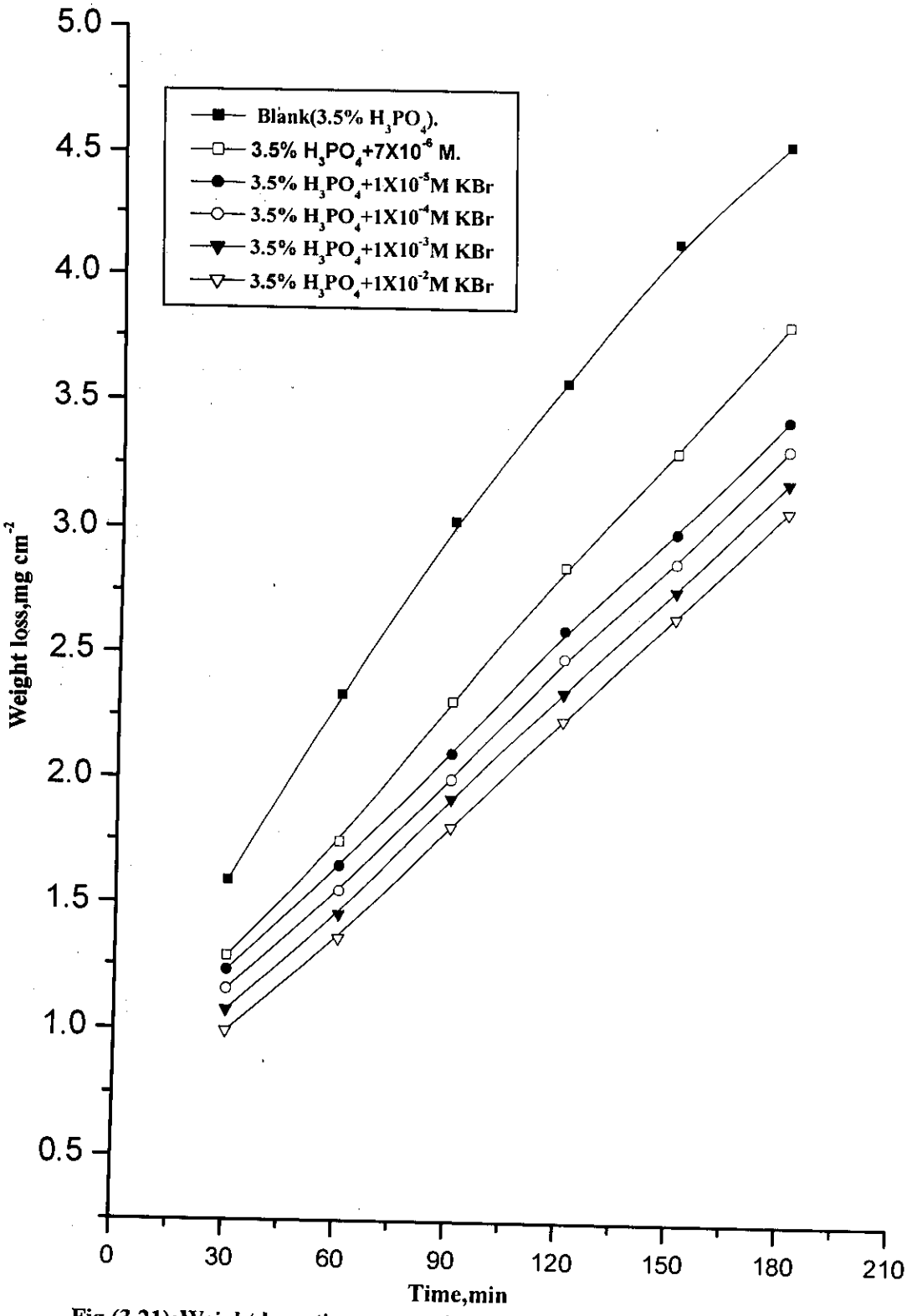


Fig.(3.21):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KBr and at 7x10^{-6}M of compound(IV) at 30°C.

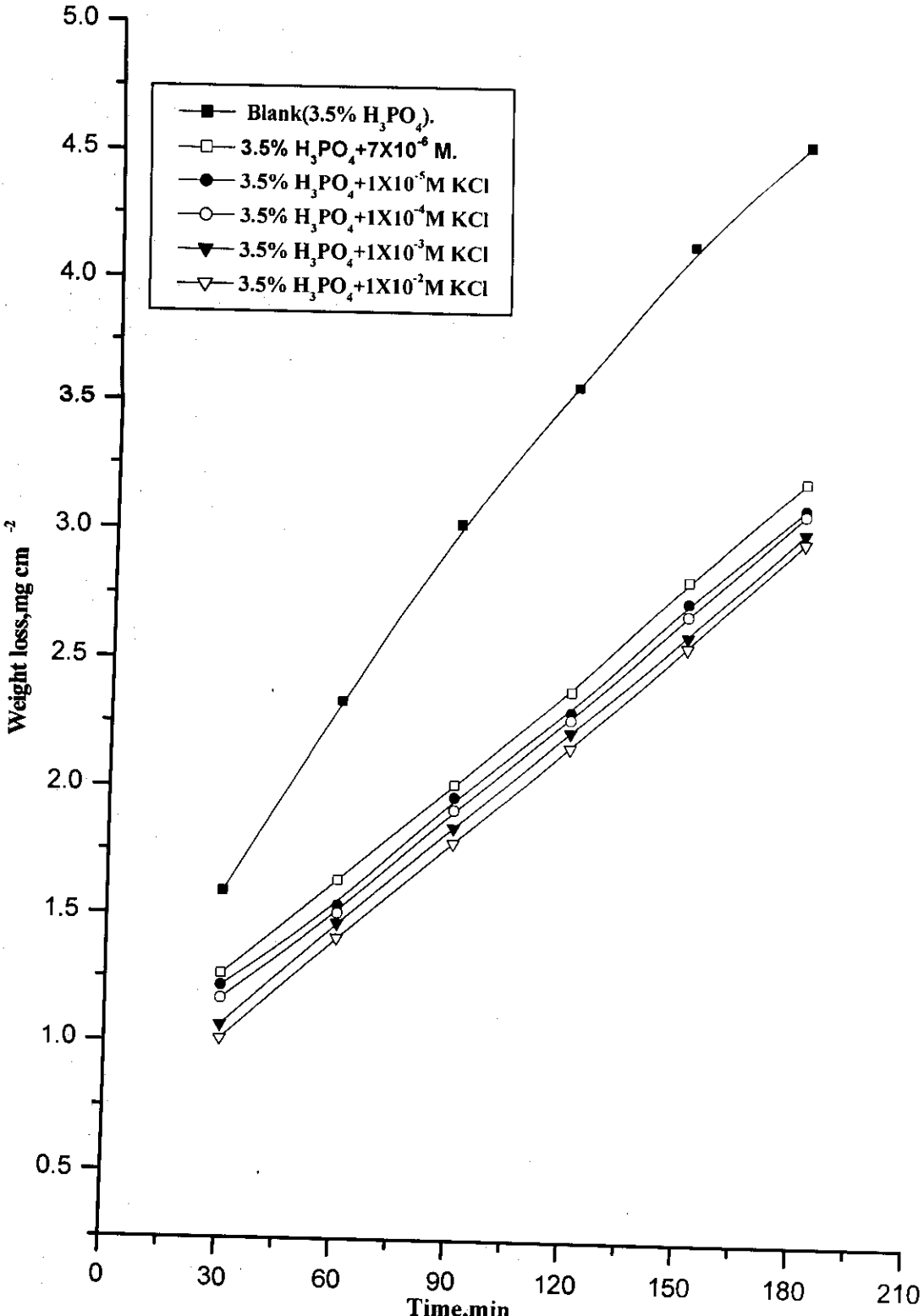


Fig.(3.22): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KCl and at 7x10^{-6}M of compound(1) at 30°C.

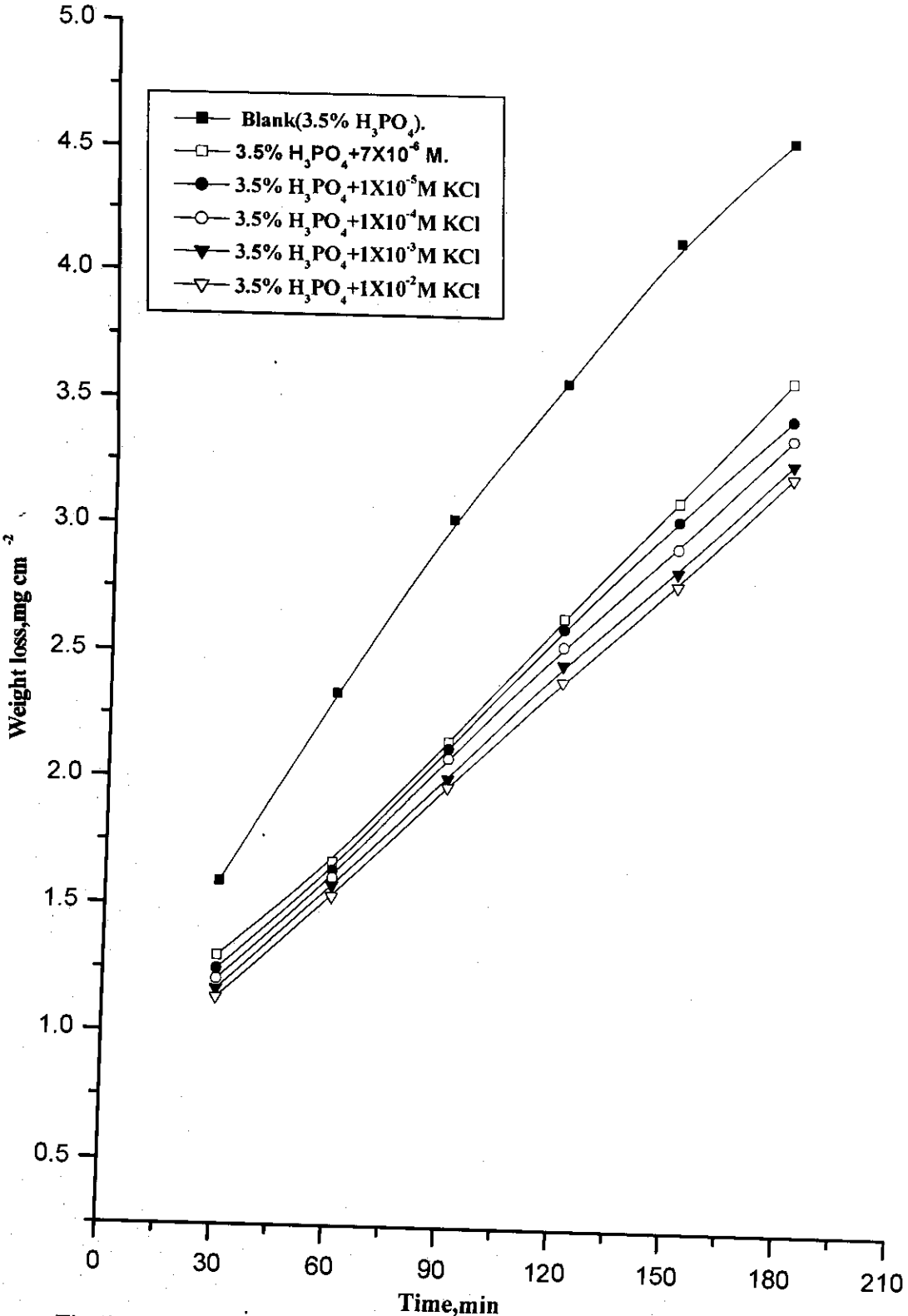


Fig.(3.23): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KCl and at 7x10^{-6}M of compound(2) at 30°C.

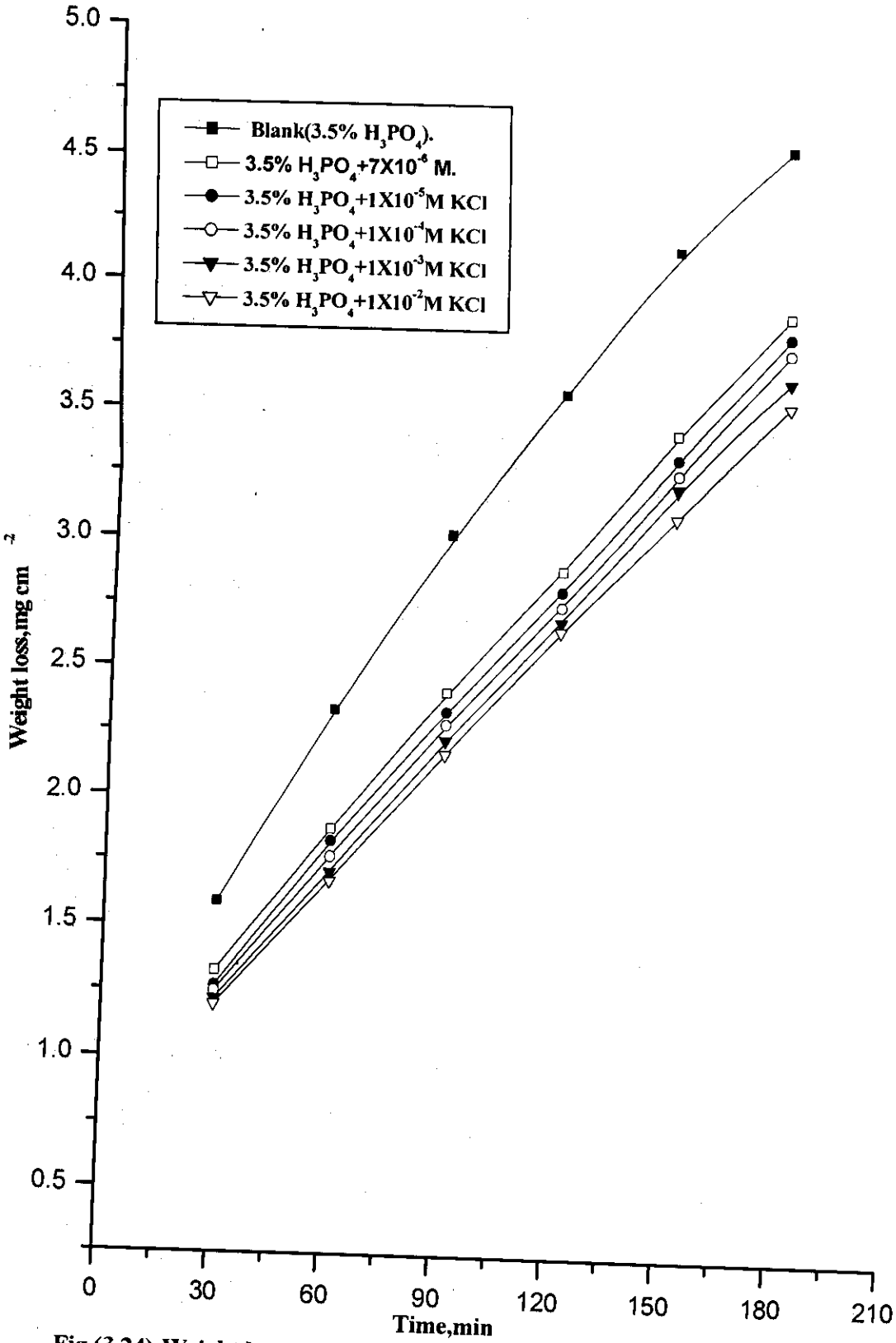


Fig.(3.24):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KCl and at 7x10^{-6}M of compound(3) at 30°C.

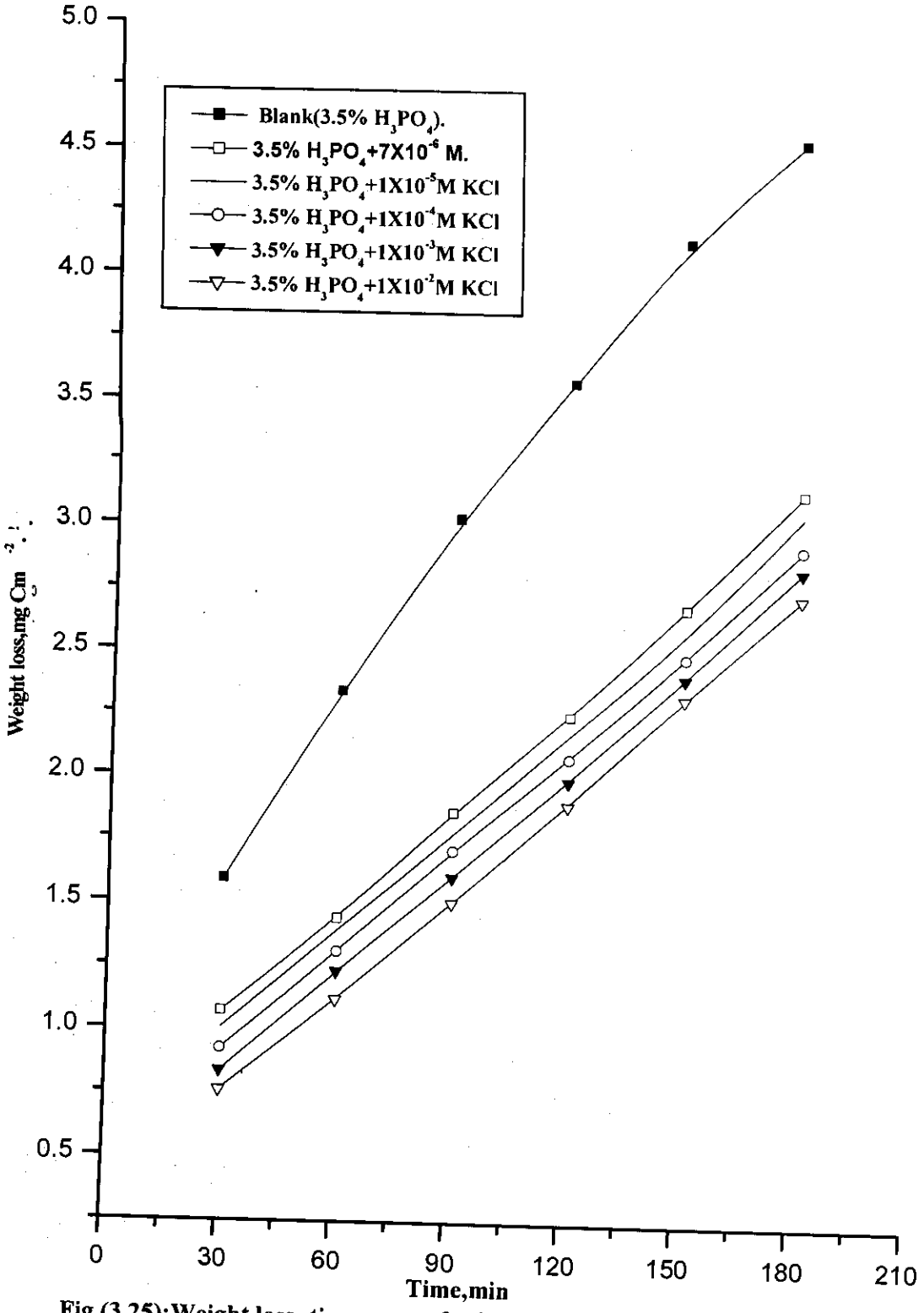


Fig.(3.25): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KCl and at 7x10^{-6}M of compound(I) at 30°C.

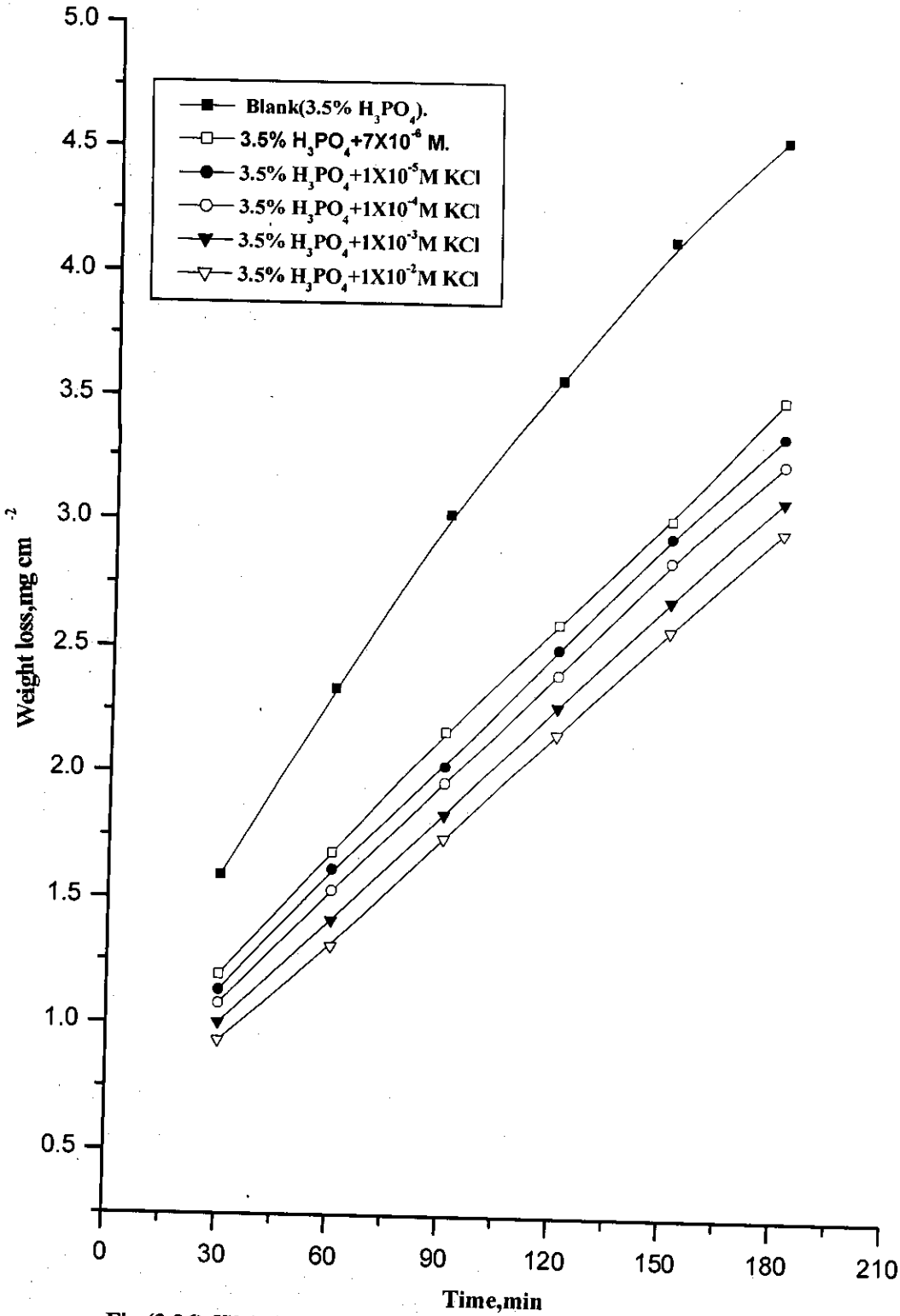


Fig.(3.26):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KCl and at 7x10^{-6}M of compound(II) at 30°C.

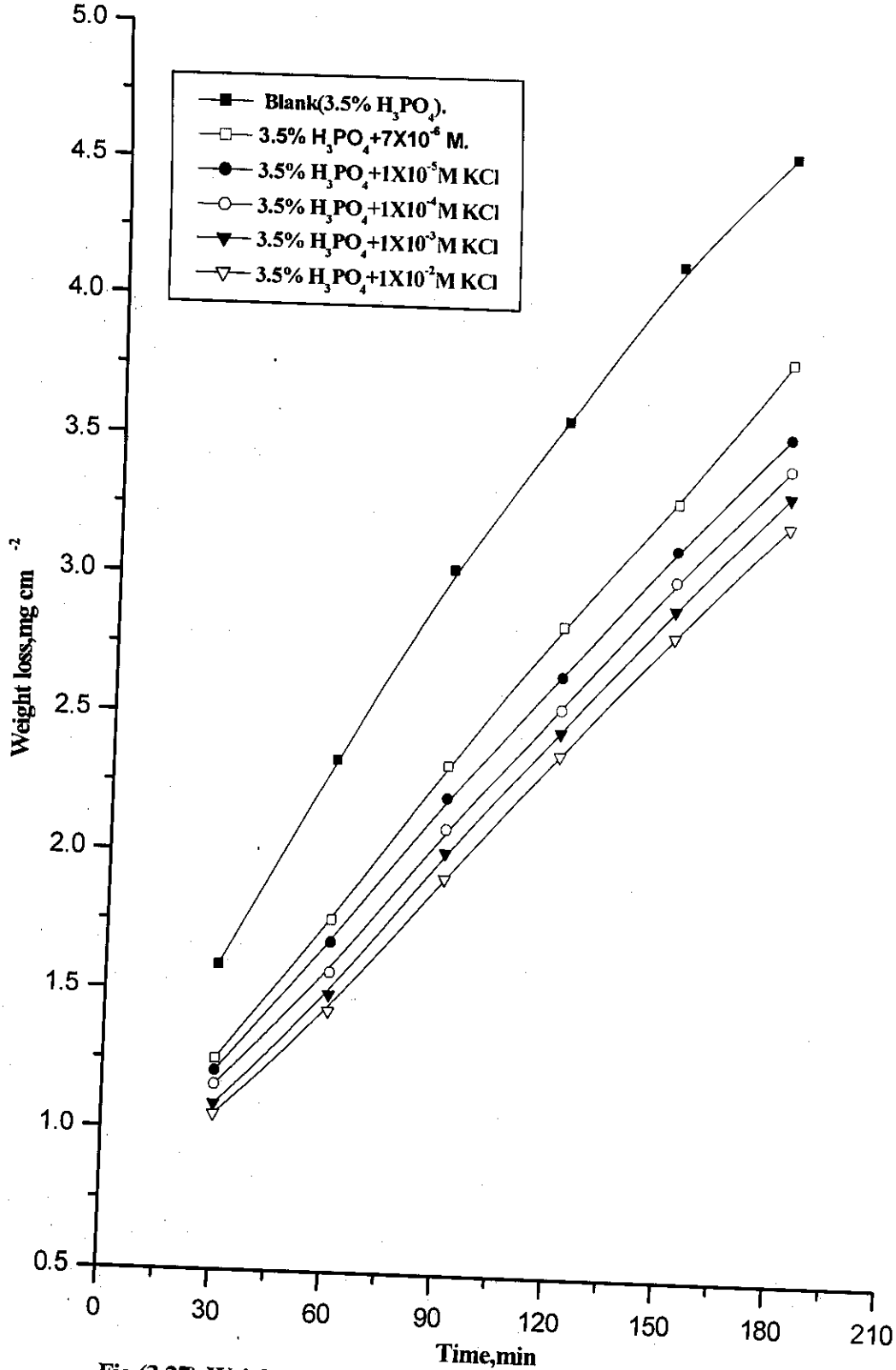


Fig.(3.27): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KCl and at 7x10^{-6}M of compound(III) at 30°C.

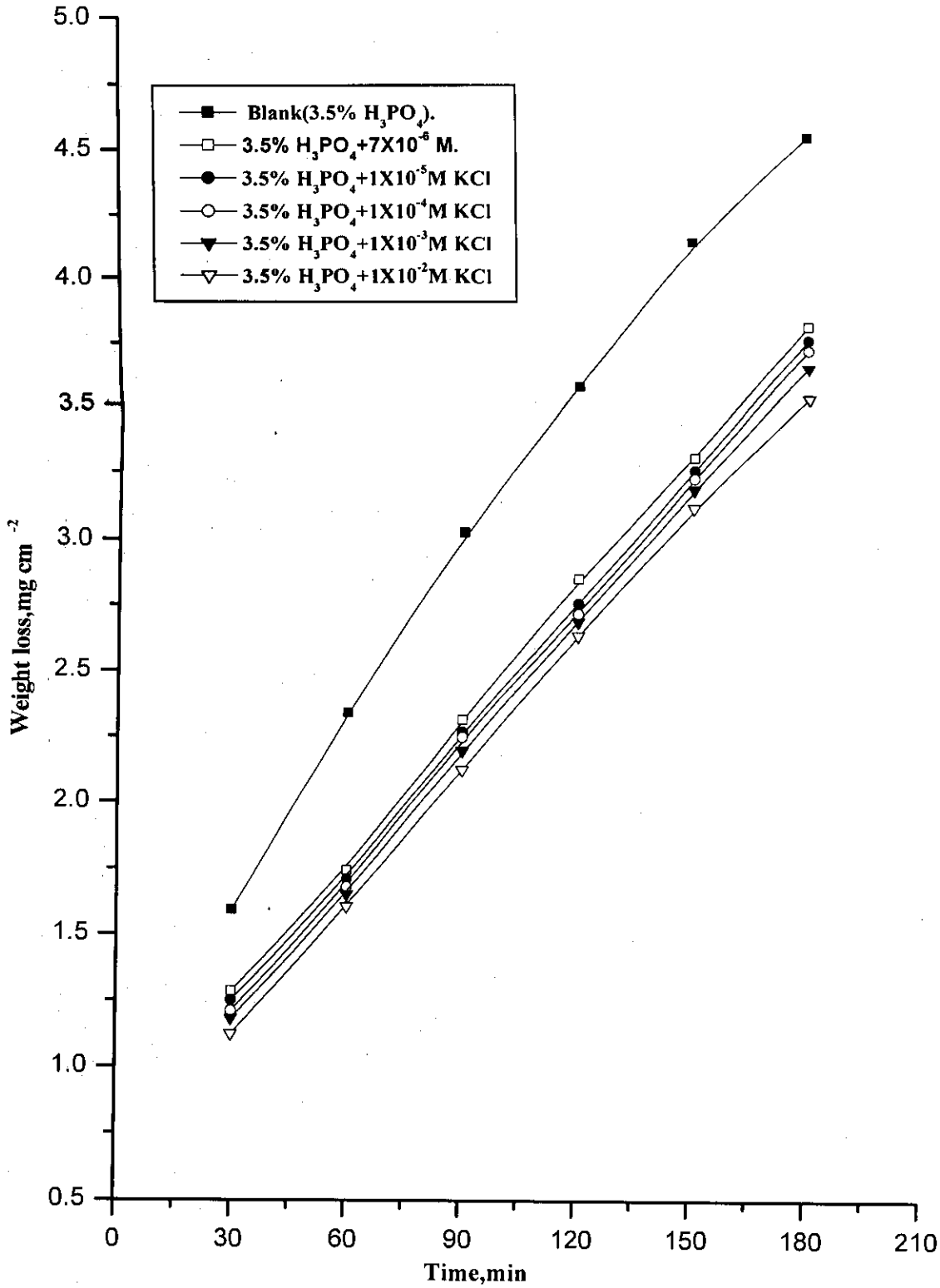


Fig.(3.28):Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of different concentrations of KCl and at 7x10^{-6}M of compound(IV) at 30°C.

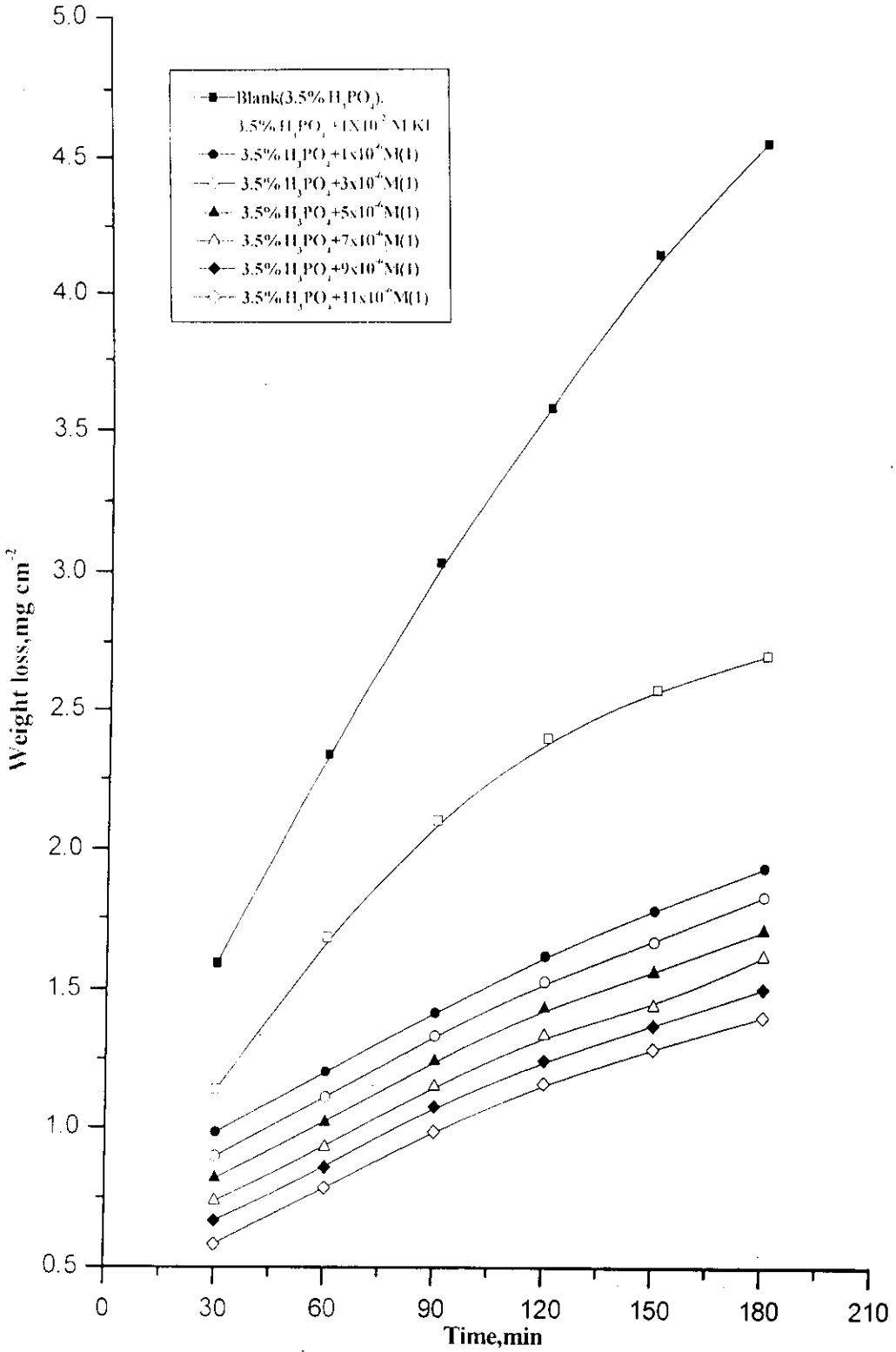


Fig.(3.29): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KI and at different concentrations of compound(1) at 30°C.

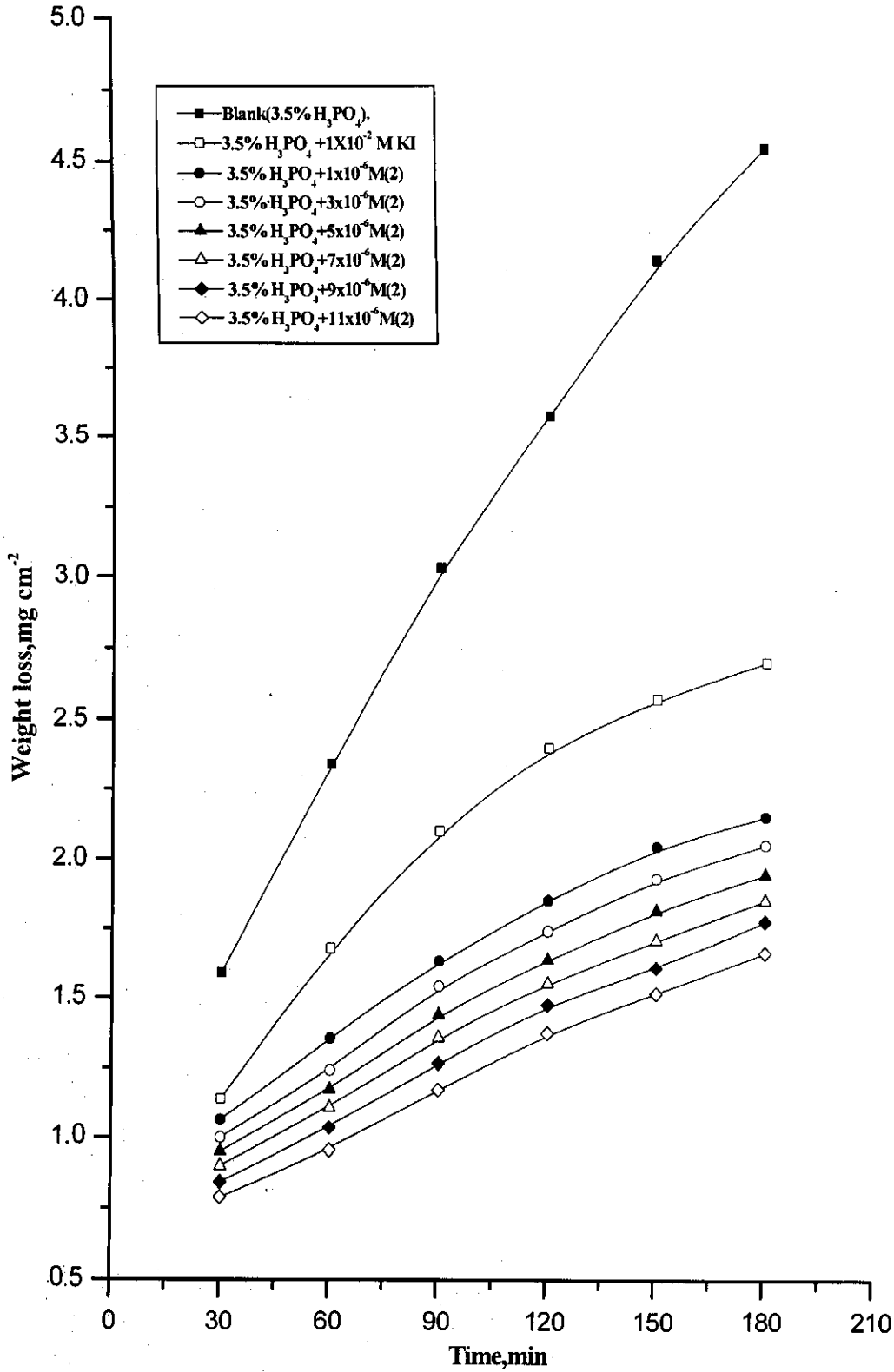


Fig.(3.30): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KI and at different concentrations of compound(2) at 30^{o}C.

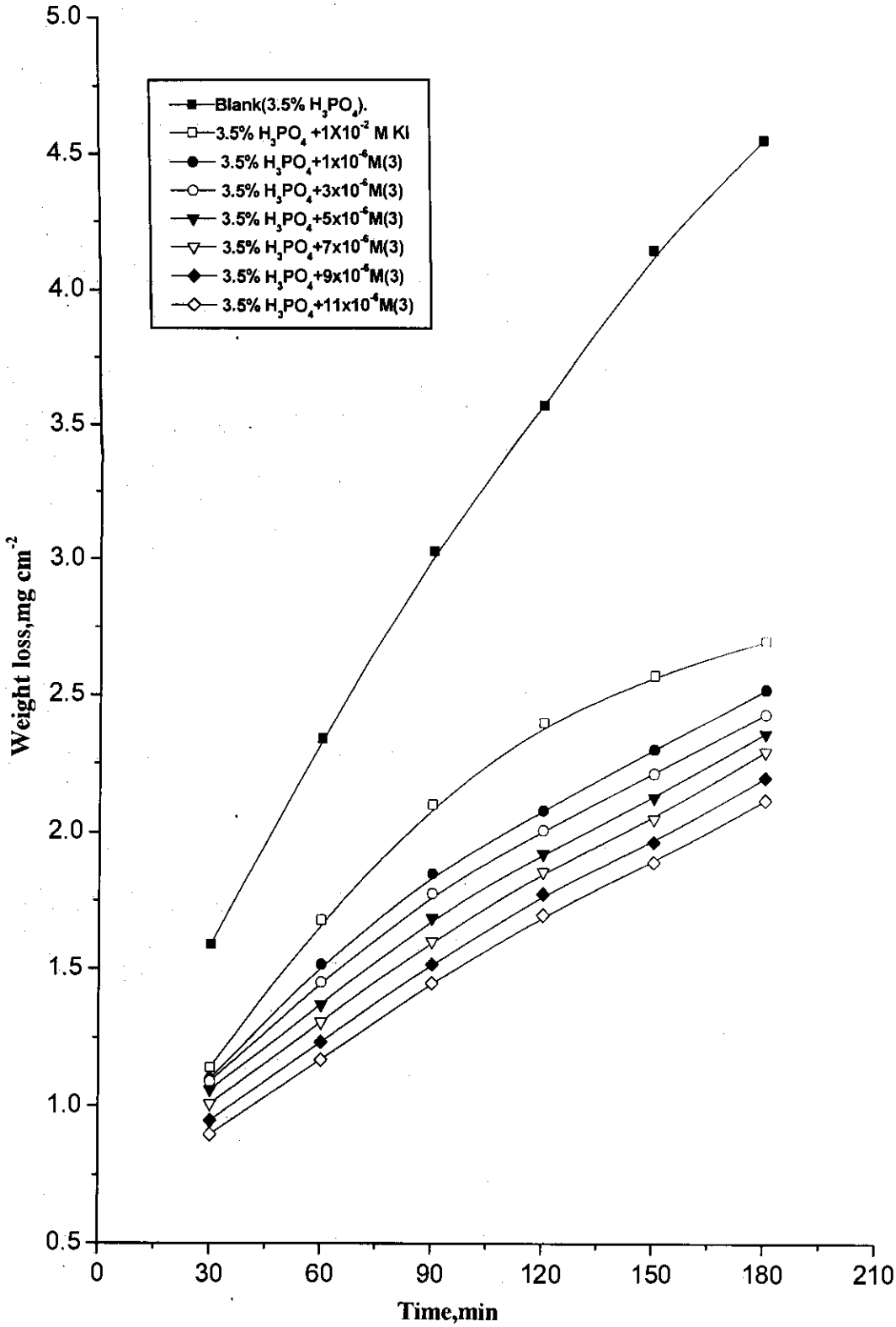


Fig.(3.31): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KI and at different concentrations of compound(3) at 30^{O}C.

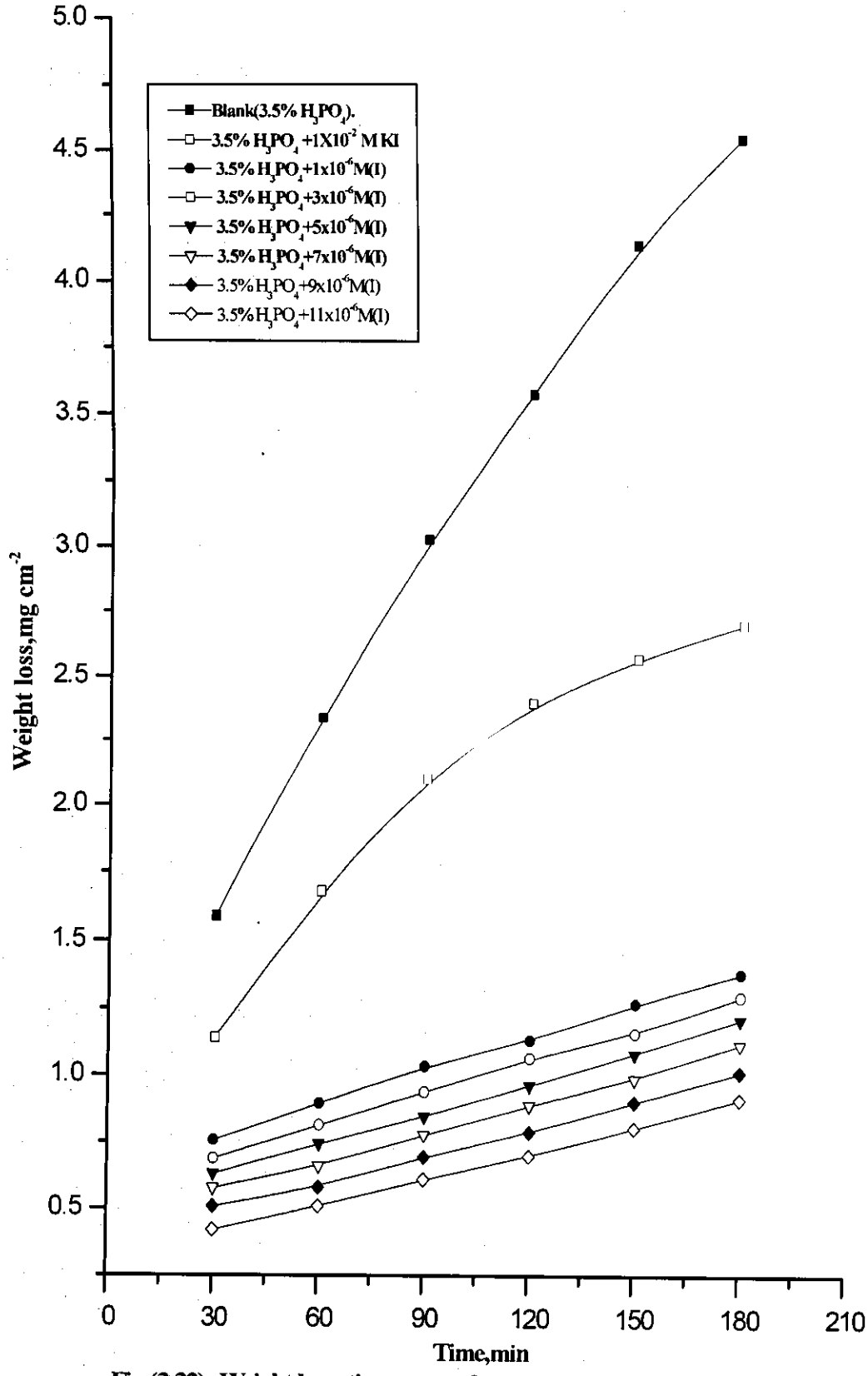


Fig.(3.32): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KI and at different concentrations of compound(I) at 30^{o}C.

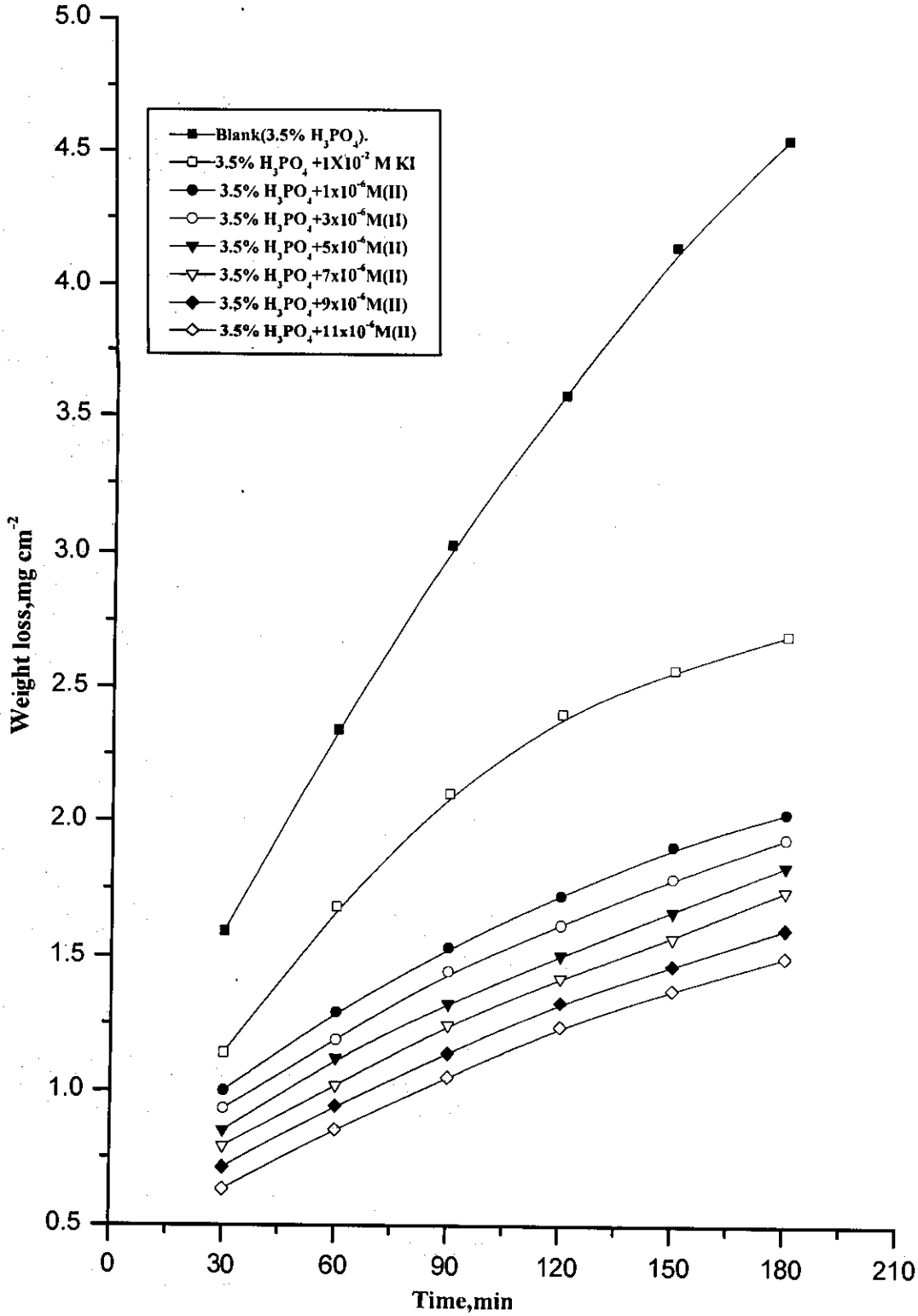


Fig.(3.33): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KI and at different concentrations of compound(II) at 30^{O}C.

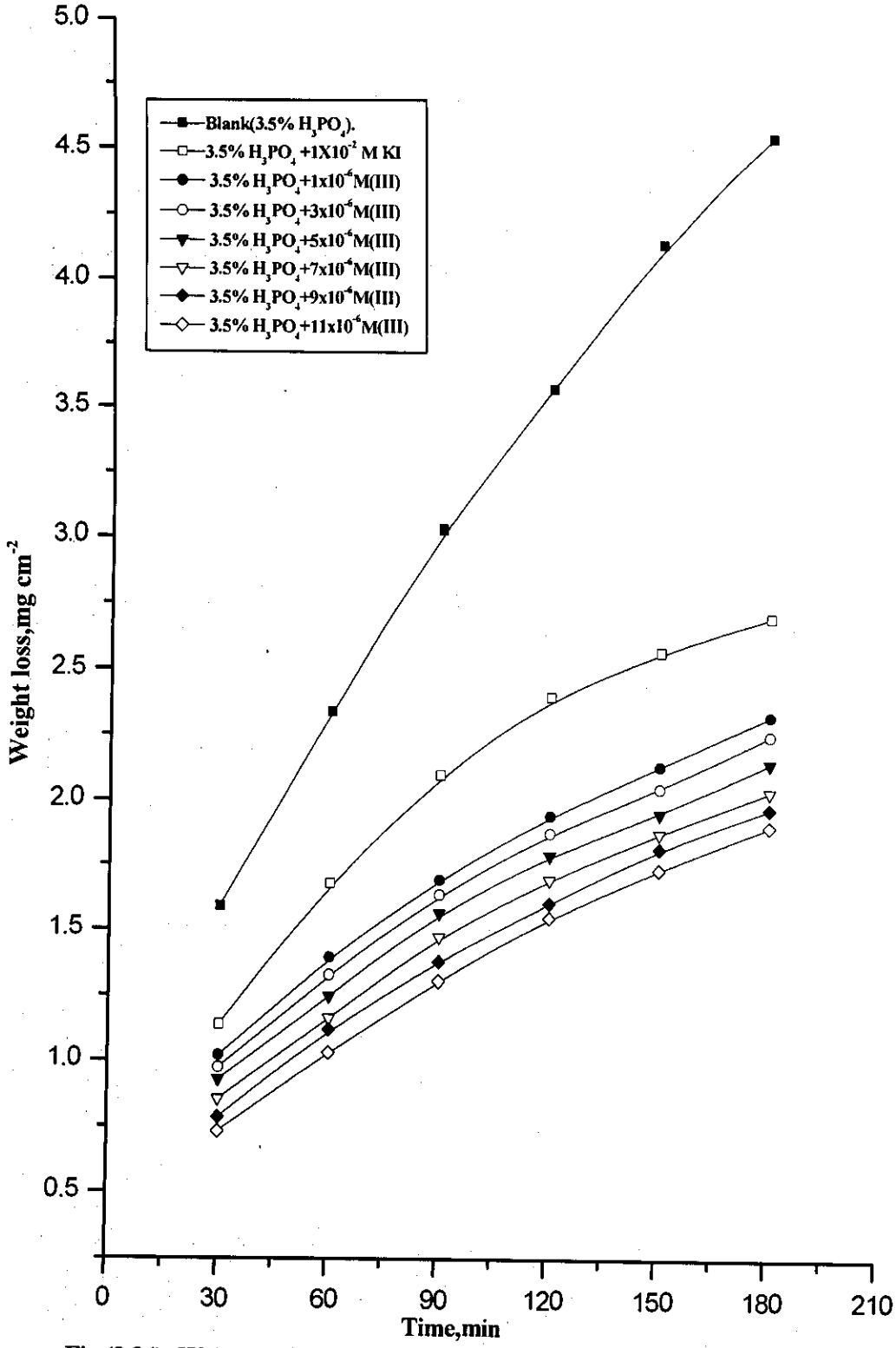


Fig.(3.34): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KI and at different concentrations of compound(III) at 30^{o}C.

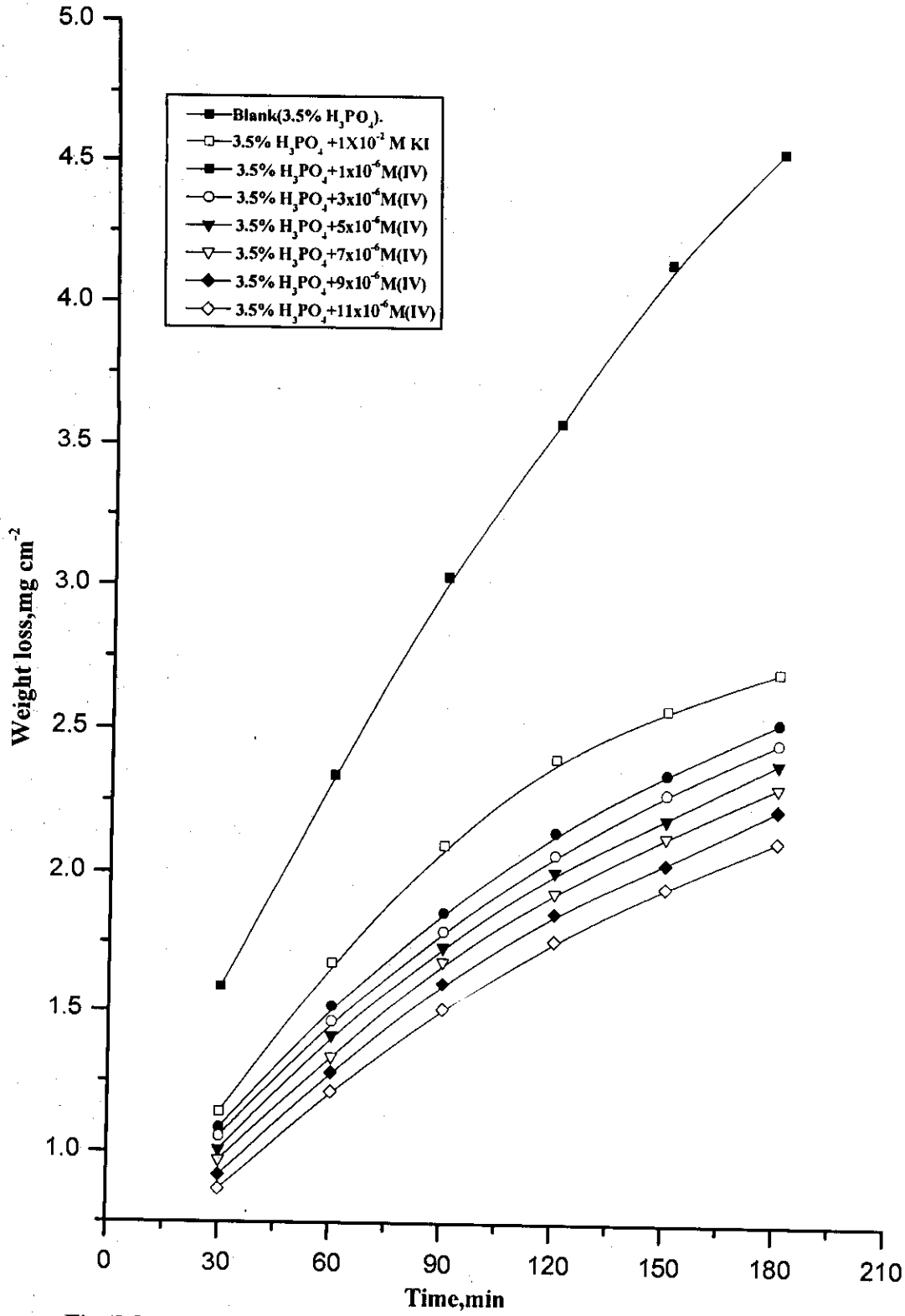


Fig.(3.35): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KI and at different concentrations of compound(IV) at 30^{o}C.

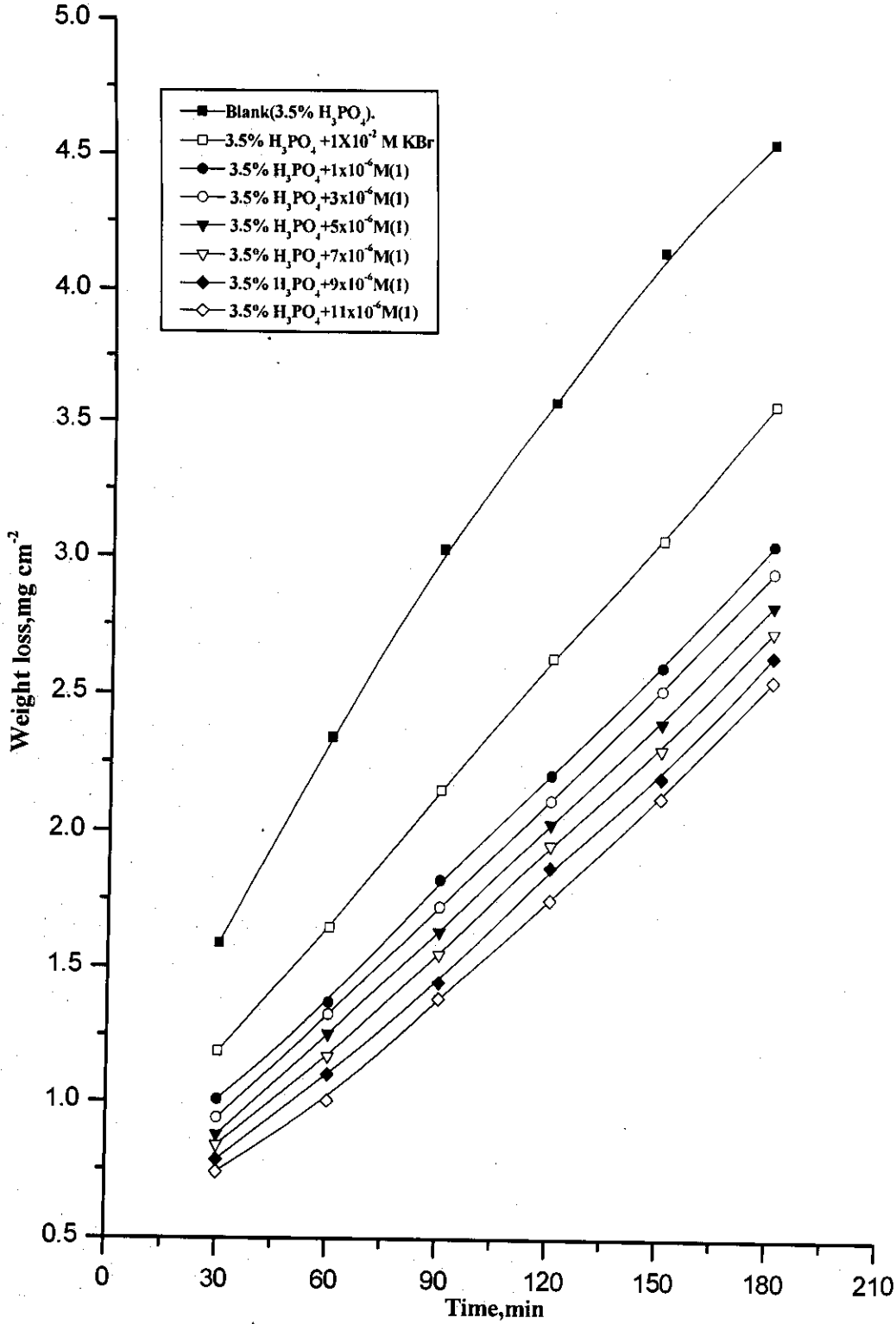


Fig.(3.36): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KBr and at different concentrations of compound(1) at 30°C.

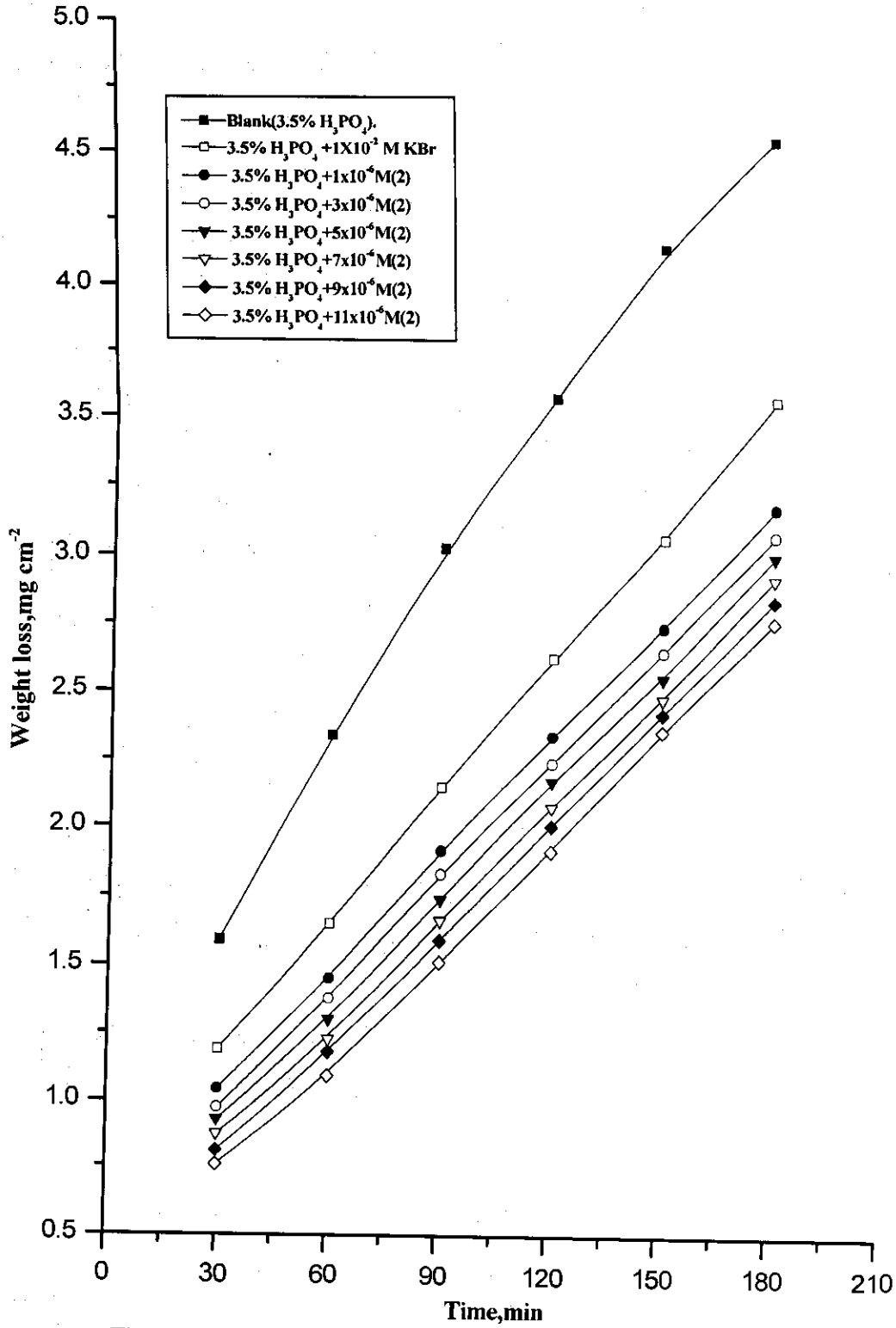


Fig.(3.37): Weight loss -time curves for iron dissolution in 3.5%H_3PO_4 in absence and presence of 1x10^{-2}M KBr and at different concentrations of compound(2) at 30°C.

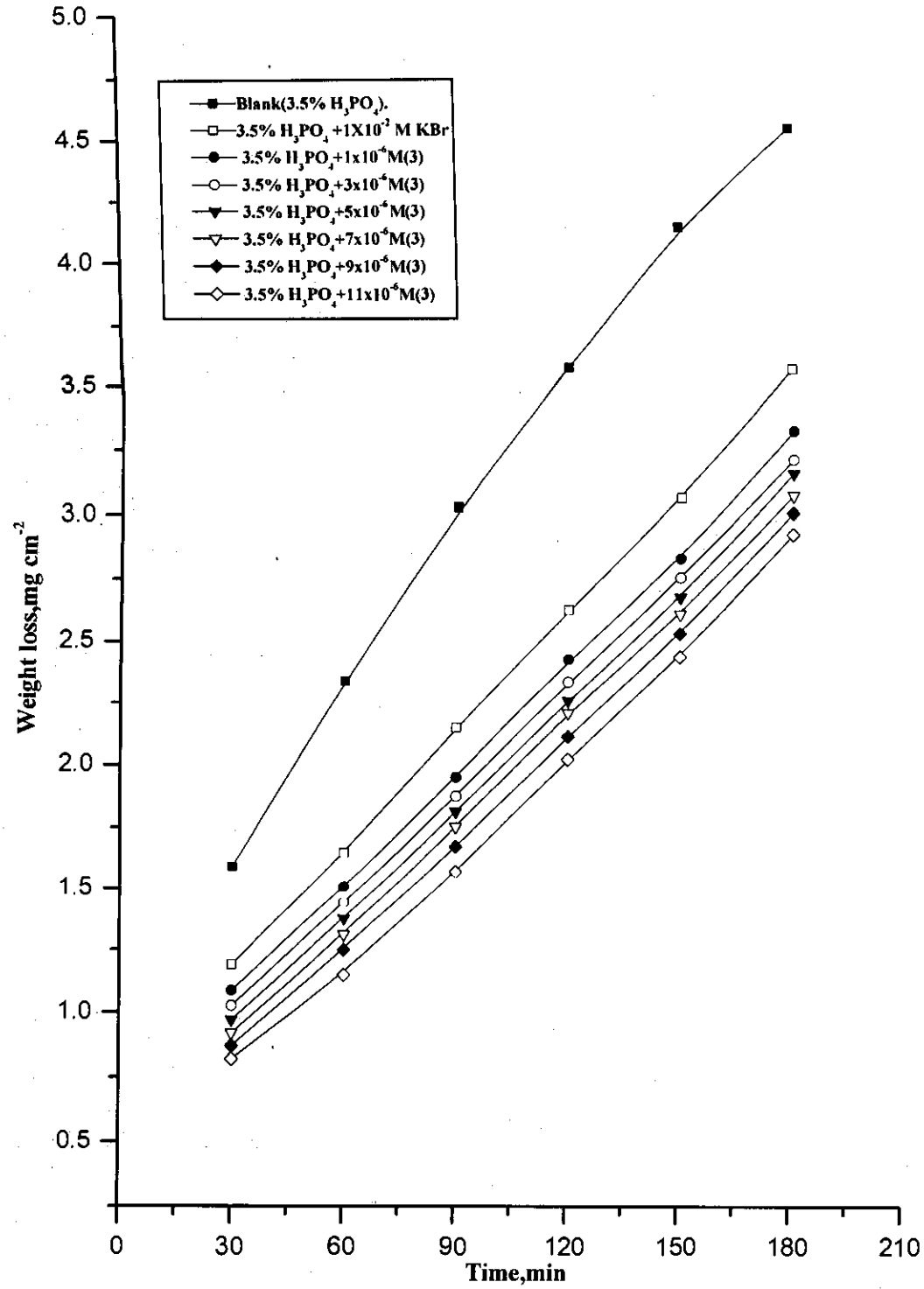


Fig.(3.38): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KBr and at different concentrations of compound(3) at 30°C.

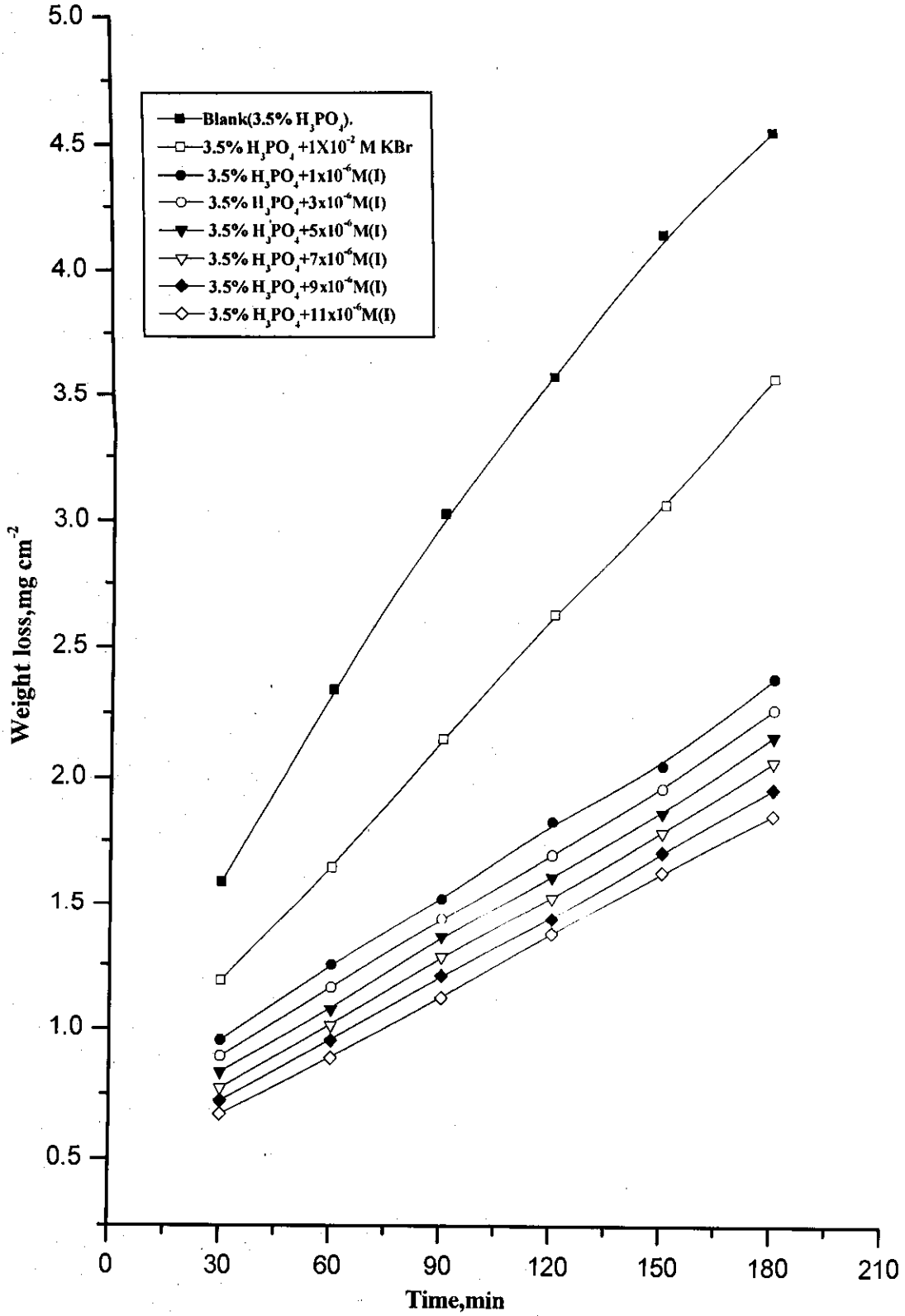


Fig.(3.39): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KBr and at different concentrations of compound(I) at 30°C.

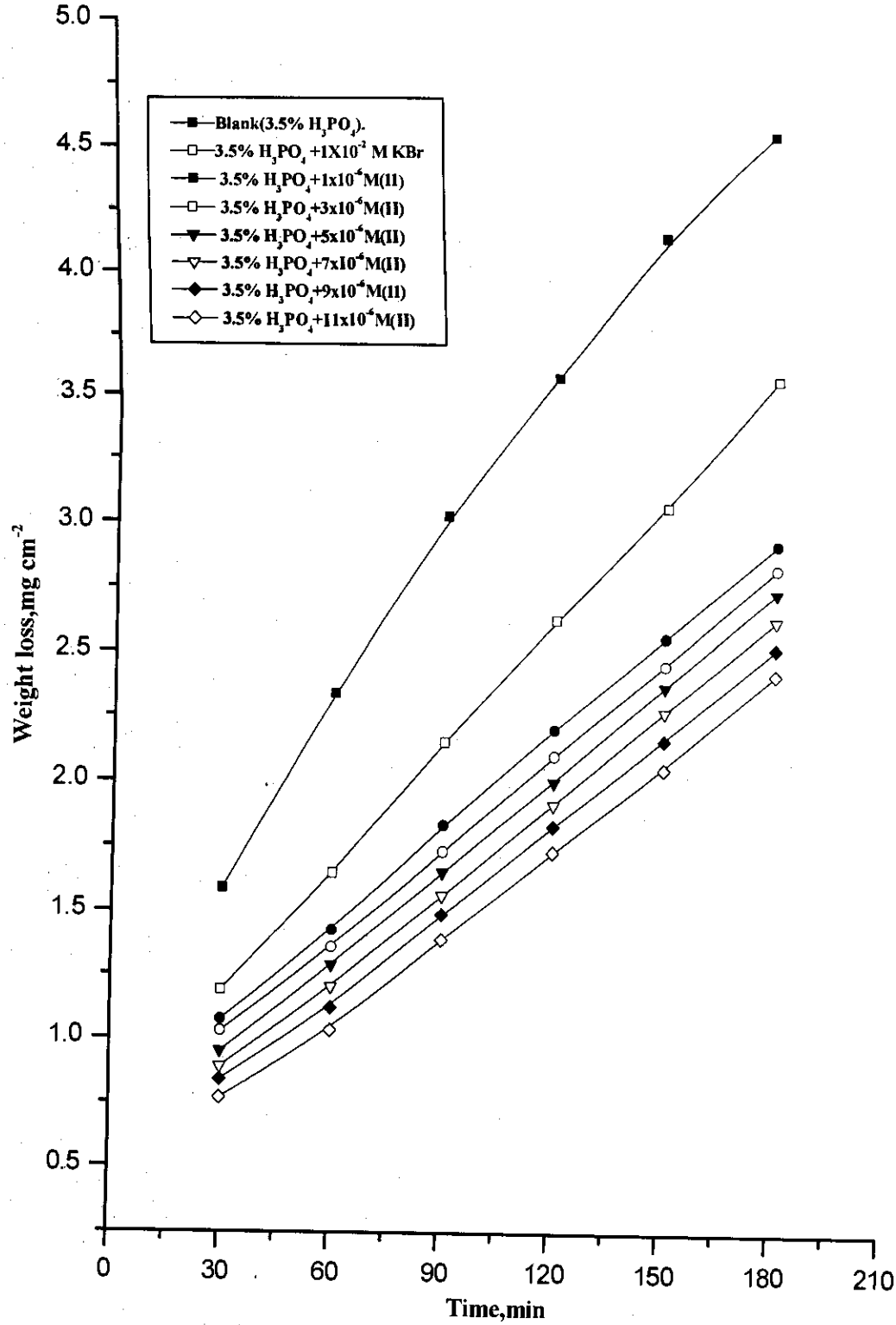


Fig.(3.40): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KBr and at different concentrations of compound(II) at 30°C.

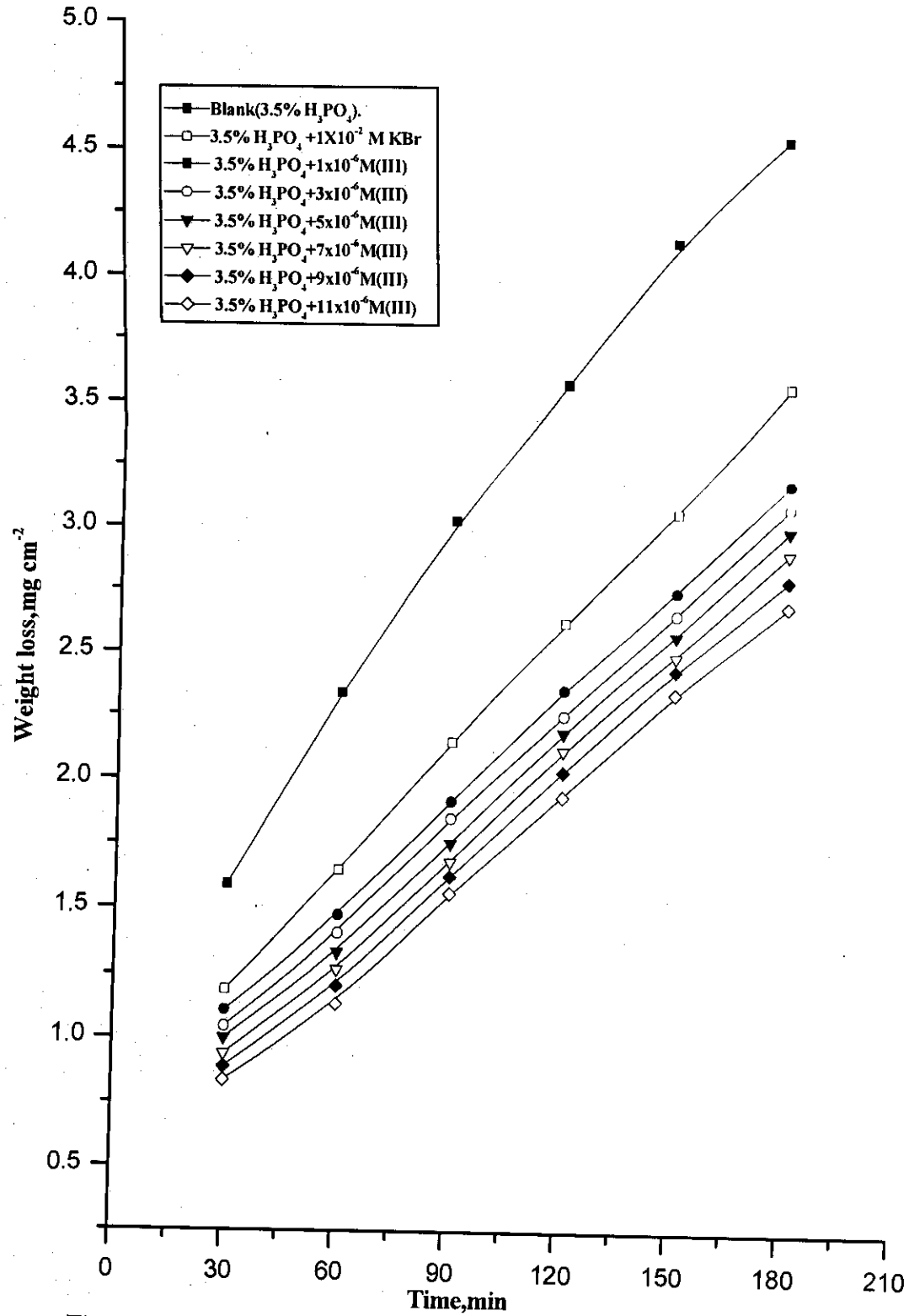


Fig.(3.41): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KBr and at different concentrations of compound(III) at 30°C.

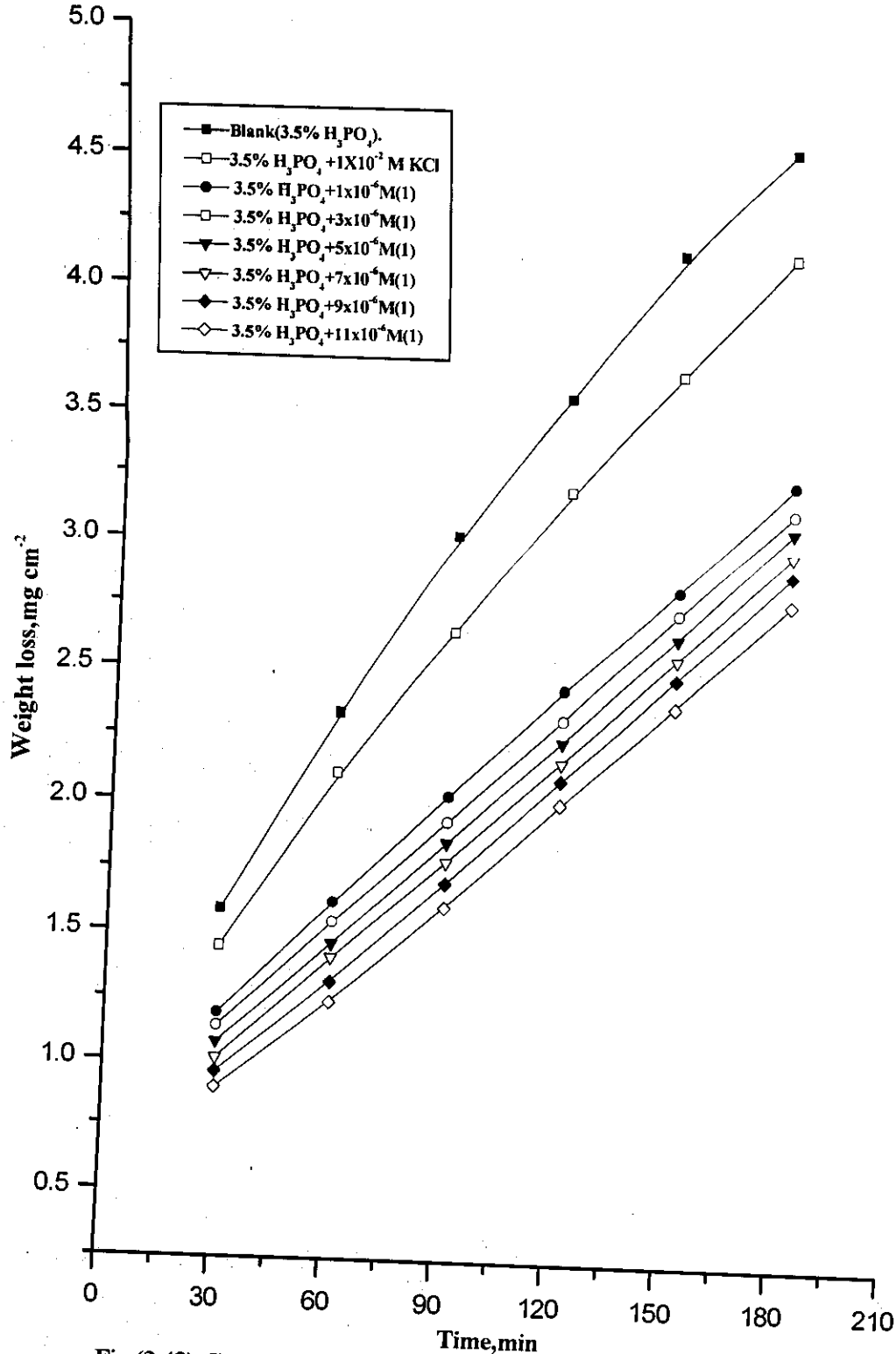


Fig.(3.43): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KCL and at different concentrations of compound(1) at 30°C.

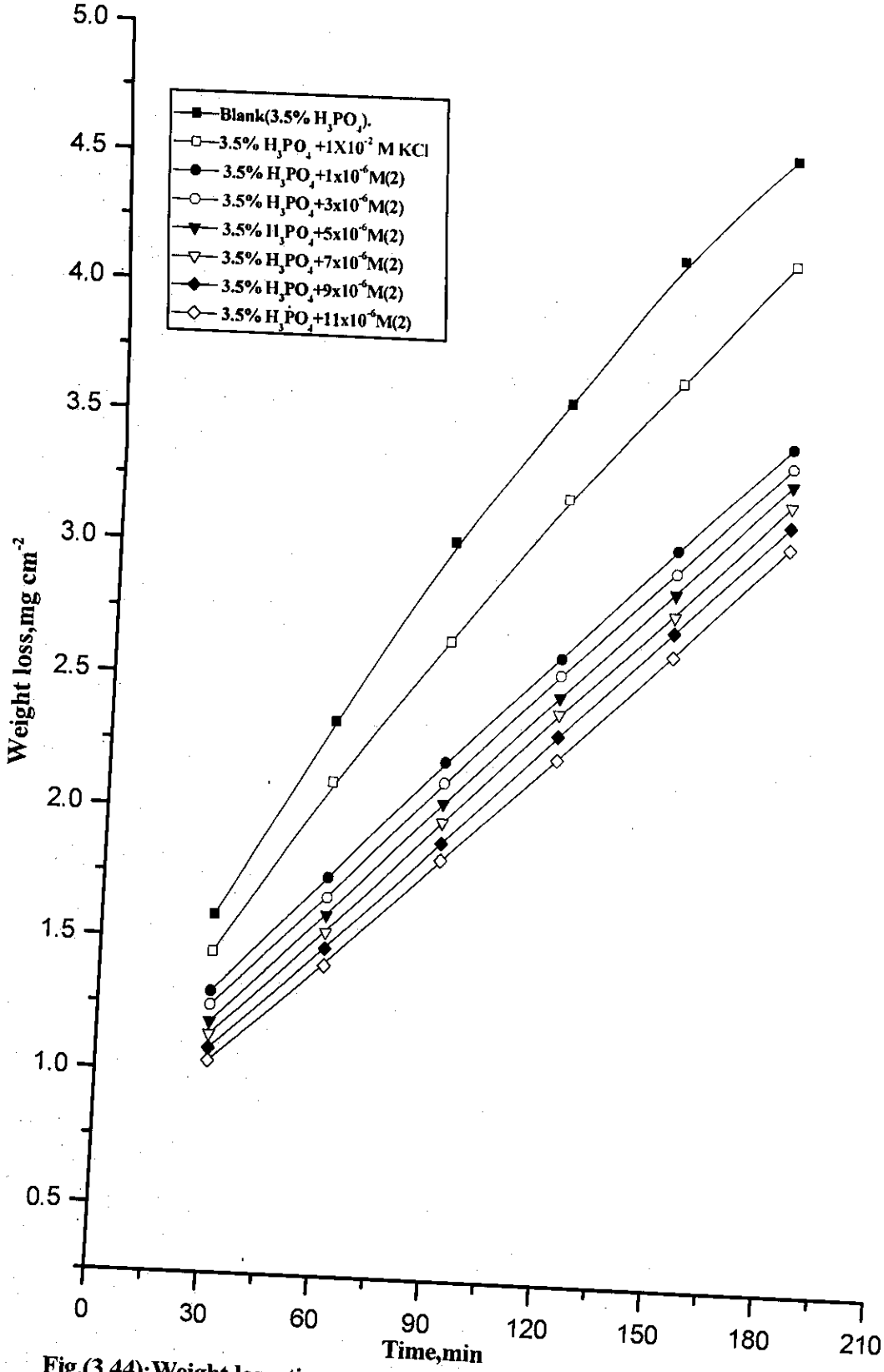


Fig.(3.44): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KCL and at different concentrations of compound(2) at 30°C.

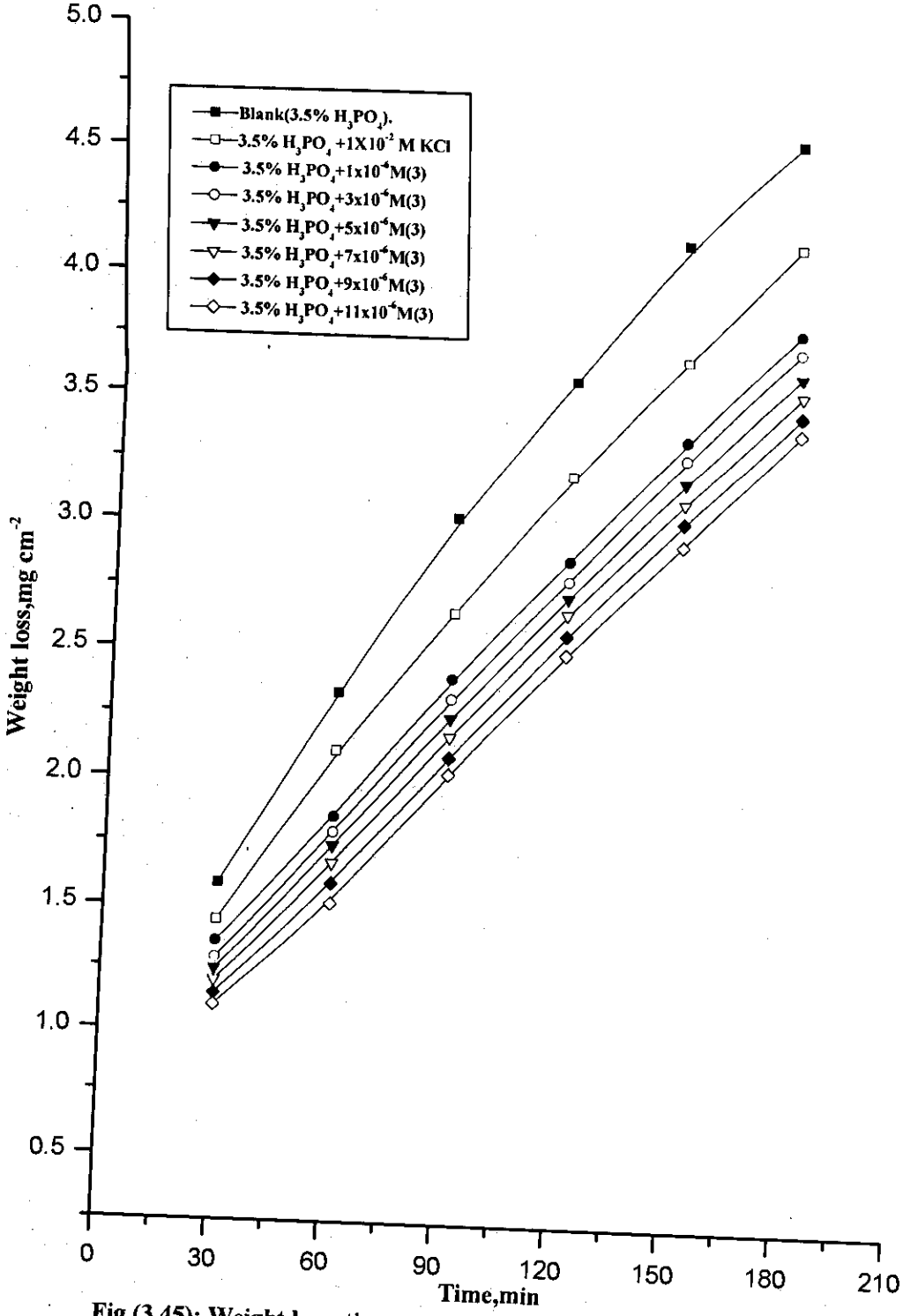


Fig.(3.45): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KCL and at different concentrations of compound(3) at 30°C.

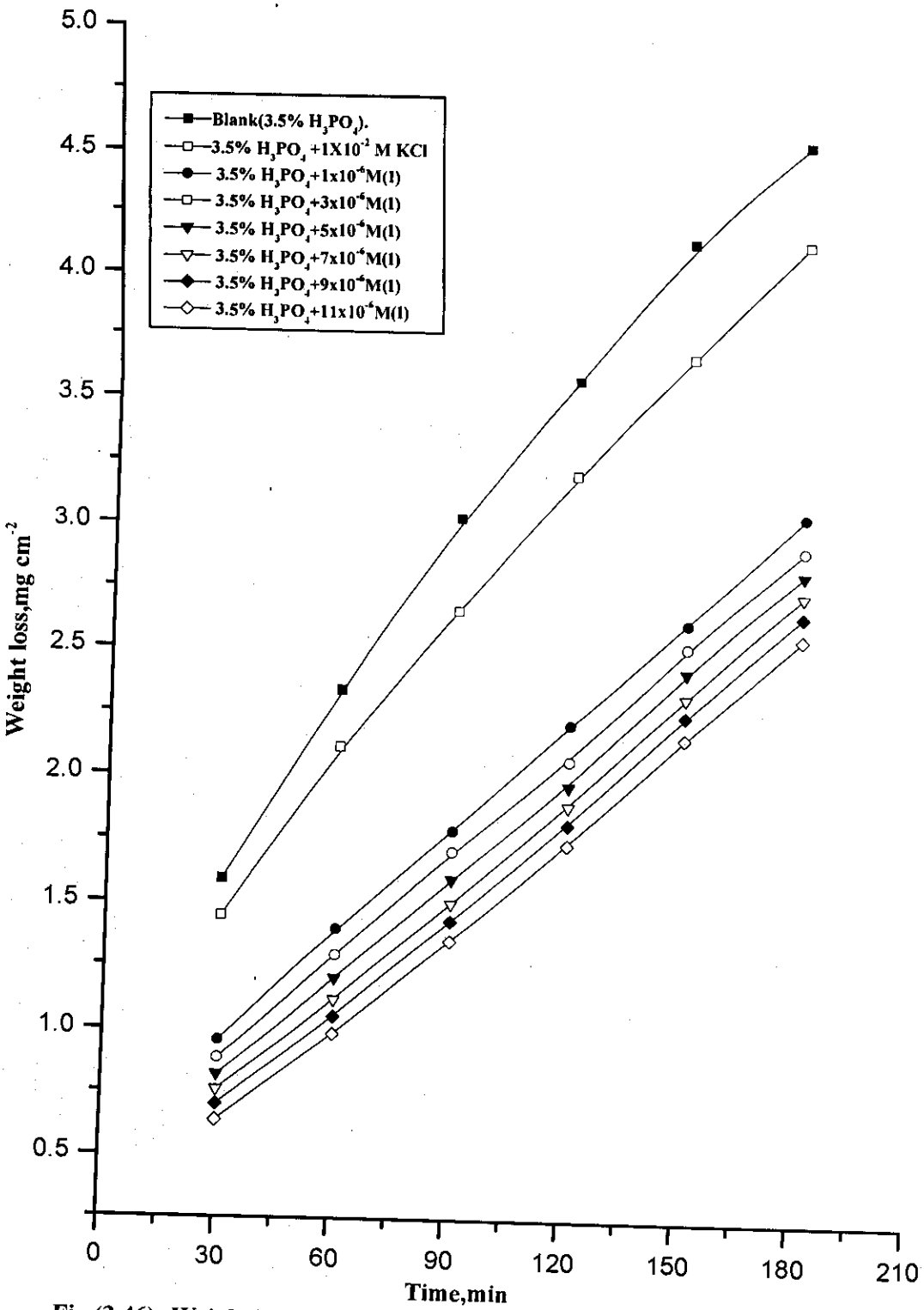


Fig.(3.46): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KCL and at different concentrations of compound(I) at 30°C.

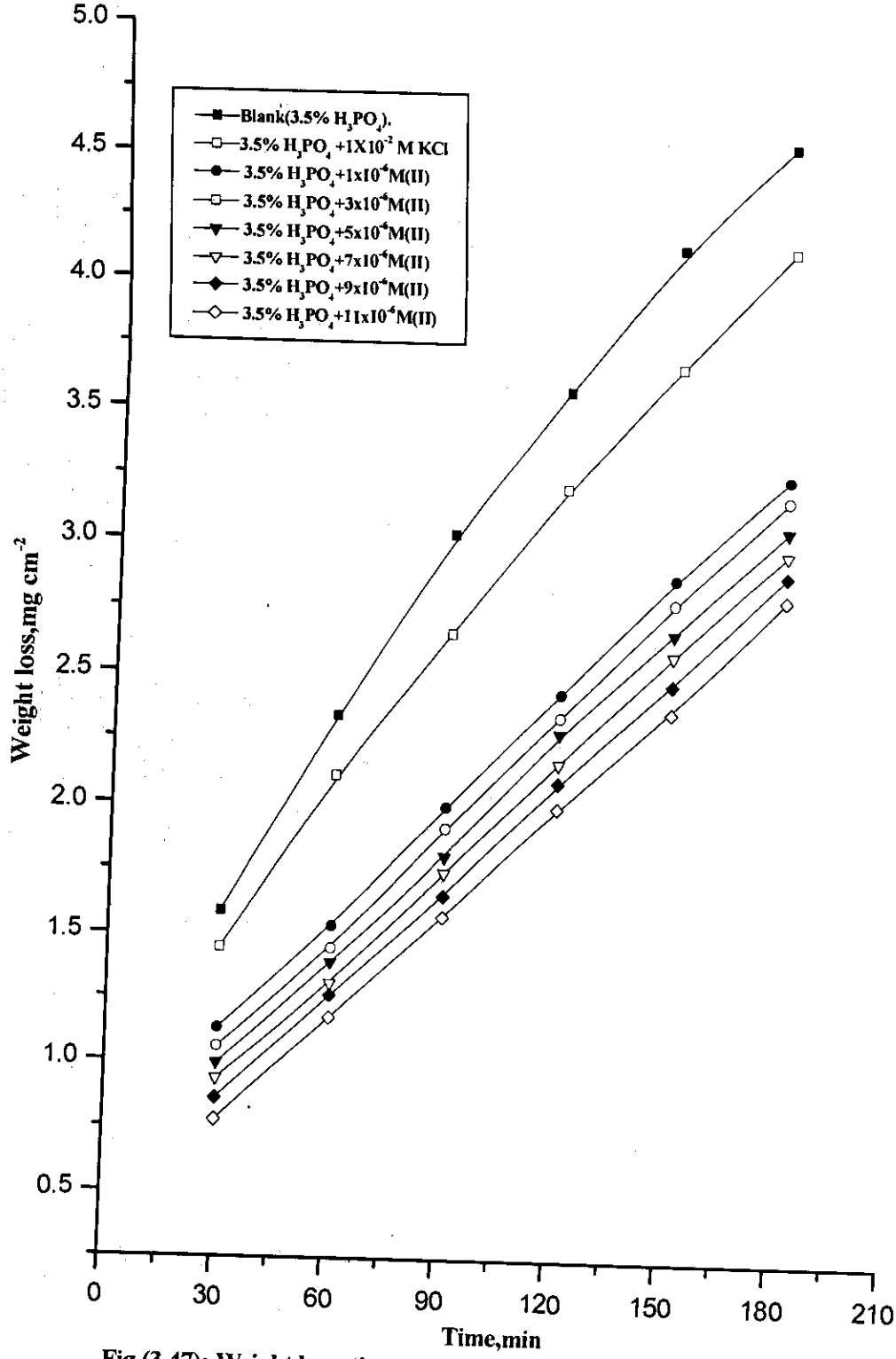


Fig.(3.47): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KCL and at different concentrations of compound(II) at 30°C.

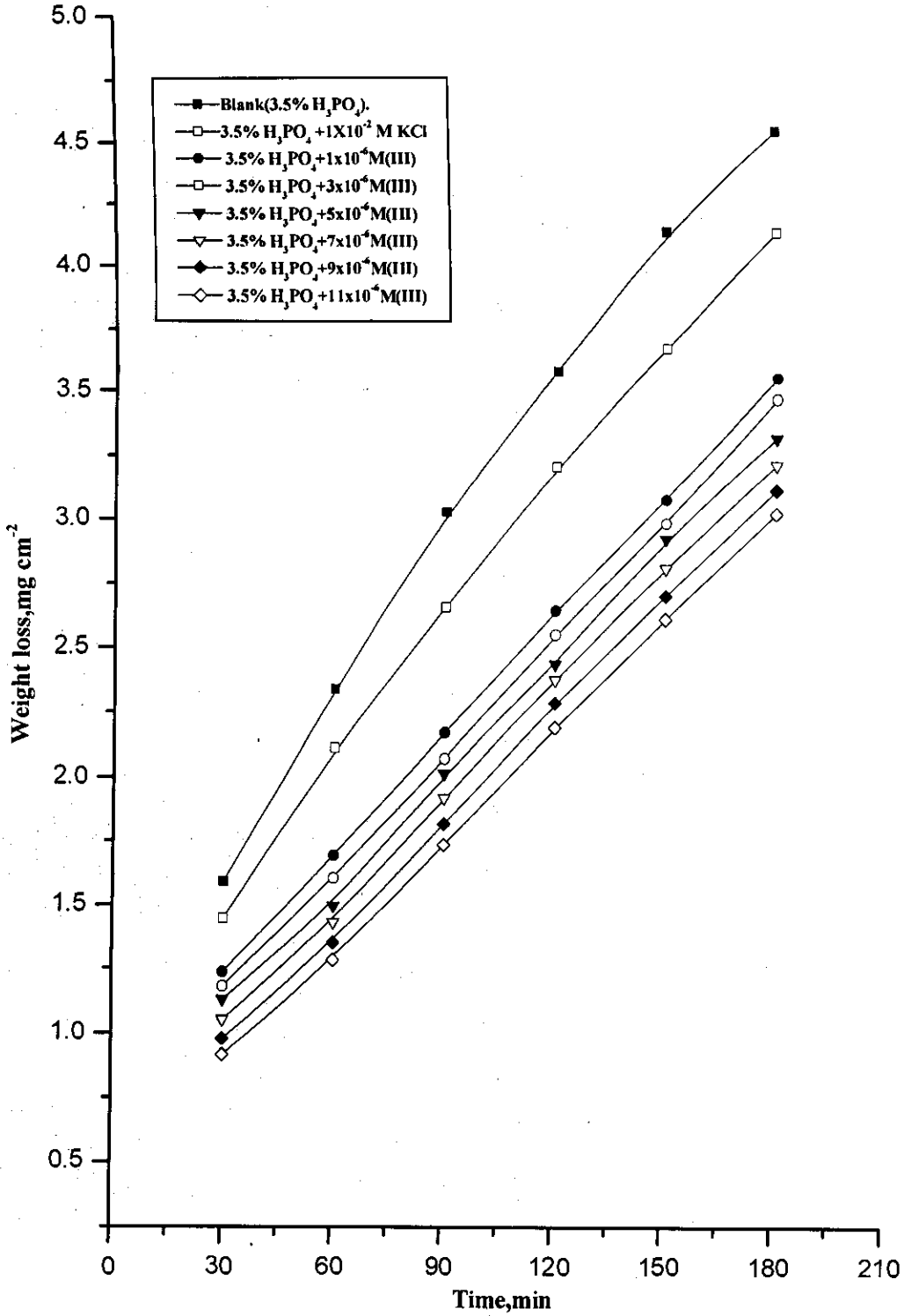


Fig.(3.48): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KCL and at different concentrations of compound(III) at 30°C.

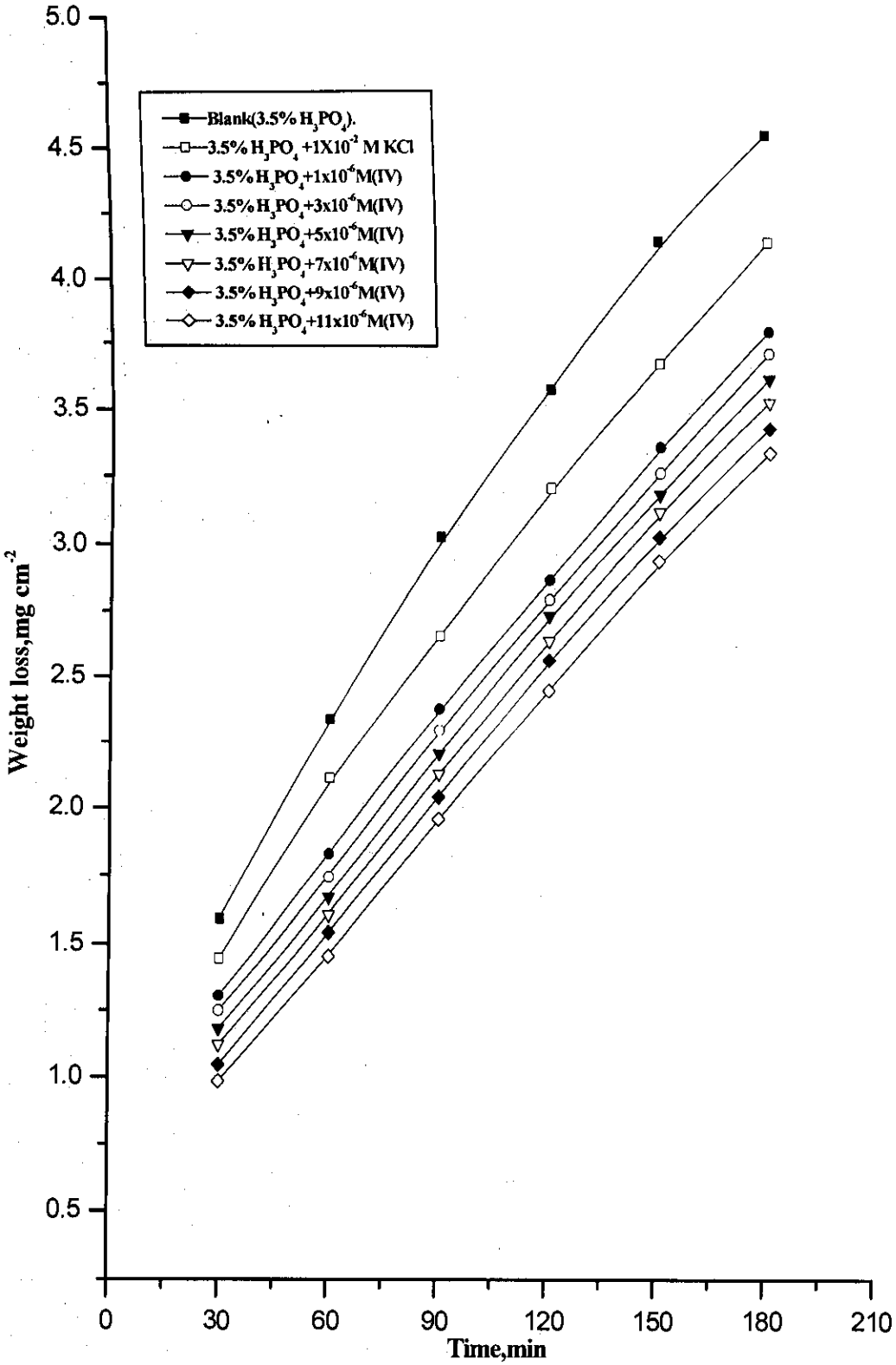


Fig.(3.49): Weight loss -time curves for iron dissolution in 3.5% H_3PO_4 in absence and presence of 1x10^{-2}M KCL and at different concentrations of compound(IV) at 30°C.

Table(3.3) :%Inhibition efficiency of iron dissolution at 120min. immersion in 3.5% H_3PO_4 in presence of $1x10^{-2}$M KI at different concentrations of first group compounds at 30°C .

Concentration M	% Inhibition		
	(1)	(2)	(3)
$1x10^{-6}$	54.8	48.3	41.9
$3x10^{-6}$	57.3	51.3	43.9
$5x10^{-6}$	60.0	54.2	46.3
$7x10^{-6}$	62.7	56.6	48.2
$9x10^{-6}$	65.2	58.8	50.4
$11x10^{-6}$	67.5	61.6	52.5

Table(3.4):%Inhibition efficiency of iron dissolution at 120min. immersion in 3.5% H_3PO_4 in presence of $1x10^{-2}$M KI at different concentrations of second group compounds at 30°C.

Concentration M	% Inhibition			
	(I)	(II)	(III)	(IV)
$1x10^{-6}$	68.4	51.9	45.6	40.0
$3x10^{-6}$	70.3	54.9	47.5	42.2
$5x10^{-6}$	73.1	57.9	49.9	43.9
$7x10^{-6}$	75.1	60.2	52.5	46.0
$9x10^{-6}$	78.0	62.9	55.1	48.1
$11x10^{-6}$	80.5	65.4	56.7	50.8

Table(3.5):%Inhibition efficiency of iron dissolution at 120 min. immersion in3.5% H_3PO_4 in presence of $1x10^{-2}$M KBr at different concentrations of first group compounds at 30°C.

Concentration M	% Inhibition		
	(1)	(2)	(3)
$1x10^{-6}$	38.4	34.6	32.1
$3x10^{-6}$	41.0	37.4	34.7
$5x10^{-6}$	43.3	39.2	36.8
$7x10^{-6}$	45.5	41.9	38.2
$9x10^{-6}$	47.8	43.9	40.9
$11x10^{-6}$	51.1	46.4	43.4

Table(3.6):%Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5%H_3PO_4 in presence of $1x10^{-2}$M KBr at different concentrations of second group compounds at 30°C.

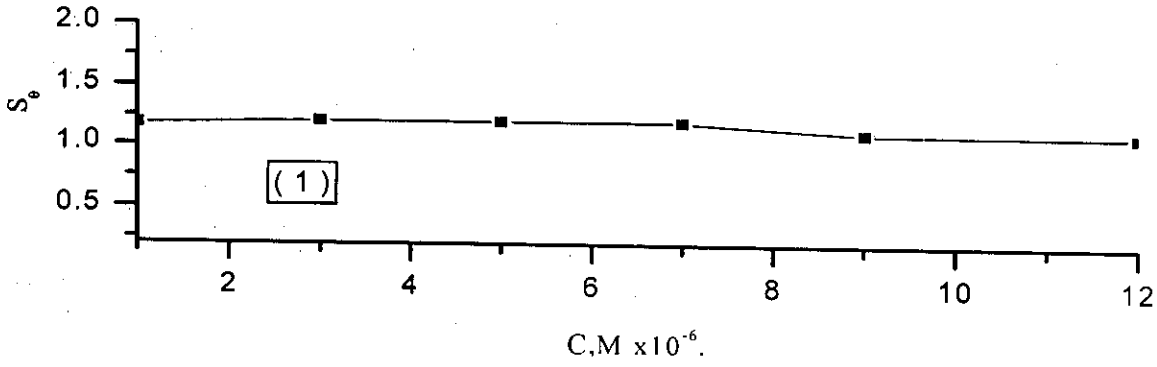
Concentration M	% Inhibition			
	(I)	(II)	(III)	(IV)
$1x10^{-6}$	48.9	38.5	34.1	31.2
$3x10^{-6}$	52.5	41.3	37.0	33.1
$5x10^{-6}$	54.9	44.1	38.8	35.4
$7x10^{-6}$	57.3	46.5	40.7	37.3
$9x10^{-6}$	59.7	48.9	43.1	39.2
$11x10^{-6}$	61.4	51.6	45.8	41.9

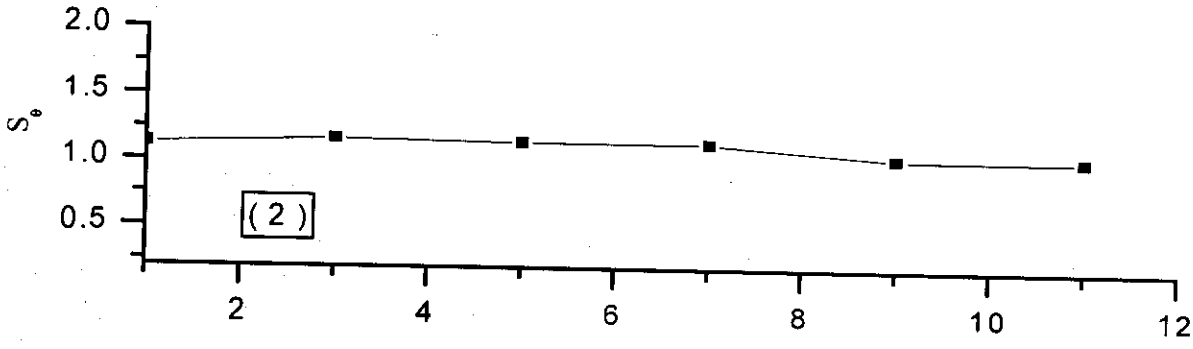
Table(3.7):%Inhibition efficiency of iron dissolution at 120min. immersion in 3.5% H_3PO_4 in presence of $1x10^{-2}$M KCl at different concentrations of first group compounds at 30°C.

Concentration M	% Inhibition		
	(1)	(2)	(3)
$1x10^{-6}$	31.8	27.0	19.6
$3x10^{-6}$	34.9	28.8	21.9
$5x10^{-6}$	37.1	31.1	23.7
$7x10^{-6}$	39.4	32.9	25.5
$9x10^{-6}$	41.3	35.2	27.8
$11x10^{-6}$	43.8	37.7	29.9

Table(3.8): %Inhibition efficiency of iron dissolution at 120min. immersion in3.5% H_3PO_4 in presence of $1x10^{-2}$M KCl at different concentrations of second group compounds at 30°C.

Concentration M	% Inhibition			
	(I)	(II)	(III)	(IV)
$1x10^{-6}$	38.2	31.9	26.1	19.8
$3x10^{-6}$	42.2	34.5	28.6	21.9
$5x10^{-6}$	44.9	36.2	31.8	23.6
$7x10^{-6}$	47.1	39.3	33.5	26.3
$9x10^{-6}$	49.2	41.4	36.1	28.3
$11x10^{-6}$	51.4	44.1	38.8	31.5





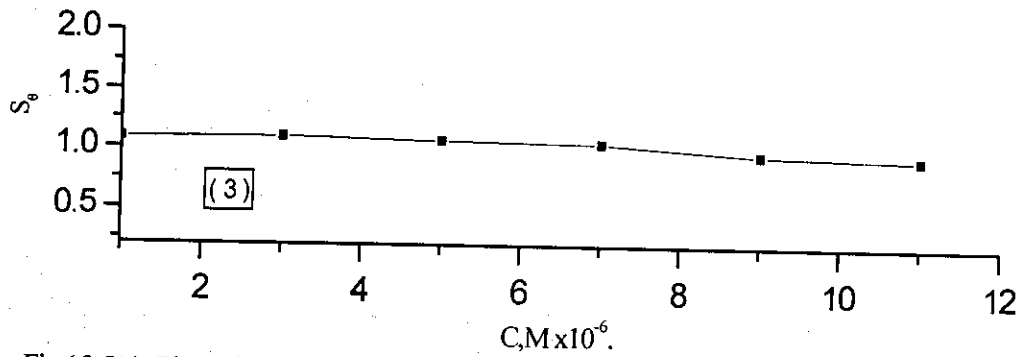
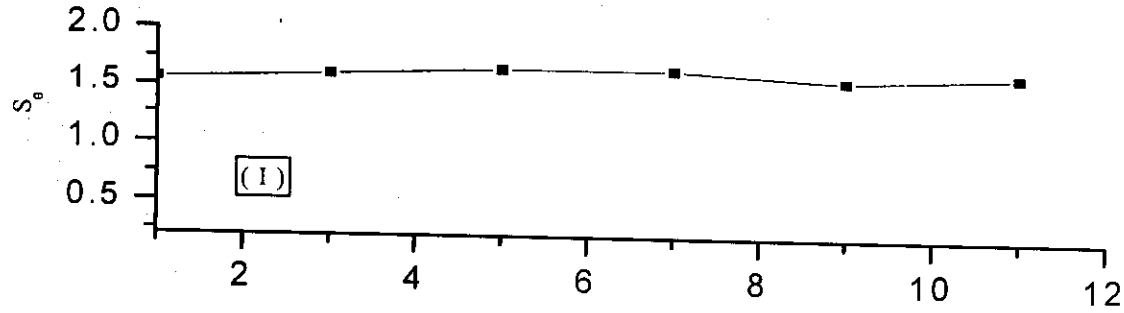
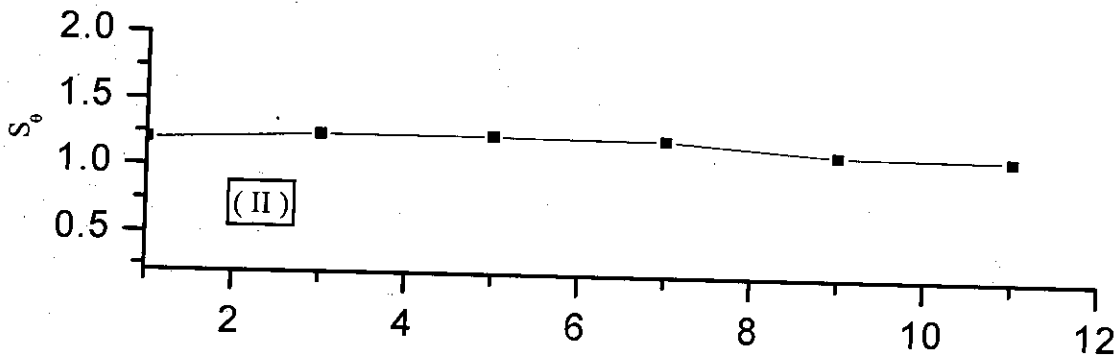
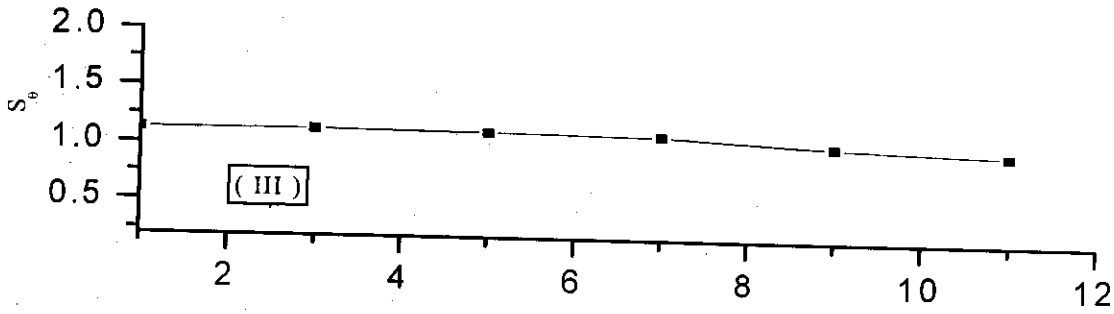


Fig.(3.50): Plots of synergism parameter(S_θ) versus concenrations of first group for iron dissolution in 3.5% H_3PO_4 with addition of 1x10^{-2}M KI at 30°C.







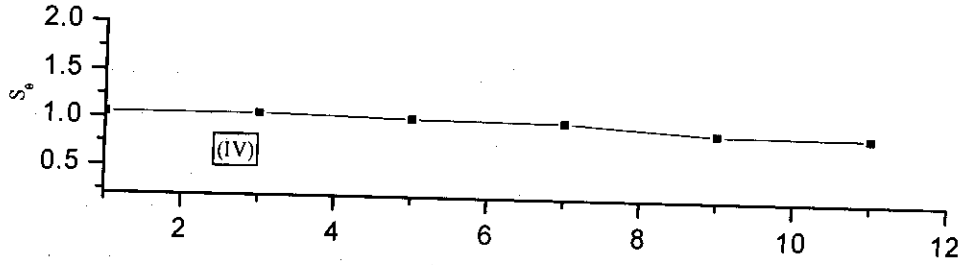
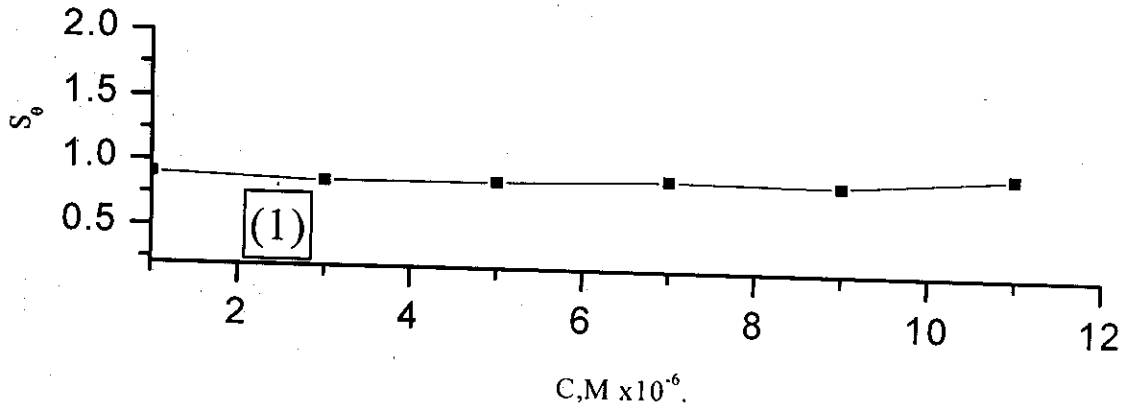
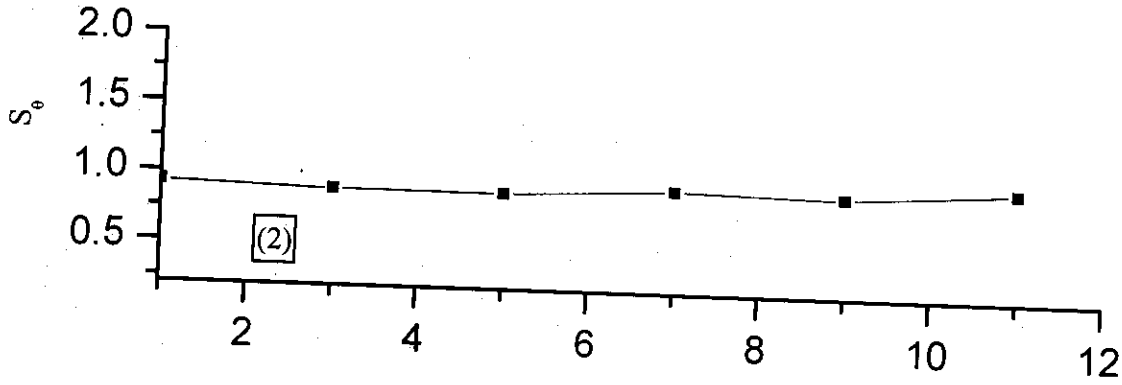


Fig.(3.51): Plots of synergism parameter(S_θ) versus concenrations of second group for iron dissolution in 3.5% H_3PO_4 with addition of 1x10^{-2}M KI at 30°C.





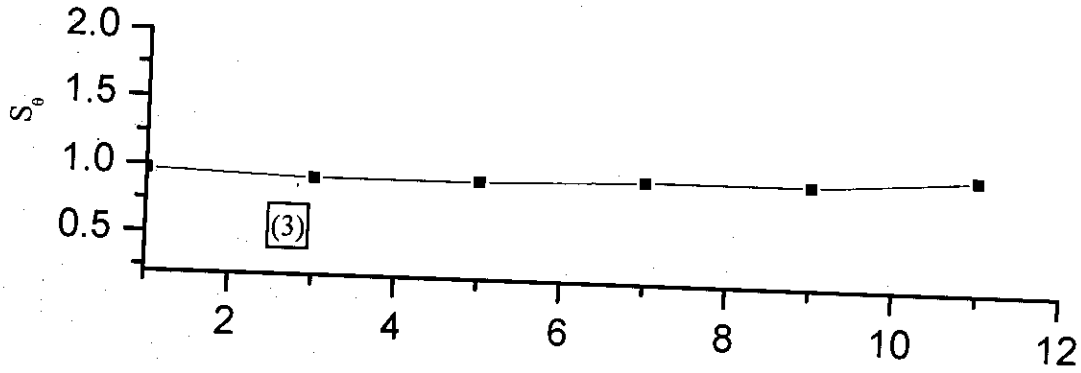


Fig.(3.52): Plots of synergism parameter(S_θ) versus concenrations of first group foriron dissolution in 3.5% H_3PO_4 with addition of1x10^{-2}M KBr at 30°C.

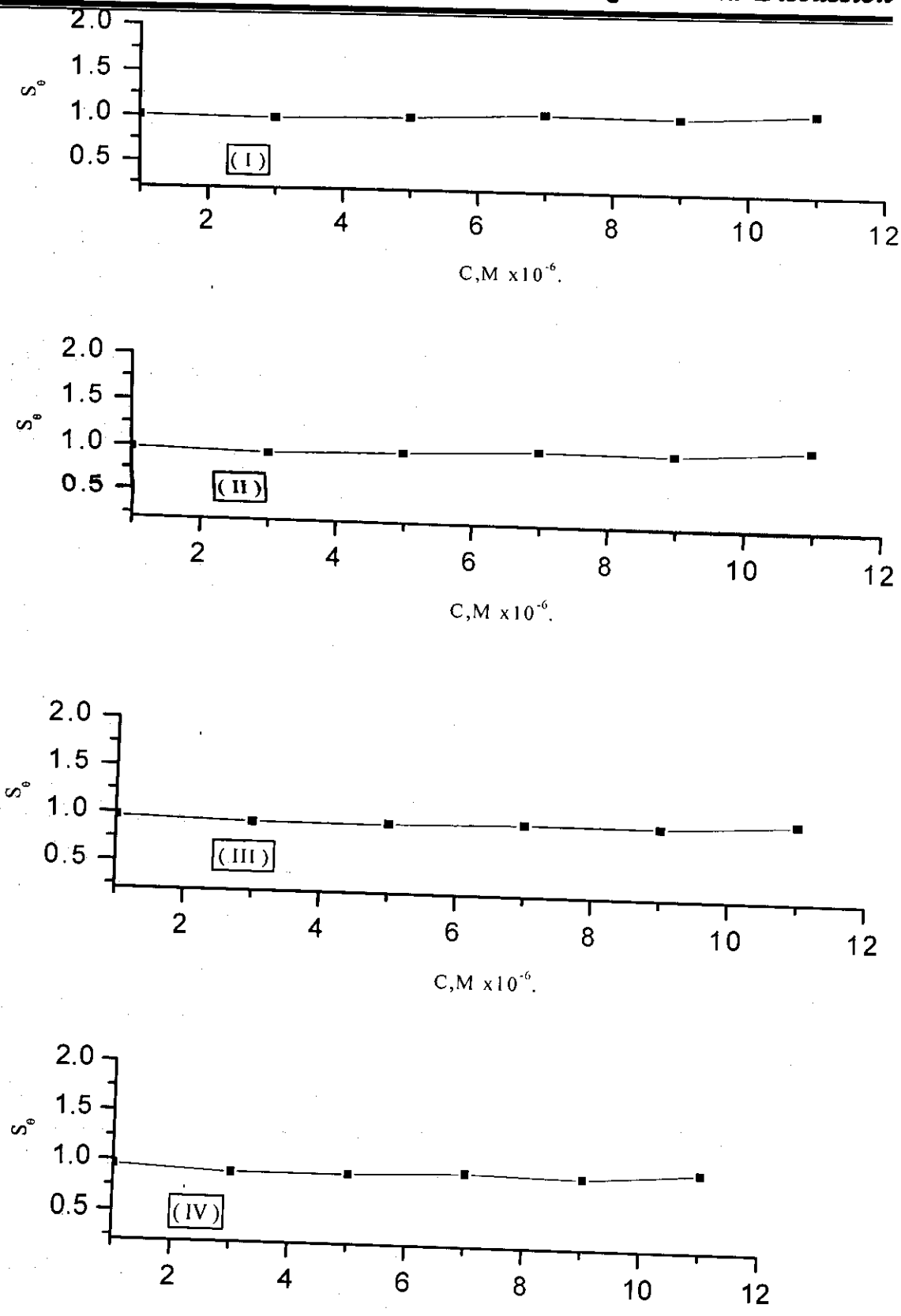
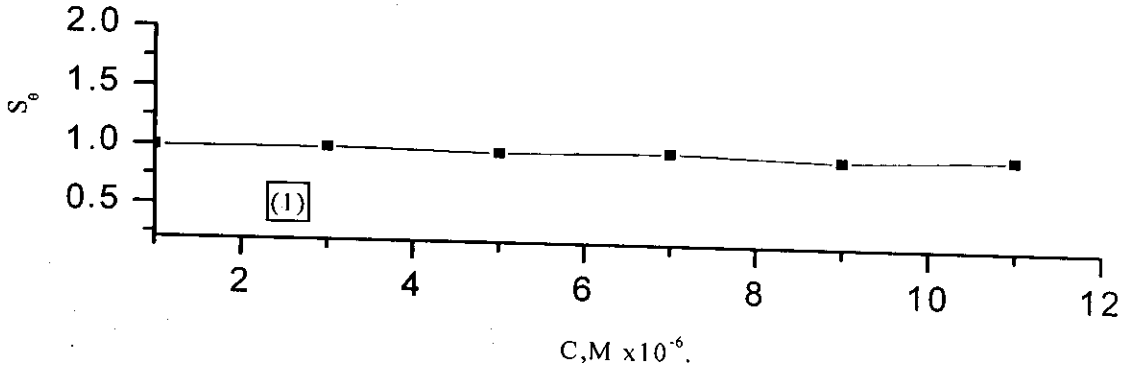
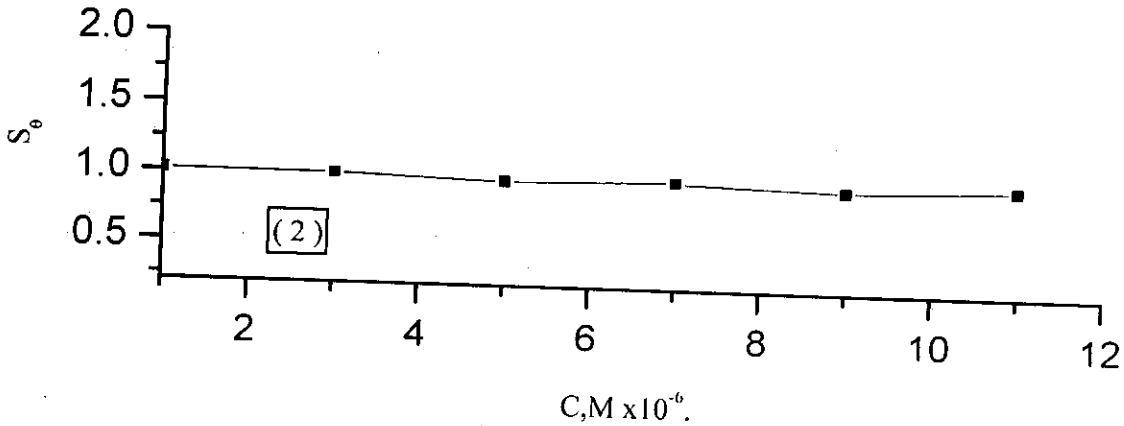


Fig.(3.53): Plots of synergism parameter(S_θ) versus concenrations of second group for iron dissolution in 3.5% H_3PO_4 with addition of1x10^{-2}M KBr at 30°C.





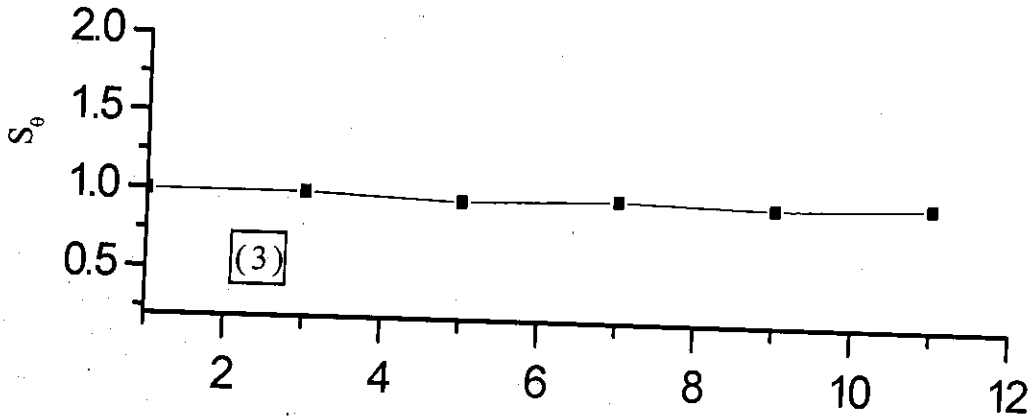


Fig.(3.54): Plots of synergism parameter(S_θ) versus concenrations of first group for iron dissolution in 3.5% H_3PO_4 with addition of $1x10^{-2}$M KCl at 30°C.

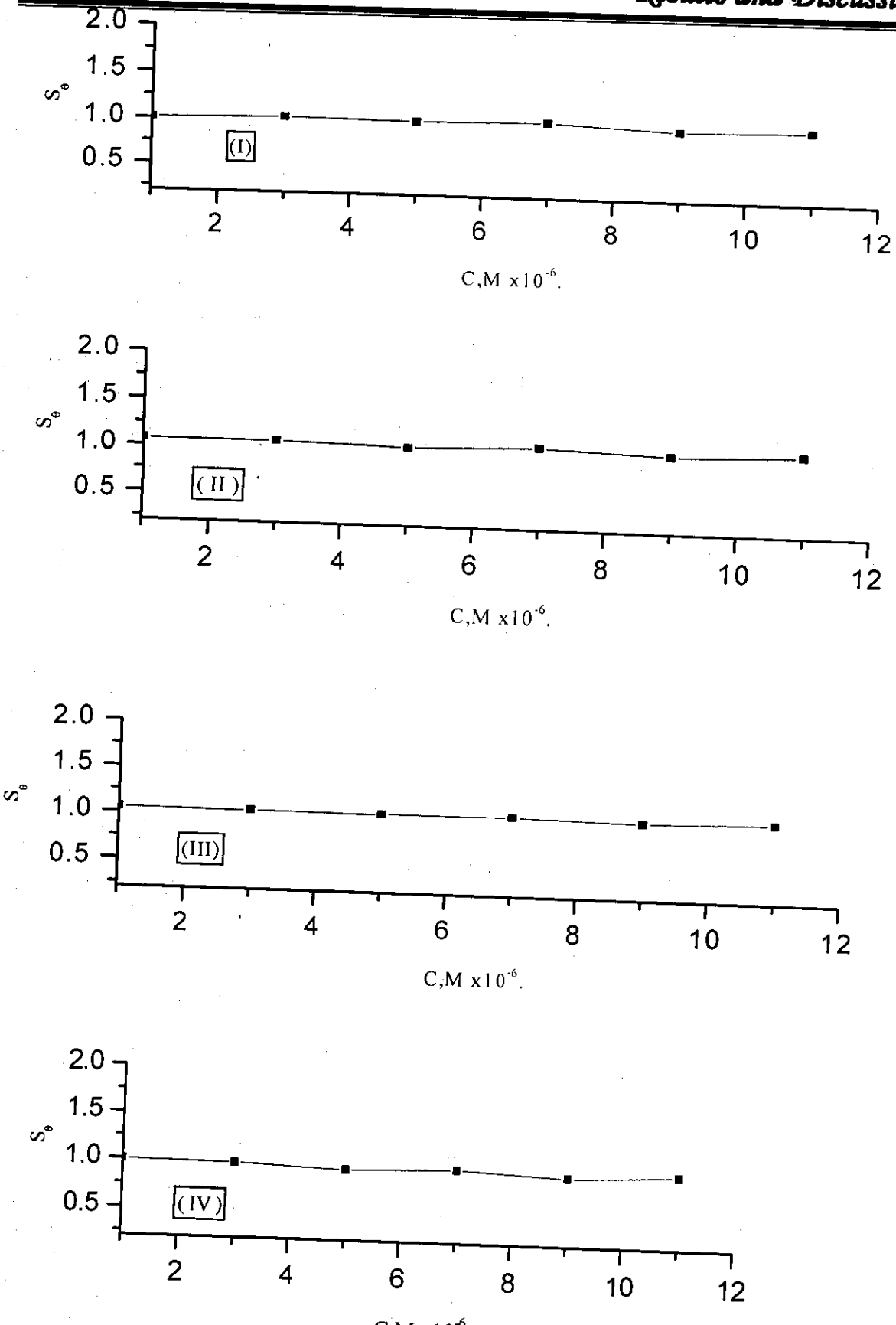


Fig.(3.55): Plots of synergism parameter(S_θ) versus concenrations of second group for iron dissolution in 3.5% H_3PO_4 with addition of 1x10^{-2}M KCl at 30°C.

Table(3.9): Synergism parameter (S_θ) for different concentrations of first group for iron dissolution in 3.5% H_3PO_4 with addition of $1x10^{-2}$M KI at 30°C.

Concentration M	Synergism parameter (S_θ)		
	(1)	(2)	(3)
$1X10^{-6}$	1.2	1.1	1.1
$3X10^{-6}$	1.2	1.2	1.1
$5X10^{-6}$	1.2	1.1	1.1
$7X10^{-6}$	1.2	1.1	1.1
$9X10^{-6}$	1.1	1.0	1.0
$11X10^{-6}$	1.1	1.0	1.0

Table(3.10): Synergism parameter (S_θ) for different concentrations of second group for iron dissolution in 3.5% H_3PO_4 with addition of $1x10^{-2}$M KI at 30°C.

Concentration M	Synergism parameter (S_θ)			
	(I)	(II)	(III)	(IV)
$1X10^{-6}$	1.6	1.2	1.1	1.0
$3X10^{-6}$	1.6	1.2	1.1	1.0
$5X10^{-6}$	1.6	1.2	1.1	1.0
$7X10^{-6}$	1.6	1.2	1.1	1.0
$9X10^{-6}$	1.6	1.1	1.0	1.0
$11X10^{-6}$	1.6	1.1	1.0	1.0

Table(3.11): Synergism parameter (S_θ) for different concentrations of first group for iron dissolution in 3.5% H_3PO_4 with addition of $1x10^{-2}$M KBr at 30°C.

Concentration M	Synergism parameter (S_θ)		
	(1)	(2)	(3)
$1X10^{-6}$	0.9	0.9	1.0
$3X10^{-6}$	0.9	0.9	0.9
$5X10^{-6}$	0.9	0.9	0.9
$7X10^{-6}$	0.9	0.9	1.0
$9X10^{-6}$	0.9	0.9	1.0
$11X10^{-6}$	1.0	1.0	1.0

Table(3.12): Synergism parameter (S_θ) for different concentrations of second group for iron dissolution in 3.5% H_3PO_4 with addition of $1x10^{-2}$M KBr at 30°C.

Concentration M	Synergism parameter (S_θ)			
	(I)	(II)	(III)	(IV)
$1X10^{-6}$	1.0	1.1	1.0	1.0
$3X10^{-6}$	1.0	0.9	0.9	0.9
$5X10^{-6}$	1.0	1.1	0.9	0.9
$7X10^{-6}$	1.1	1.0	1.0	0.9
$9X10^{-6}$	1.0	1.0	1.0	0.9
$11X10^{-6}$	1.1	1.1	1.0	1.0

Table(3.13):Synergism parameter (S_θ) for different concentrations of first group for iron dissolution in 3.5% H_3PO_4 with addition of $1x10^{-2}$M KCl at 30°C.

Concentration M	Synergism parameter (S_θ)		
	(1)	(2)	(3)
$1X10^{-6}$	1.0	1.0	1.0
$3X10^{-6}$	1.0	1.0	1.0
$5X10^{-6}$	1.0	1.0	1.0
$7X10^{-6}$	1.0	1.0	1.0
$9X10^{-6}$	0.9	0.9	0.9
$11X10^{-6}$	1.0	1.0	1.0

Table(3.14): Synergism parameter (S_θ) for different concentrations of second group for iron dissolution in 3.5% H_3PO_4 with addition of $1x10^{-2}$M KCl at 30°C.

Concentration M	Synergism parameter (S_θ)			
	(I)	(II)	(III)	(IV)
$1X10^{-6}$	1.0	1.1	1.1	1.0
$3X10^{-6}$	1.0	1.1	1.0	1.0
$5X10^{-6}$	1.0	1.0	1.0	0.9
$7X10^{-6}$	1.0	1.1	1.1	1.0
$9X10^{-6}$	1.0	1.0	1.0	0.9
$11X10^{-6}$	1.0	1.1	1.1	1.0

3.2-Adsorption Isotherm

Organic molecules like hydrazone molecules inhibit the corrosion process by the adsorption on the metal surface. Theoretically, the adsorption process can be regarded as a single substitutional process in which an inhibitor molecule, I, in the aqueous phase substitutes an "x" number of water molecules adsorbed on the metal surface [112] vis,

$$I_{(aq)} + xH_2O_{(sur)} \longrightarrow I_{(sur)} + xH_2O_{(aq)} \qquad (3.3)$$

where x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. The adsorption depends on the structure of the inhibitor, the type of the metal and the nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal-solution interface. Also, the adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface. Actually an adsorbed molecule may make the surface more difficult or less difficult for another molecule to become attached to a neighboring site and multilayer adsorption may take place. There may be more or less than one inhibitor molecule per surface site. Finally, various surface sites could have varying degrees of activation. For these reasons a number of mathematical adsorption isotherm expressions have been developed to take into consideration some of non-ideal effects {see Table(1.1)}.

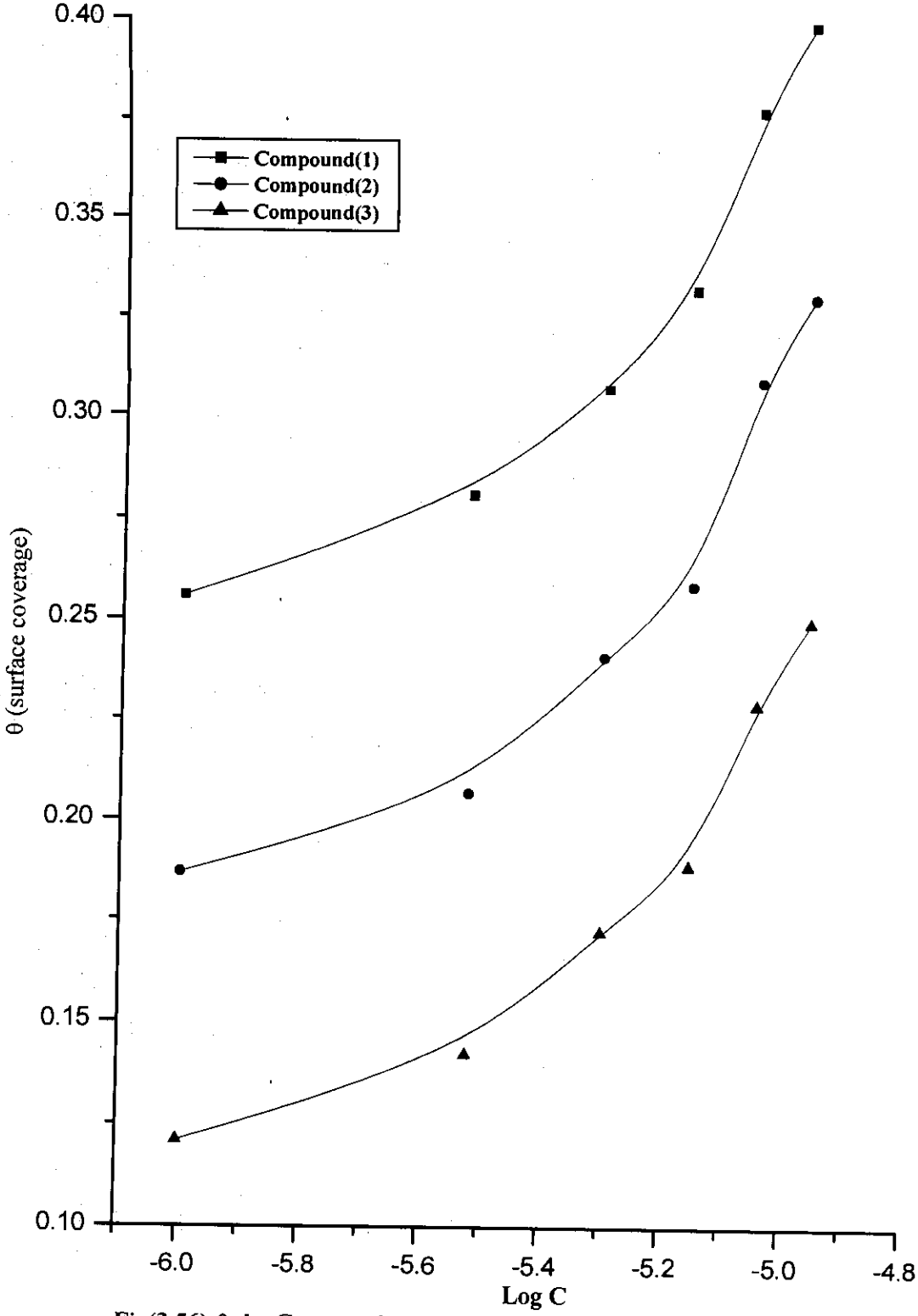
The variation of surface coverage determined by weight loss, θ, with the logarithm of the inhibitor concentration is represented in Figs. (3.56 and 3.57), and of S- shape obeying the Furmkin's adsorption isotherm[113] and is in good agreement with the Frumkin equation (3.4). As shown from these Figures, one can conclude that the degree of surface coverage increases as the

concentration of the inhibitor increases and hence, the inhibition efficiency increases.

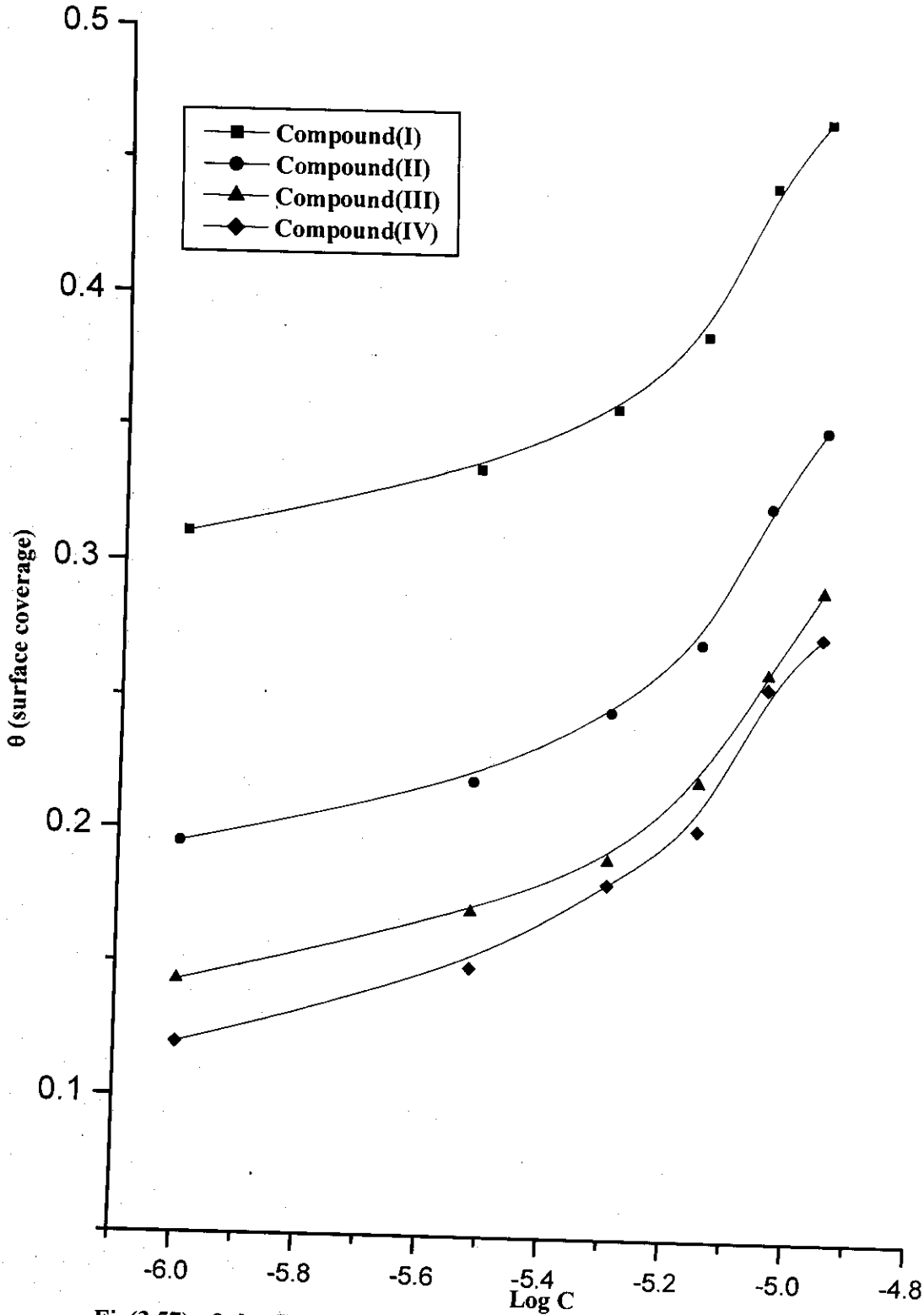
Frumkin equation is :

$$[\Theta / 1-\Theta) \exp (-2a \Theta) = KC \qquad (3.4)$$

where (a) is a molecular interaction parameter depending on the molecular interaction in the adsorption layer and on the degree of heterogeneity of the surface; it is a measure of steepness of adsorption isotherm; the more positive the value of (a) the steeper the adsorption isotherm, Θ is the degree of surface coverage, C is the inhibitor concentration in the bulk of solution, K is the equilibrium constant of the adsorption reaction.



Fig(3.56):θ -logC curves for iron dissolution in 3.5%H_3PO_4 in presence of first group compounds from weight loss measurements at 30^{o}C.



Fig(3.57): θ -logC curves for iron dissolution in 3.5%H_3PO_4 in presence of secomd group compounds from weight loss measurements at 30°C.

3.3 -Effect of Temperature and Activation Parameter

The effect of temperature is of a great importance to study the corrosion of iron, beside the effect of pH and medium composition. For that the effect of temperature has been studied from 35-50°C,which is shown in Figures.(3.58-3.85).

The effect of temperature is studied in the absence and presence of different concentrations of inhibitors. From all these Figs. One can observe that ,in the case of acid only (blank) corrosion rate is high, on the other hand when add different concentrations of hydrazone derivatives , the corrosion rate is decreased. This means that these derivatives act as inhibitors.

The increasing in the temperature has a reverse relationship with the percentage inhibition efficiency, This means that the adsorption of the investigated hydrazone derivatives on the metal surface is physically.

The results of Tables (3.15-3.22) show the percentage inhibition efficiency is decreased with increasing the temperature ,this behavior can be explained on the basis that the increase of the temperature leads to desorption of the adsorbed molecules of the inhibitors from the metal surface.

The apparent activation energy E_a^*, the enthalpy of activation ΔH^* and the entropy of activation ΔS^* for the corrosion of iron samples in 3.5% H_3PO_4 solutions in the absence and presence of different concentrations of hydrazone derivatives at 30, 35,40,45,50°C were calculated from Arrhenius-type equation:

$$\text{Rate} = A \exp(-E_a^*/RT) \qquad (3.1)$$

and transition-state equation:

$$\text{Rate} = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (3.2)$$

where A is the frequency factor, h is the Plank's constant, N is Avogadro's number and R is the universal gas constant. A plot of log Rate vs. 1/T and log (Rate/T) vs. 1/T give straight lines with slope of - $E_a^*/2.303R$, and - $\Delta H^*/2.303R$, respectively. The intercepts will be A and log R/Nh + $\Delta S^*/2.303R$ for Arrhenius and transition state equations, respectively.

Figures (3.86-3.99) represent plots of the log rate vs. 1/T and log (rate/T) vs. 1/T data. The calculated values of the apparent activation energy, E_a^*, activation entropies, $\Delta S^*$and activation enthalpies, ΔH^* are given in Tables (3.23-3.28) .

The almost similar values of E_a^* suggest that the inhibitors are similar in the mechanism of action and the order of efficiency may be related to the preexponential factor A in equation (3.1). This is further related to concentration, steric effects, metal surface characters.

The order of the inhibition efficiency of the investigated hydrazone derivative as gathered from the increase in Ea* and ΔH^* values and decrease in ΔS^* values is:

First group is:

(1) > (2) > (3)

Second group is:

(I) > (II) > (III) > (IV)

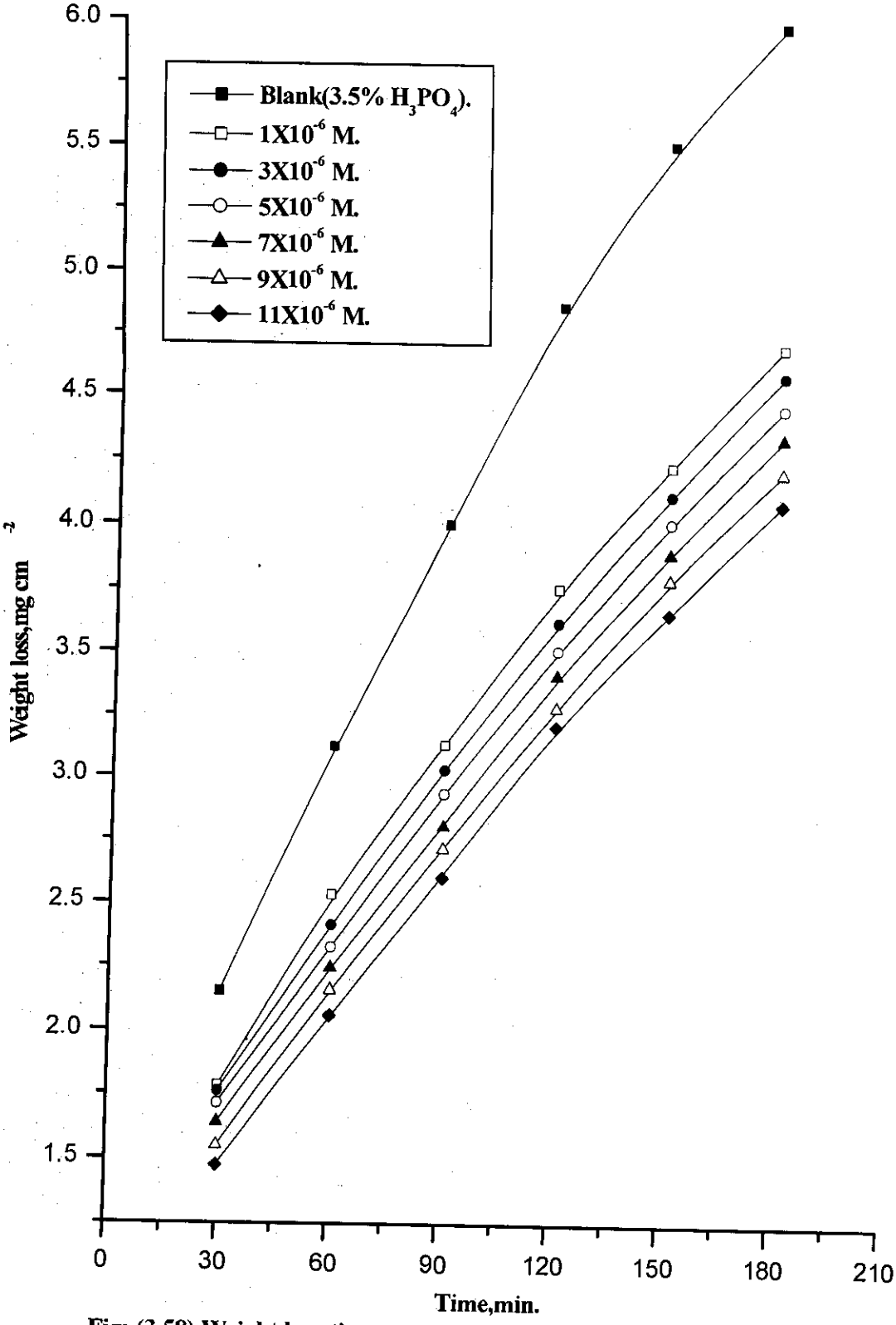


Fig: (3.58).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (1) at 35^{o}C.

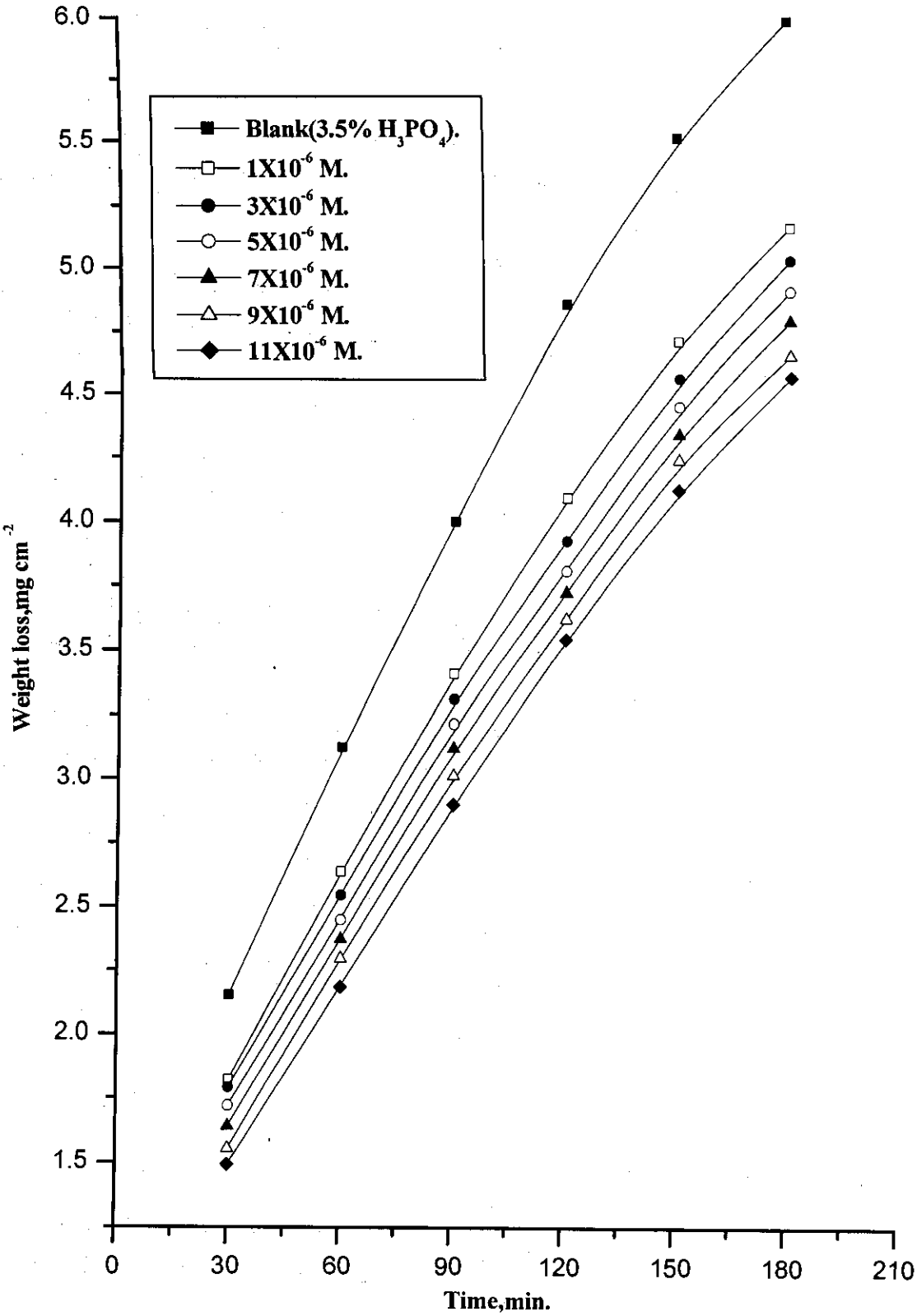


Fig: (3.59).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (2) at 35^{O}C.

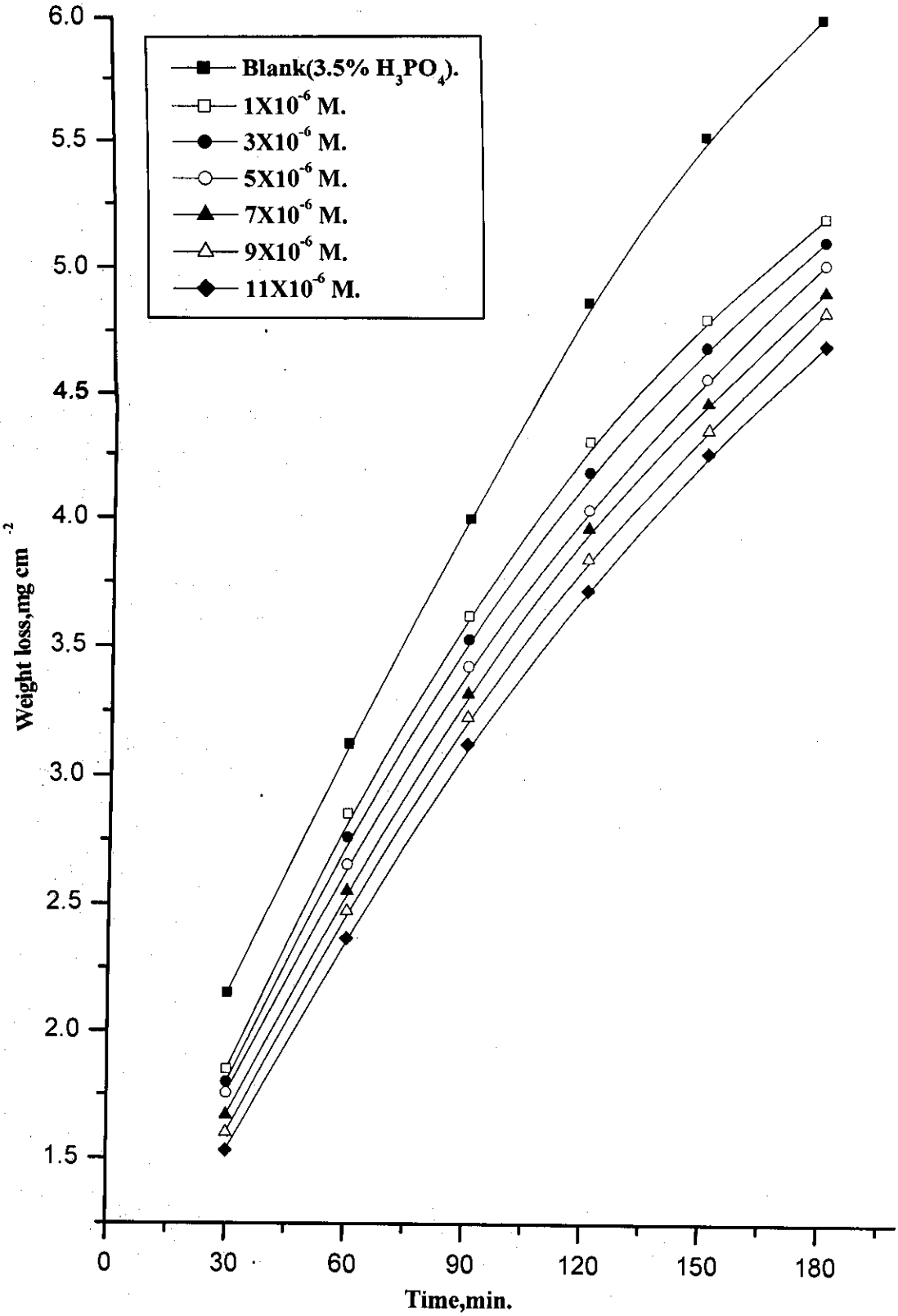


Fig: (3.60).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (3) at 35^{O}C.

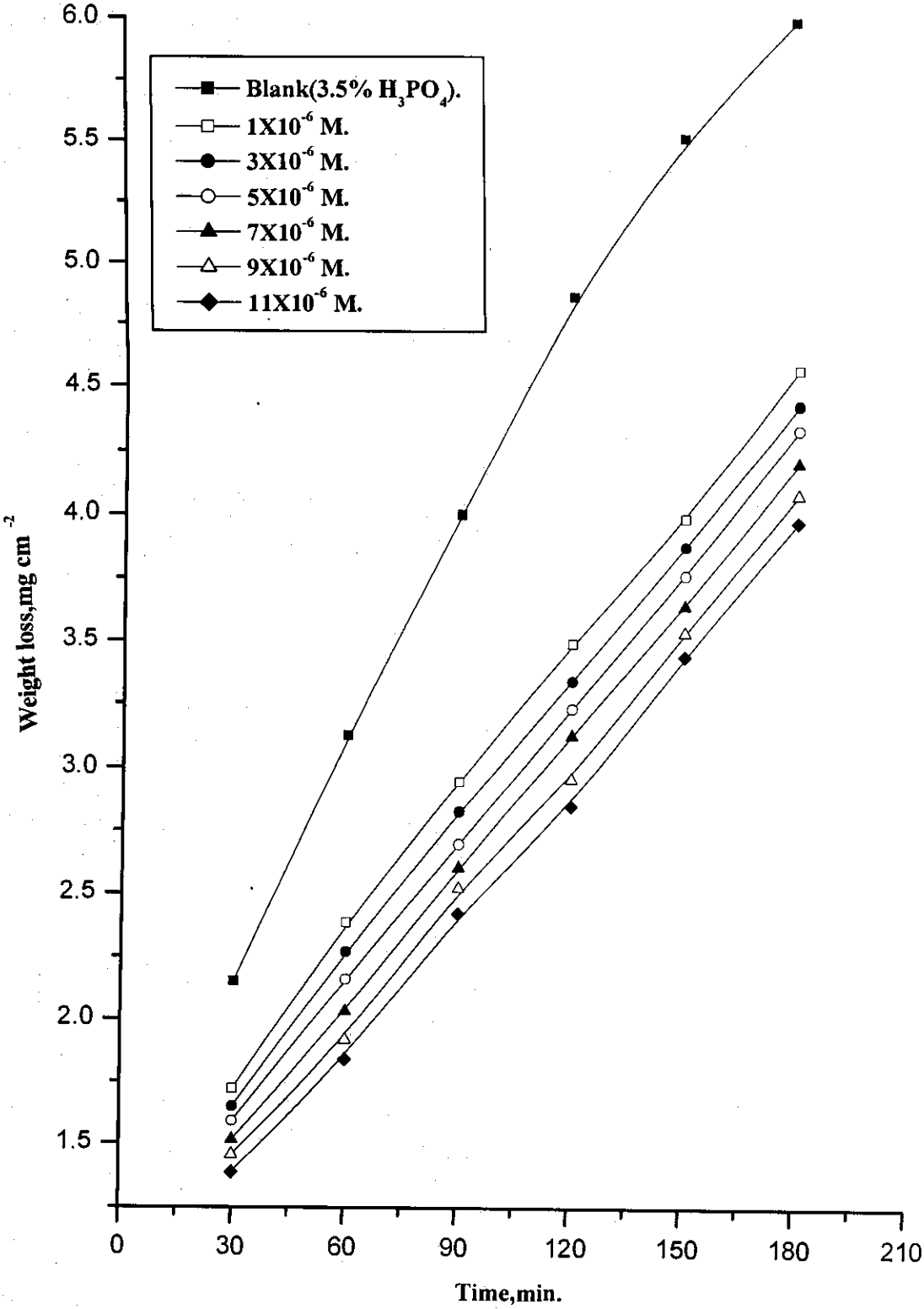


Fig: (3.61).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (I) at 35°C.

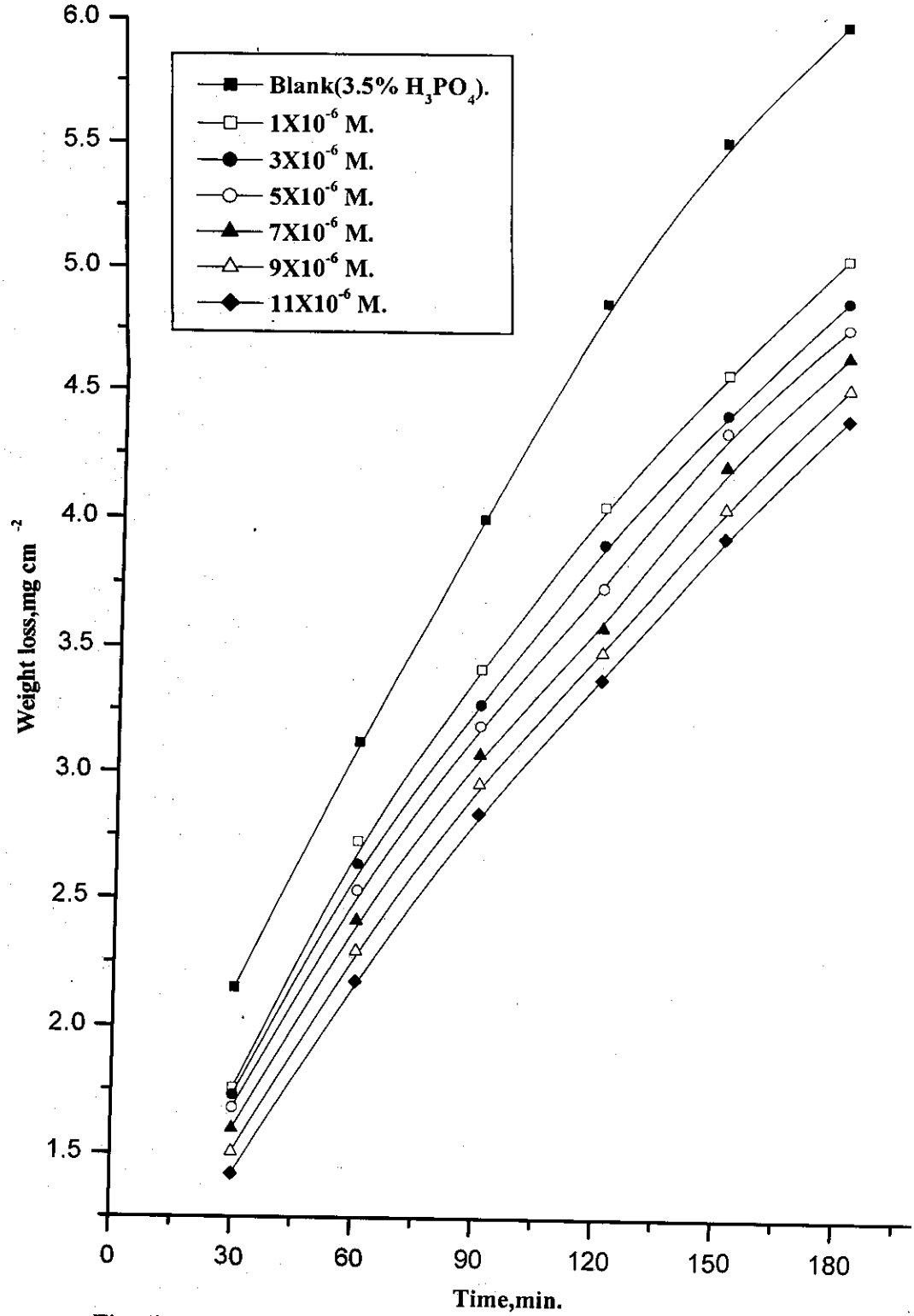


Fig: (3.62).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (II) at 35^{o}C.

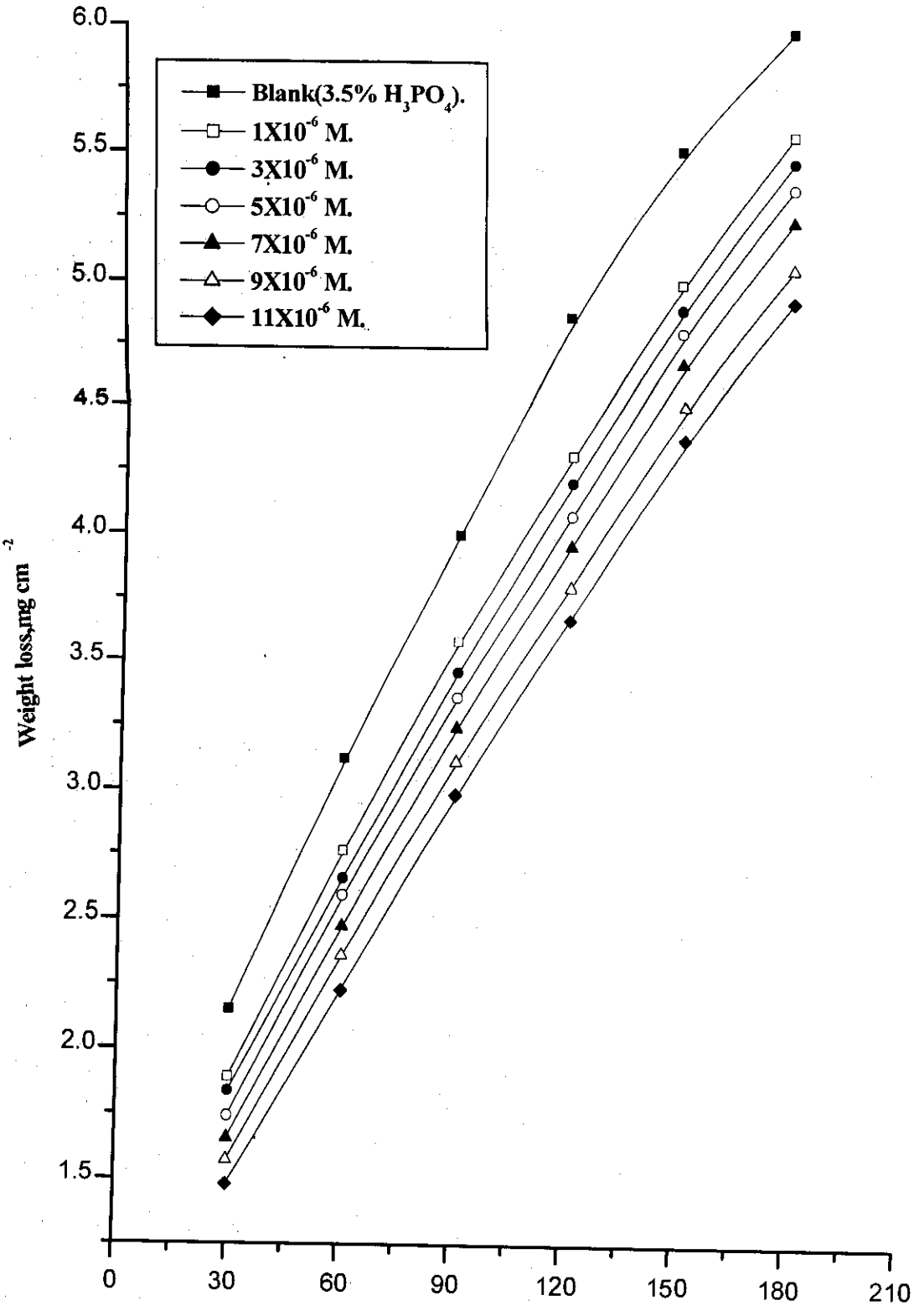


Fig: (3.63).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (III) at 35°C.

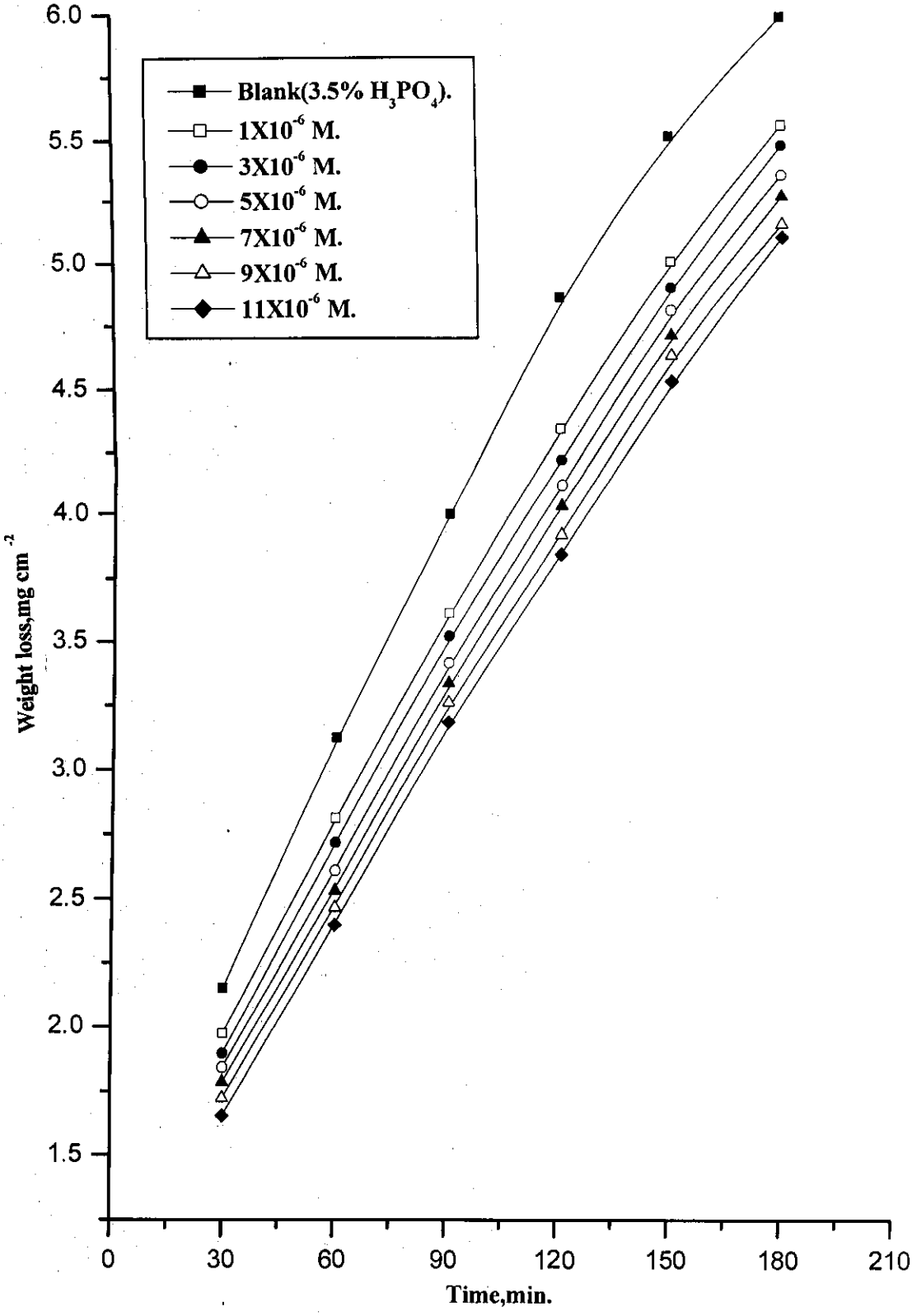


Fig: (3.64).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (VI) at 35^{O}C.

Table(3.15): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of first group compounds at 35°C.

Concentration M	%Inhibition		
	(1)	(2)	(3)
$1X10^{-6}$	22.7	15.8	11.4
$3X10^{-6}$	25.4	19.2	13.9
$5X10^{-6}$	27.8	21.6	16.9
$7X10^{-6}$	29.8	23.4	18.4
$9X10^{-6}$	32.4	25.4	20.9
$11X10^{-6}$	34.0	27.0	23.5

Table(3.16): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of second group compounds at 35°C.

Concentration M	%Inhibition			
	(I)	(II)	(III)	(IV)
$1X10^{-6}$	28.3	16.6	11.3	10.6
$3X10^{-6}$	31.3	19.6	13.4	13.2
$5X10^{-6}$	33.6	23.0	16.1	15.3
$7X10^{-6}$	35.8	26.2	18.5	17.0
$9X10^{-6}$	39.2	28.3	21.8	19.3
$11X10^{-6}$	41.5	30.5	24.5	20.9

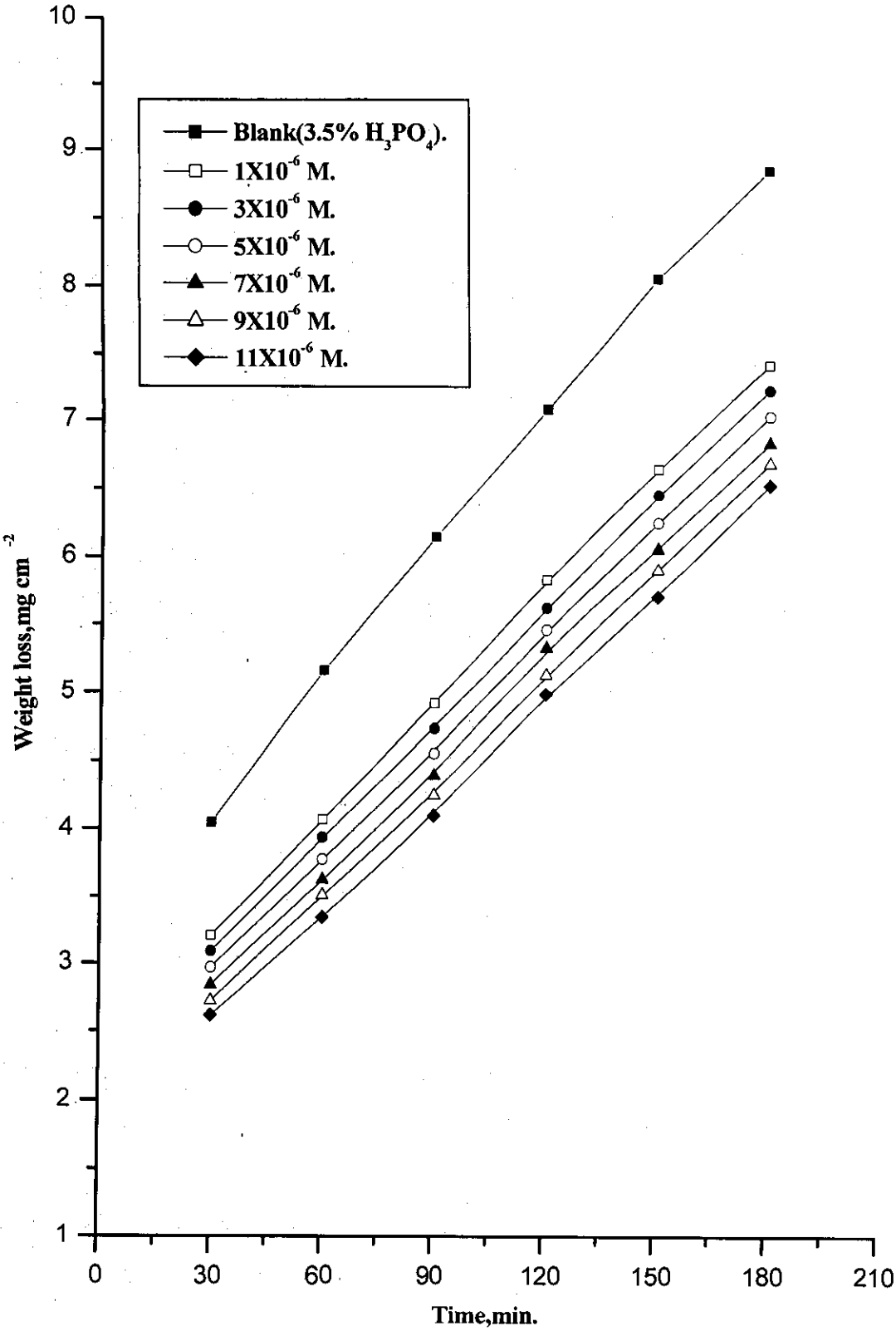


Fig: (3.65).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (1) at 40^{o}C.

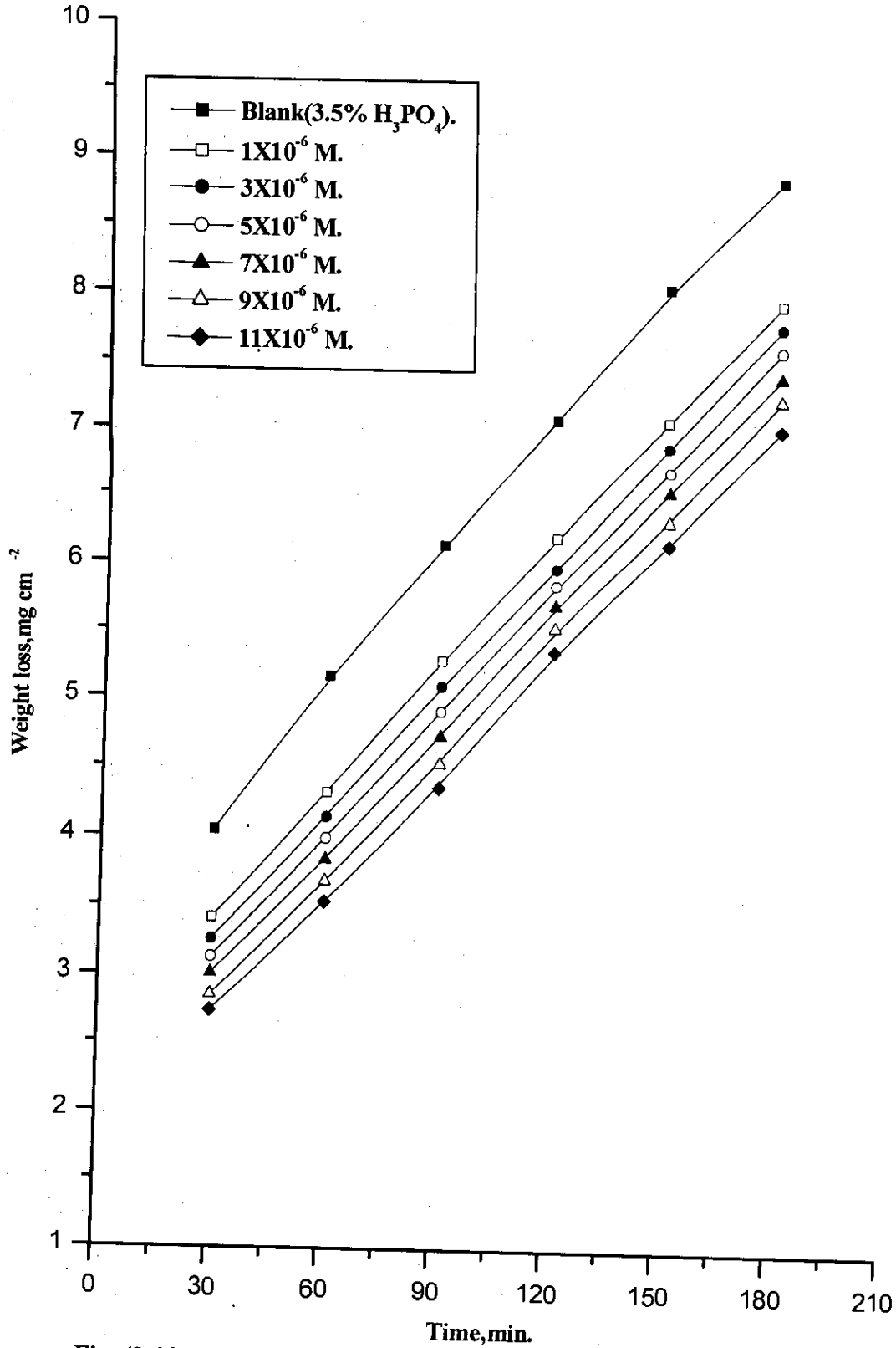


Fig: (3.66).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (2) at 40^{o}C.

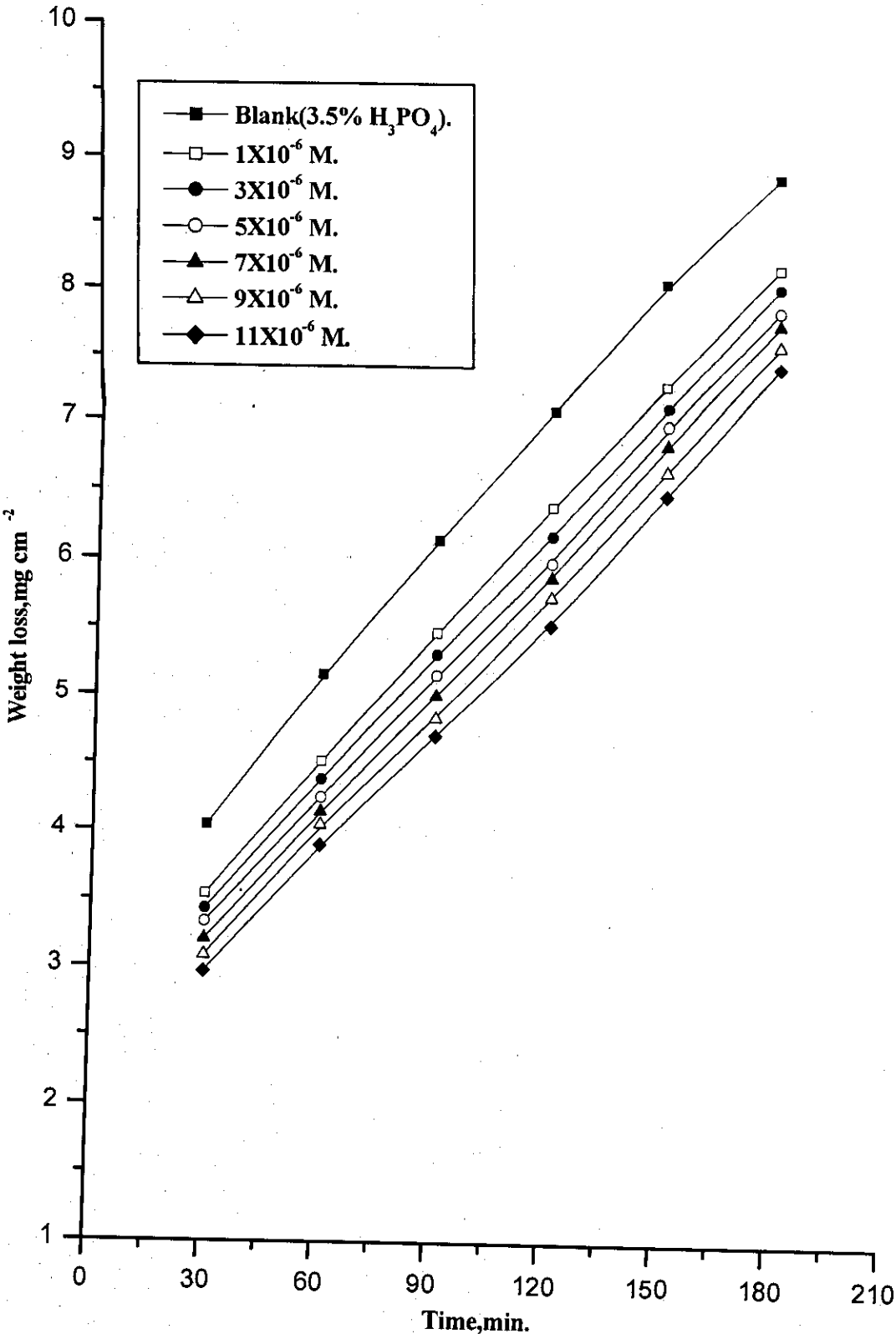


Fig: (3.67).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (3) at 40^{o}C.

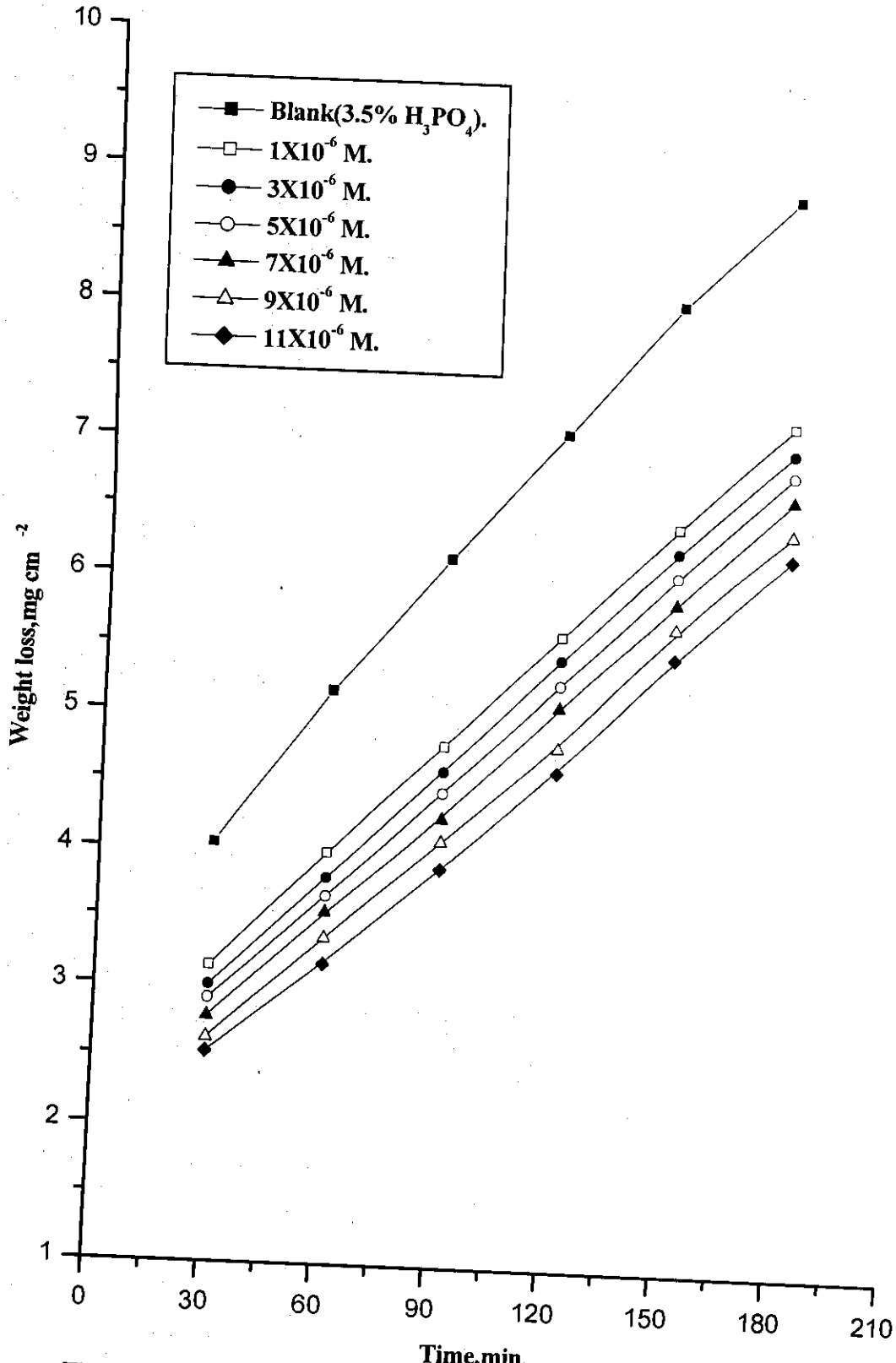


Fig: (3.68).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (I) at 40^{O}C.

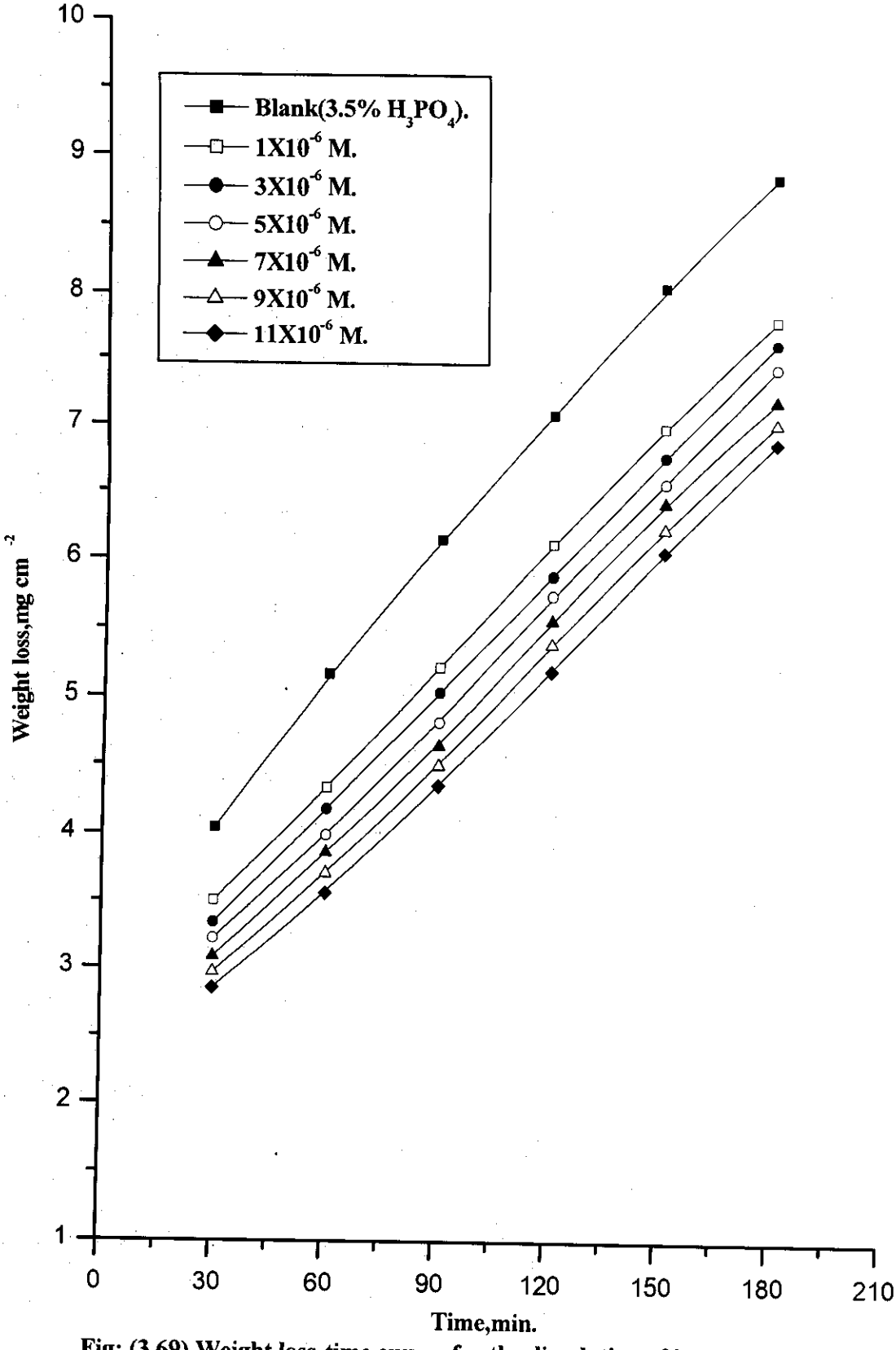


Fig: (3.69).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (II) at 40^{O}C.

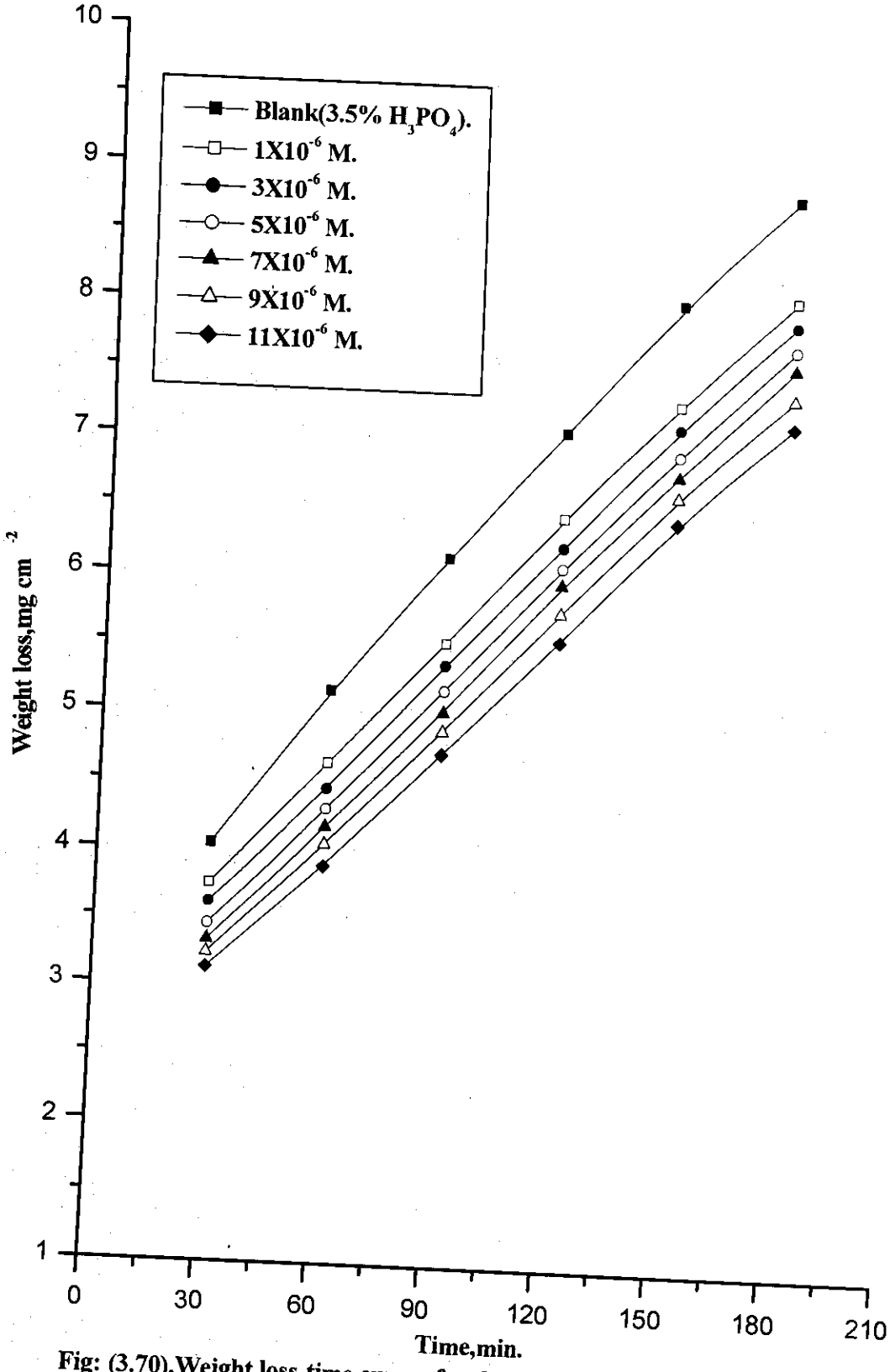


Fig: (3.70).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (III) at 40^{o}C.

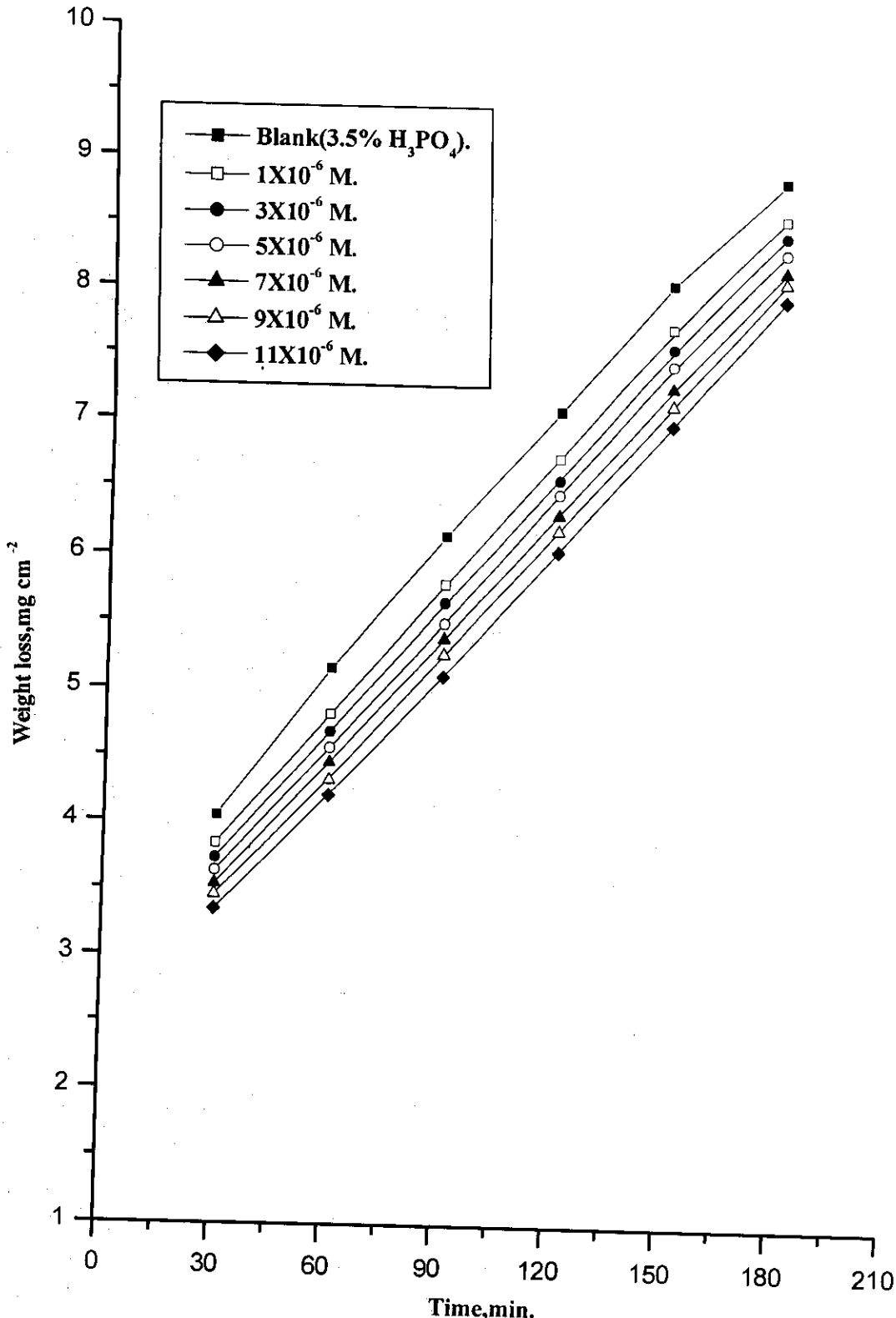


Fig: (3.71).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (IV) at 40^{o}C.

Table(3.17): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of first group compounds at 40°C.

Concentration M	%Inhibition		
	(1)	(2)	(3)
$1X10^{-6}$	17.7	12.3	9.7
$3X10^{-6}$	20.7	15.5	12.7
$5X10^{-6}$	22.9	17.3	15.4
$7X10^{-6}$	24.8	19.4	16.9
$9X10^{-6}$	27.6	21.7	18.9
$11X10^{-6}$	29.6	24.2	21.9

Table(3.18): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of second group compounds at 40°C.

Concentration M	%Inhibition			
	(I)	(II)	(III)	(IV)
$1X10^{-6}$	20.8	13.6	8.8	4.9
$3X10^{-6}$	23.3	16.9	11.8	7.2
$5X10^{-6}$	25.9	18.9	13.9	8.7
$7X10^{-6}$	28.2	21.5	15.6	10.9
$9X10^{-6}$	32.3	24.0	18.5	12.6
$11X10^{-6}$	34.8	26.7	21.4	14.7

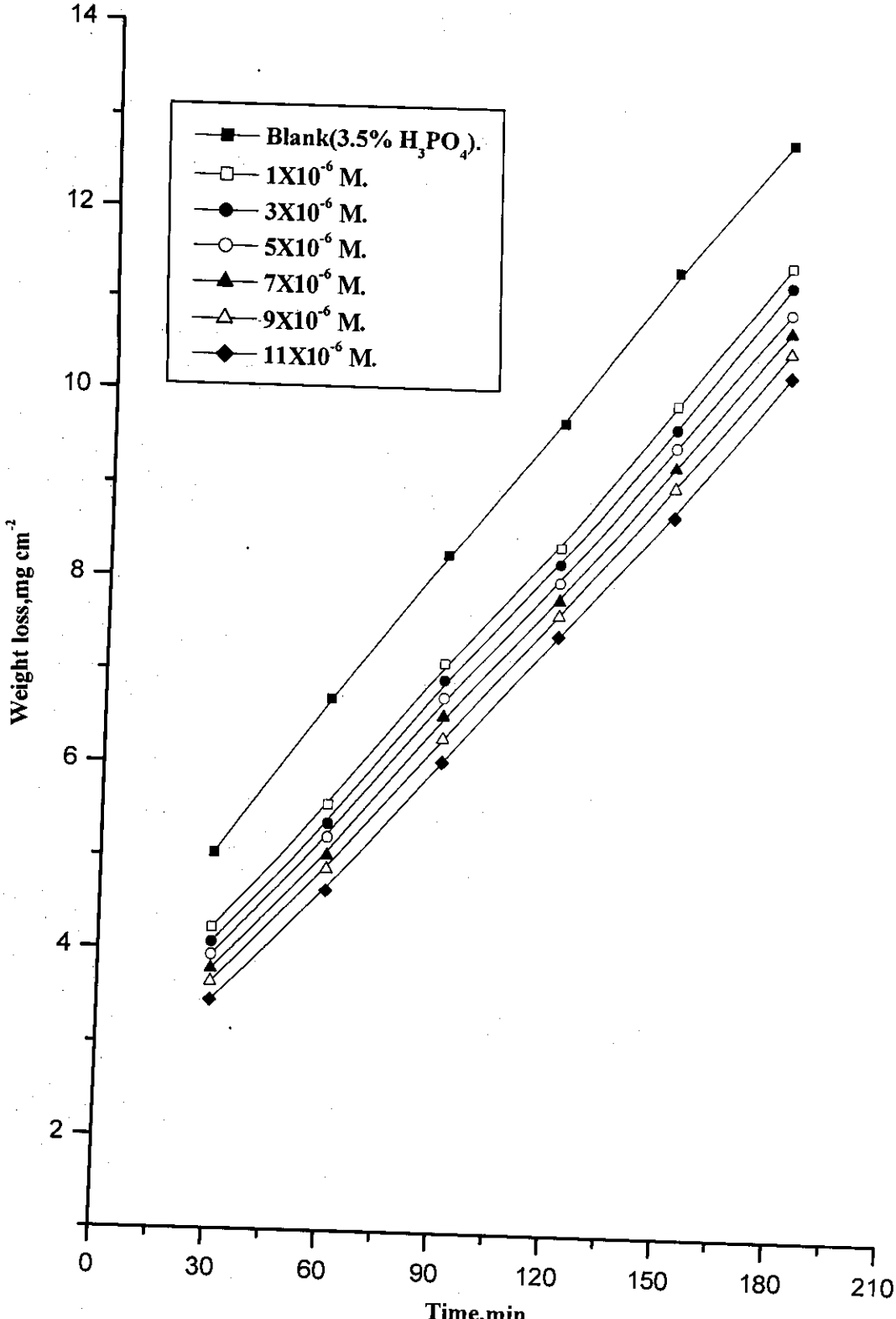


Fig: (3.72).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (1) at 45^{O}C.

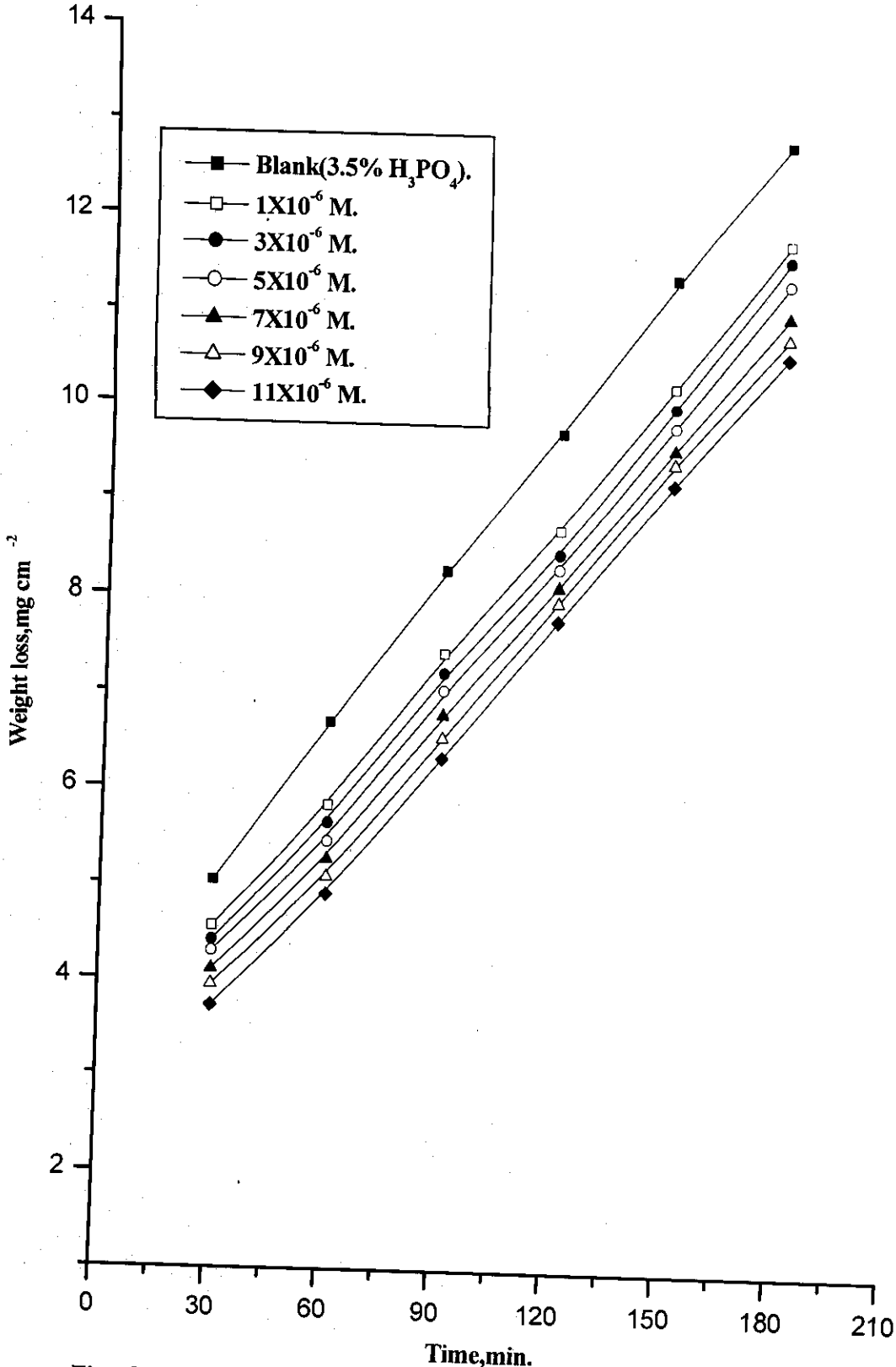


Fig: (3.73).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (2) at 45^{O}C.

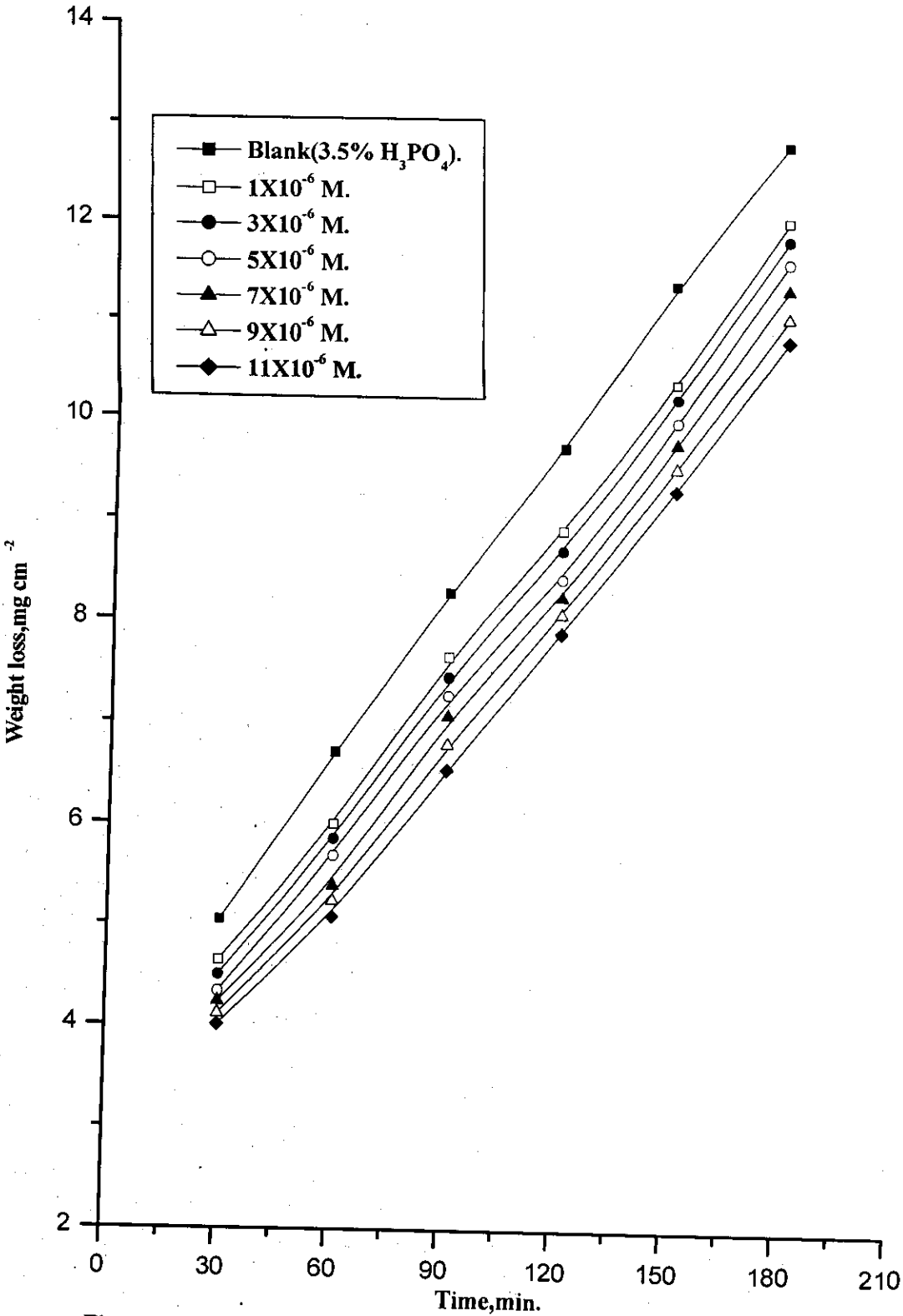


Fig: (3.74).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (3) at 45^{o}C.

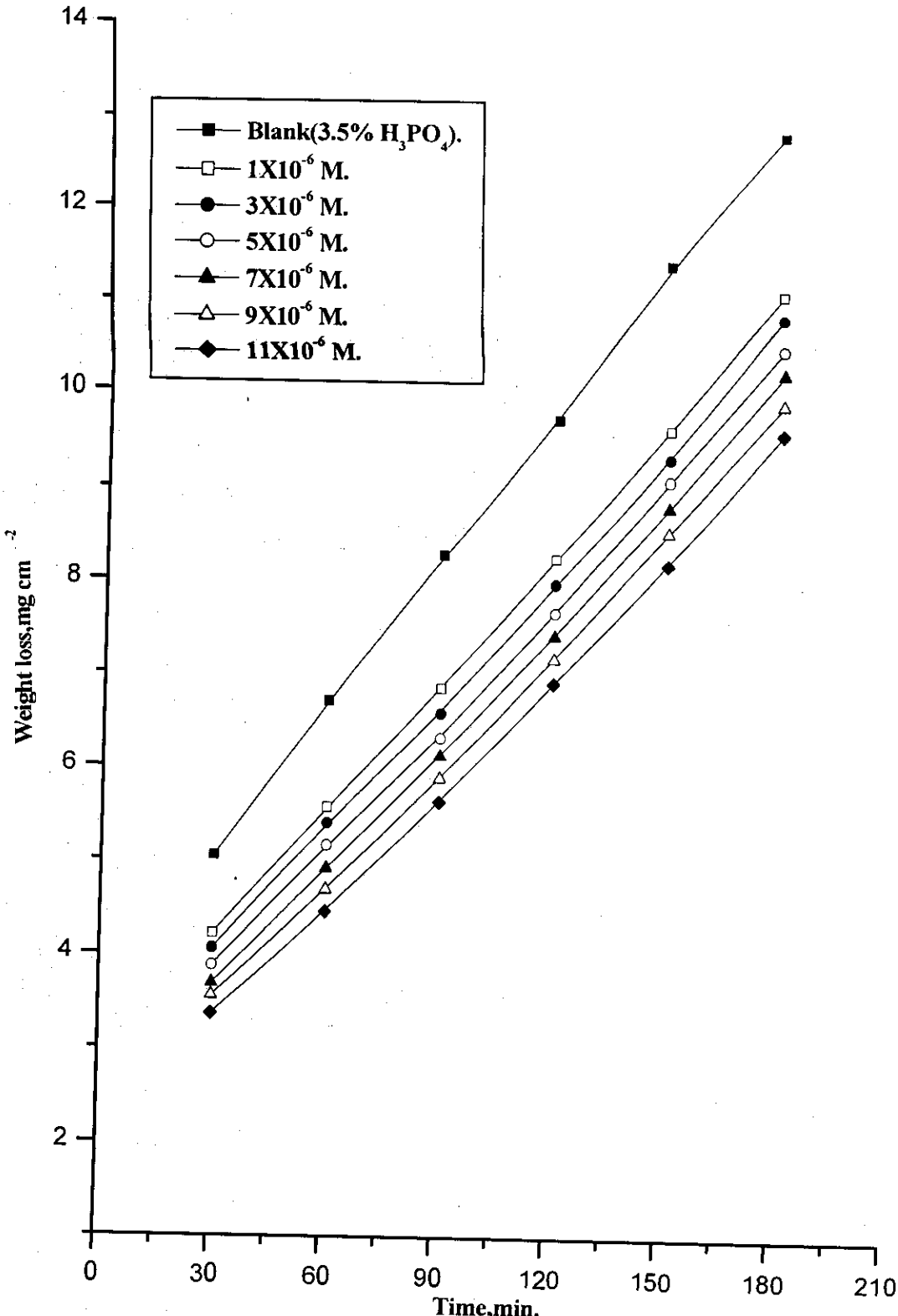


Fig: (3.75).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (I) at 45°C.

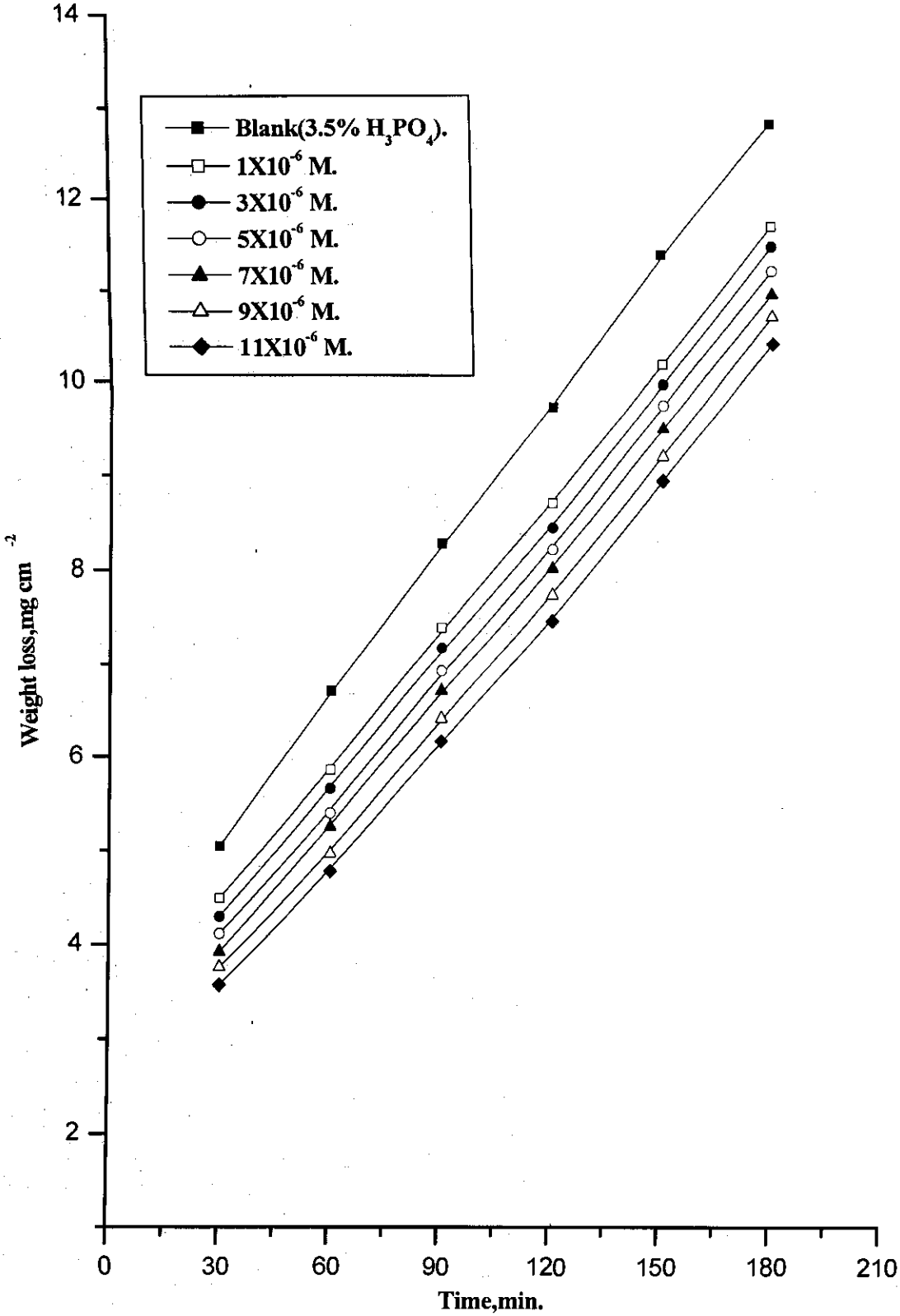


Fig: (3.76).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (II) at 45^{O}C.

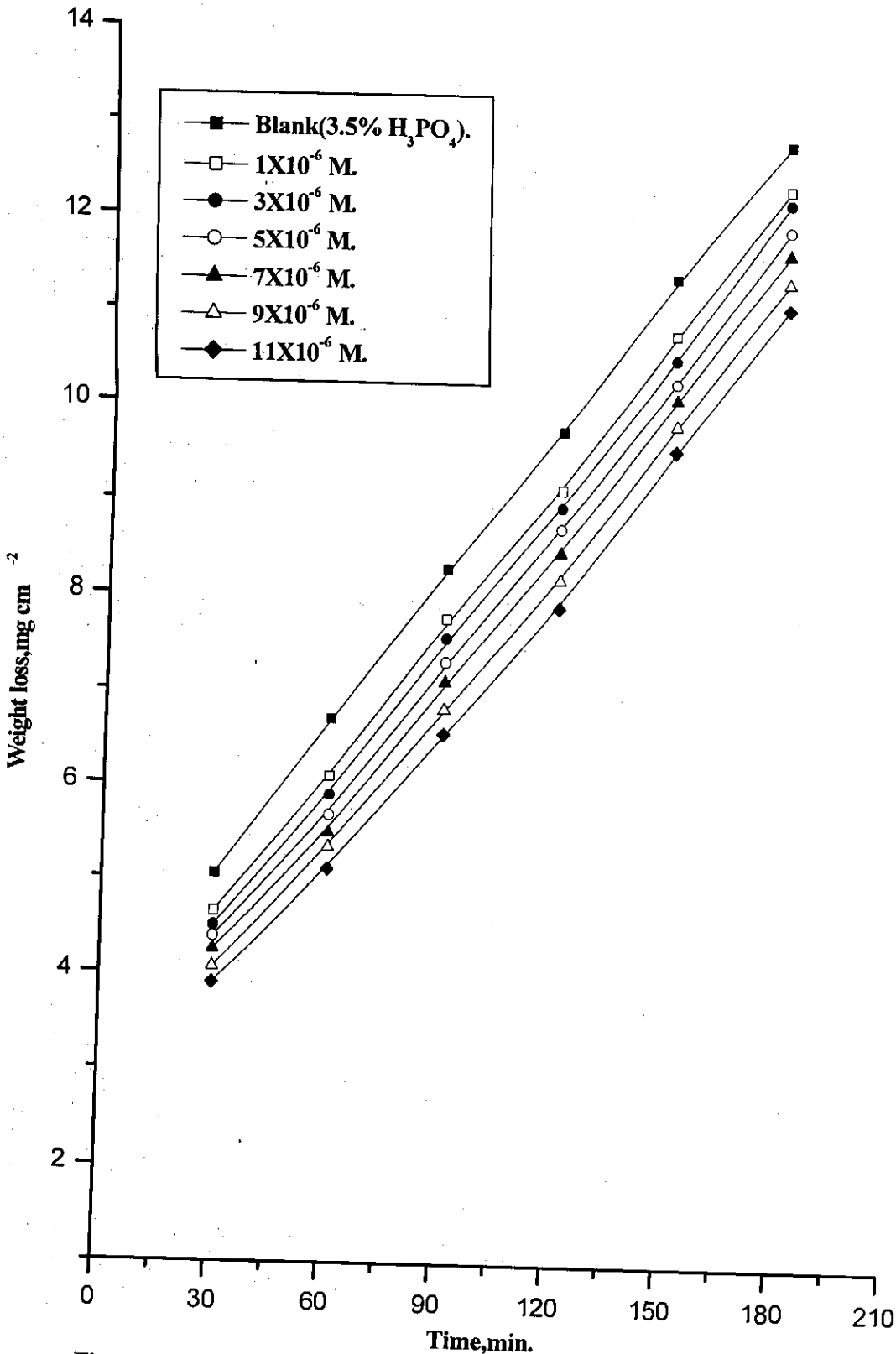


Fig: (3.77).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (III) at 45^{o}C.

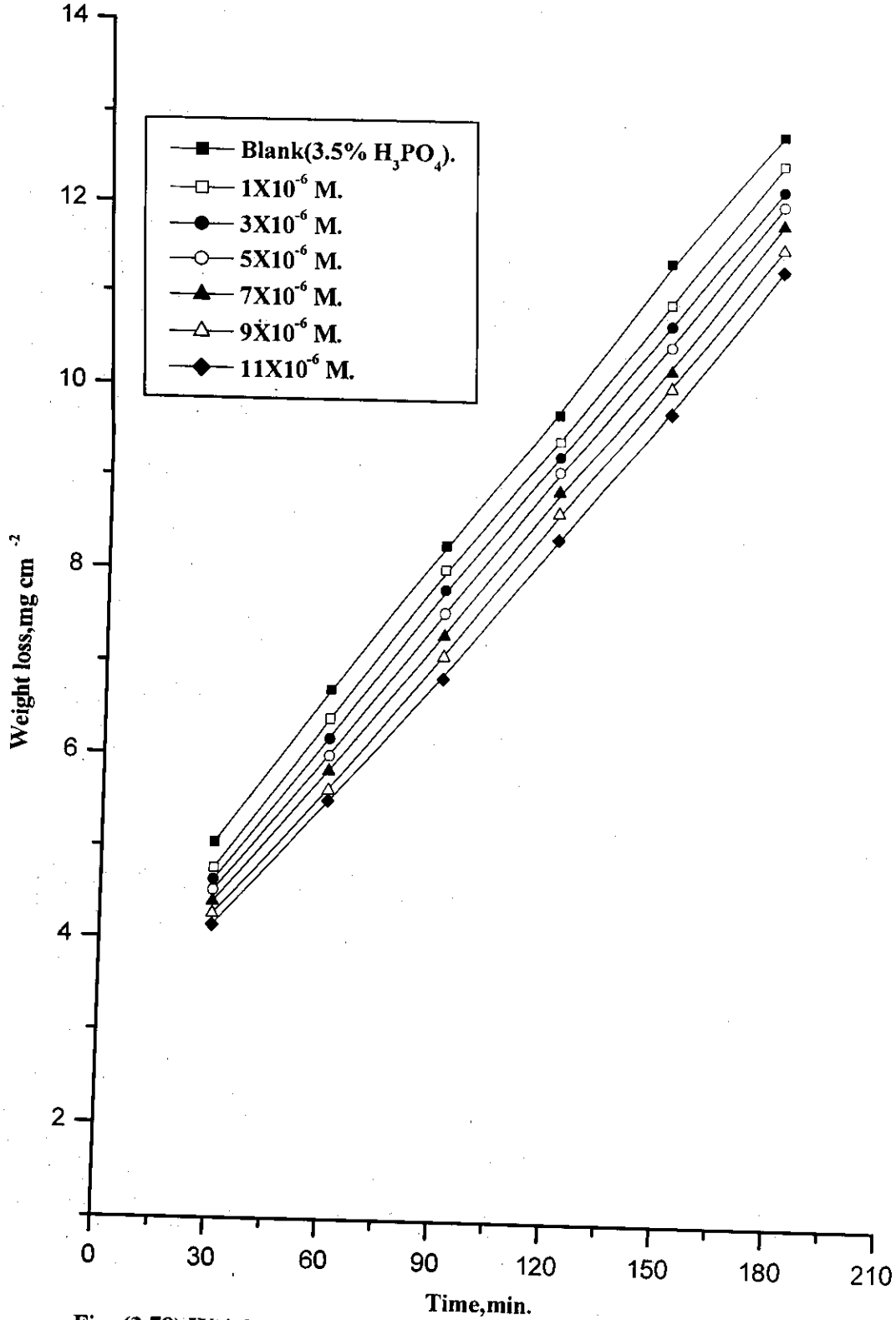


Fig: (3.78).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (IV) at 45^{o}C.

Table(3.19): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of first group compounds at 45°C.

Concentration M	%Inhibition		
	(1)	(2)	(3)
$1X10^{-6}$	13.6	10.3	8.4
$3X10^{-6}$	15.5	12.9	10.4
$5X10^{-6}$	17.6	14.4	13.3
$7X10^{-6}$	19.5	16.4	15.2
$9X10^{-6}$	21.2	18.0	17.0
$11X10^{-6}$	23.5	19.9	18.8

Table(3.20): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of second group compounds at 45°C.

Concentration M	%Inhibition			
	(I)	(II)	(III)	(IV)
$1X10^{-6}$	15.1	10.4	6.1	3.0
$3X10^{-6}$	17.9	13.1	8.0	4.8
$5X10^{-6}$	21.1	15.4	10.3	6.6
$7X10^{-6}$	23.6	17.5	12.9	8.7
$9X10^{-6}$	26.2	20.4	15.8	11.1
$11X10^{-6}$	28.9	23.1	18.8	13.9

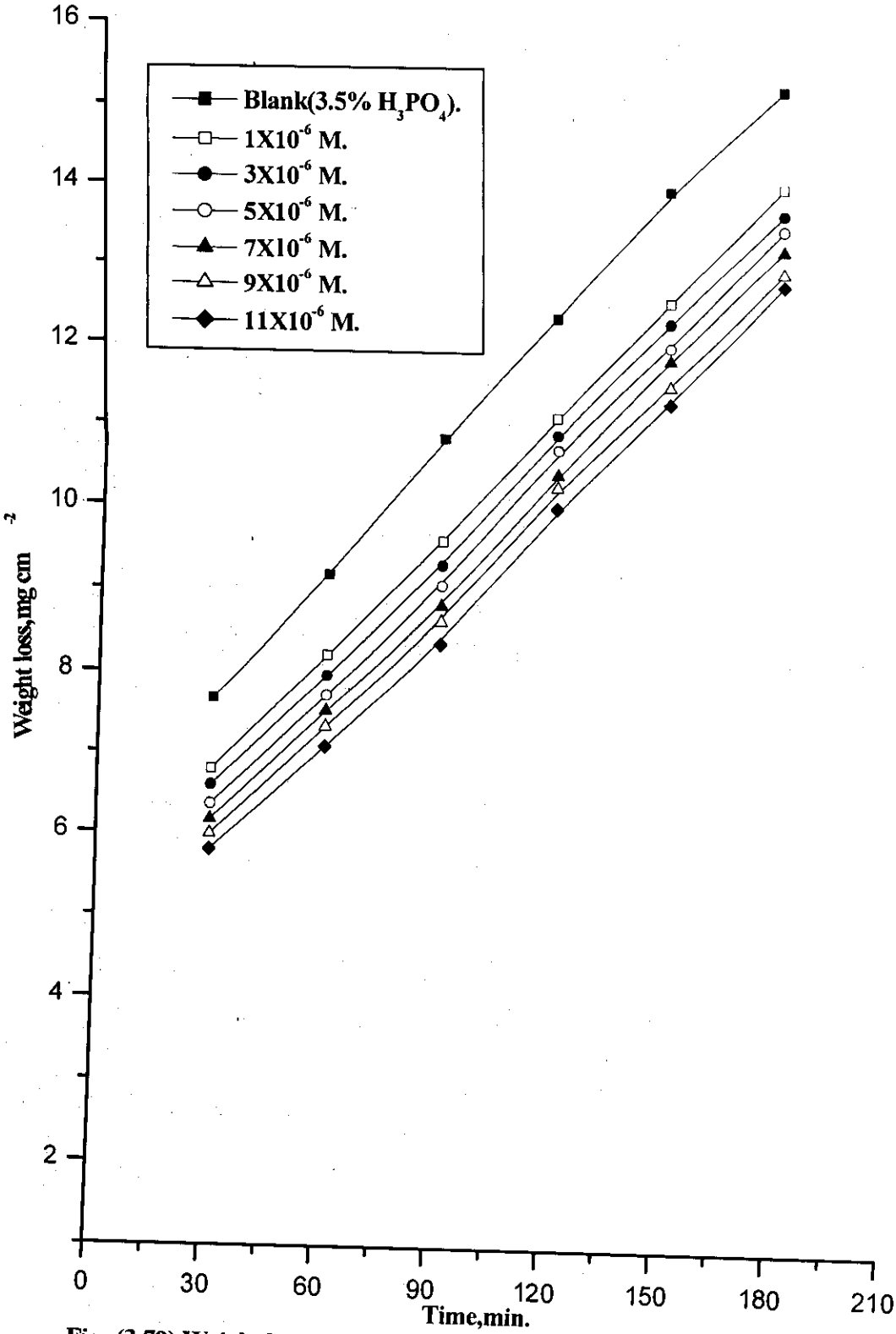


Fig: (3.79).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (1) at 50°c .

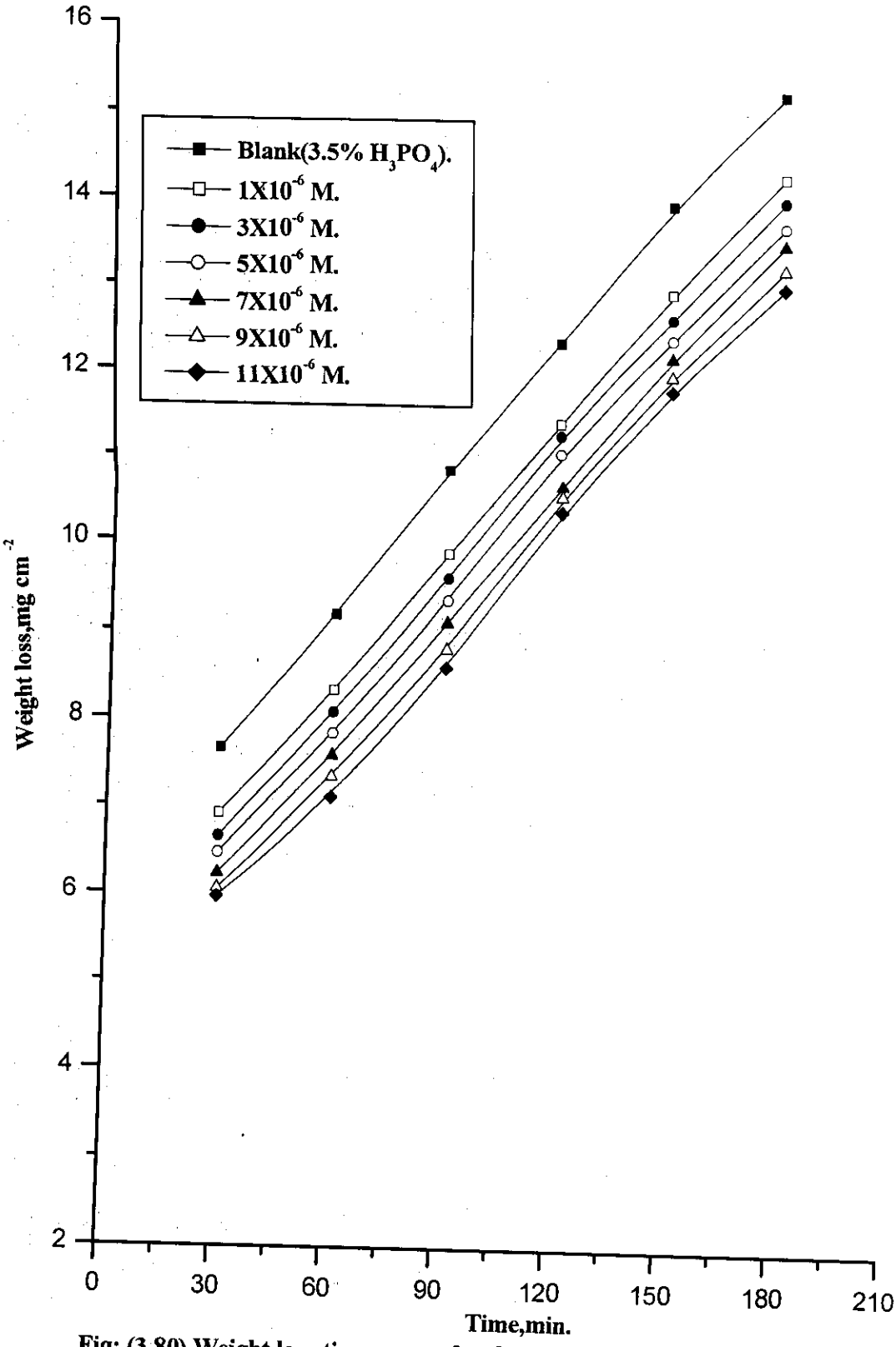


Fig: (3.80).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (2) at 50°c .

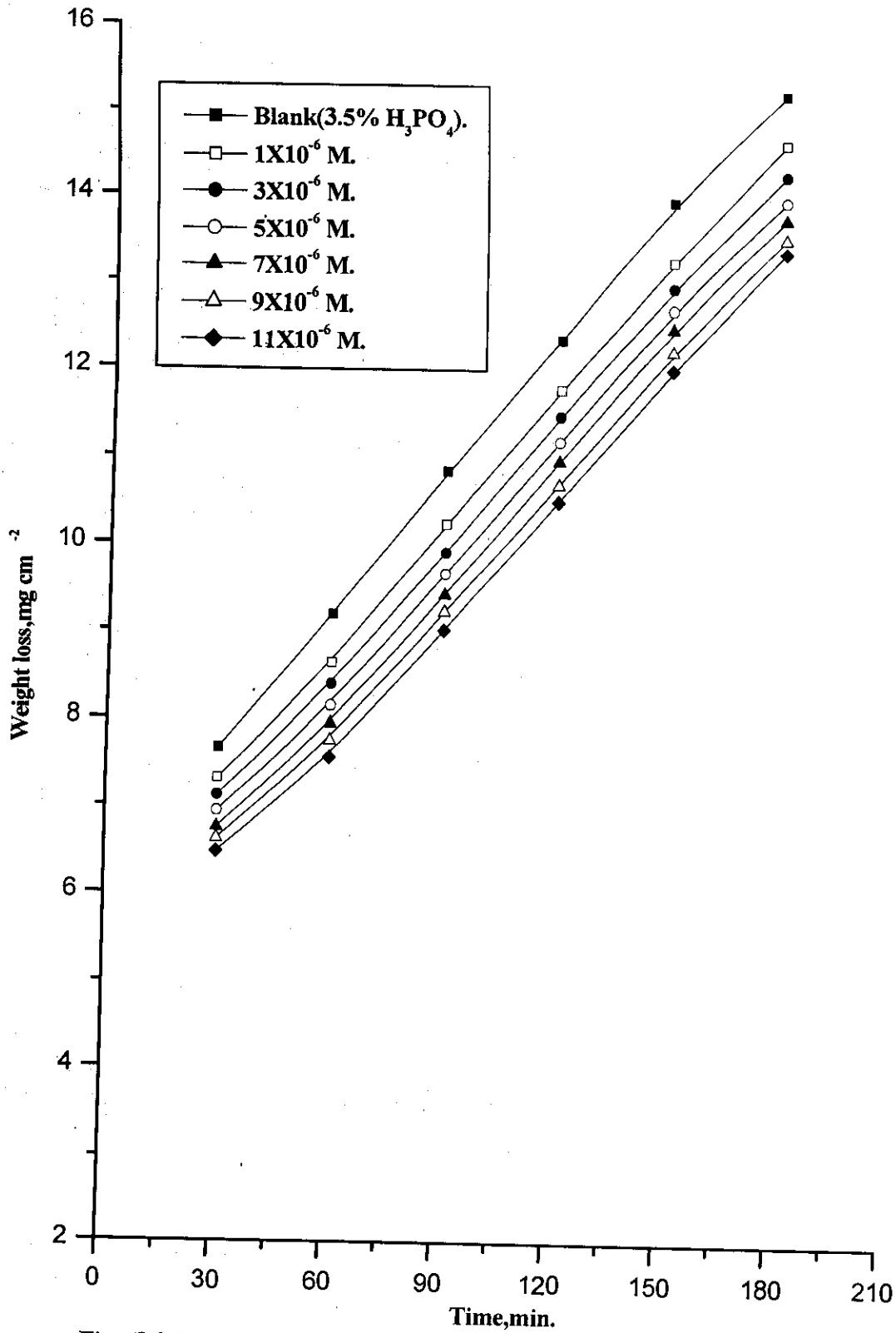


Fig: (3.81).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (3) at 50°c .

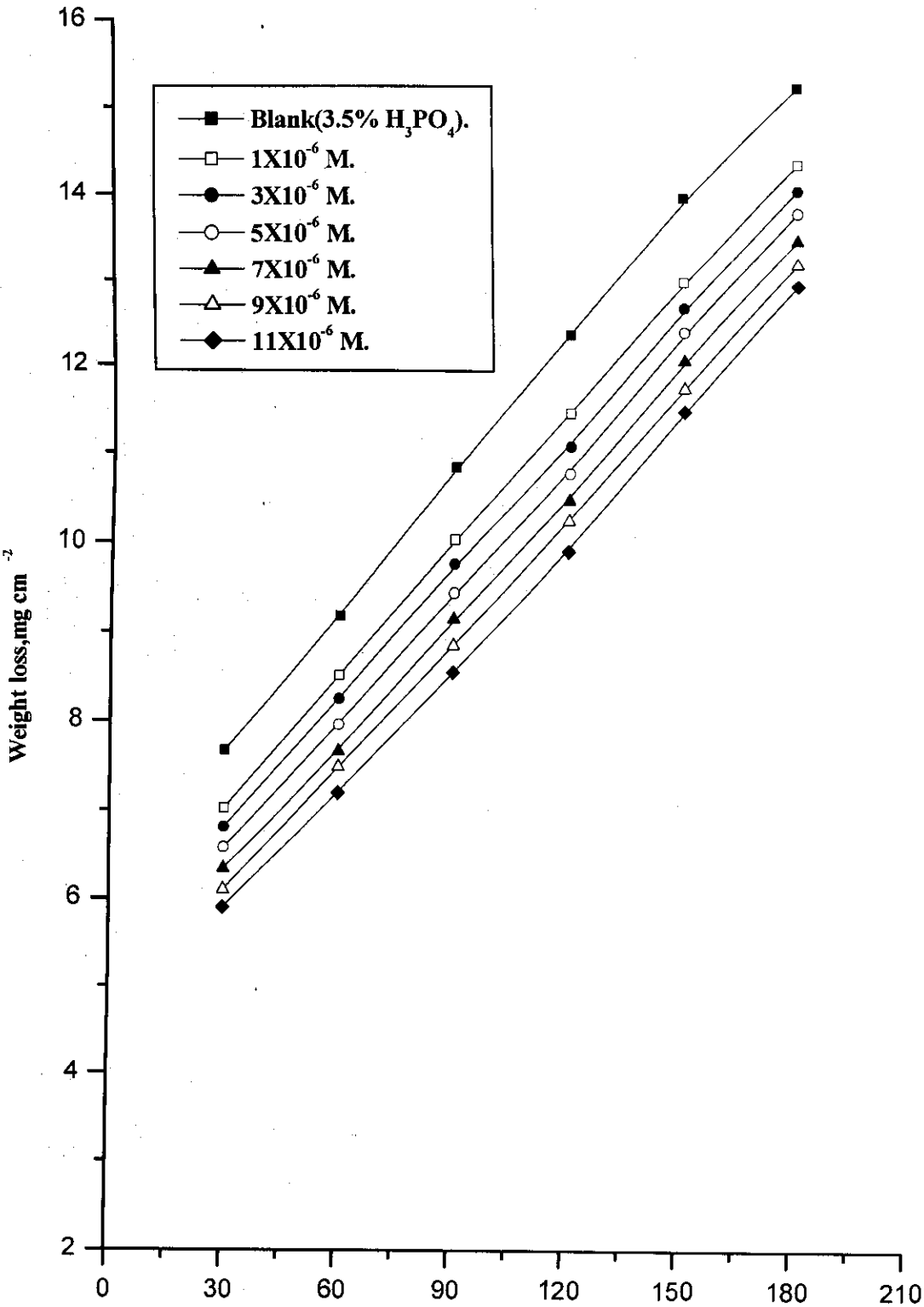


Fig: (3.83).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (II) at 50°c .

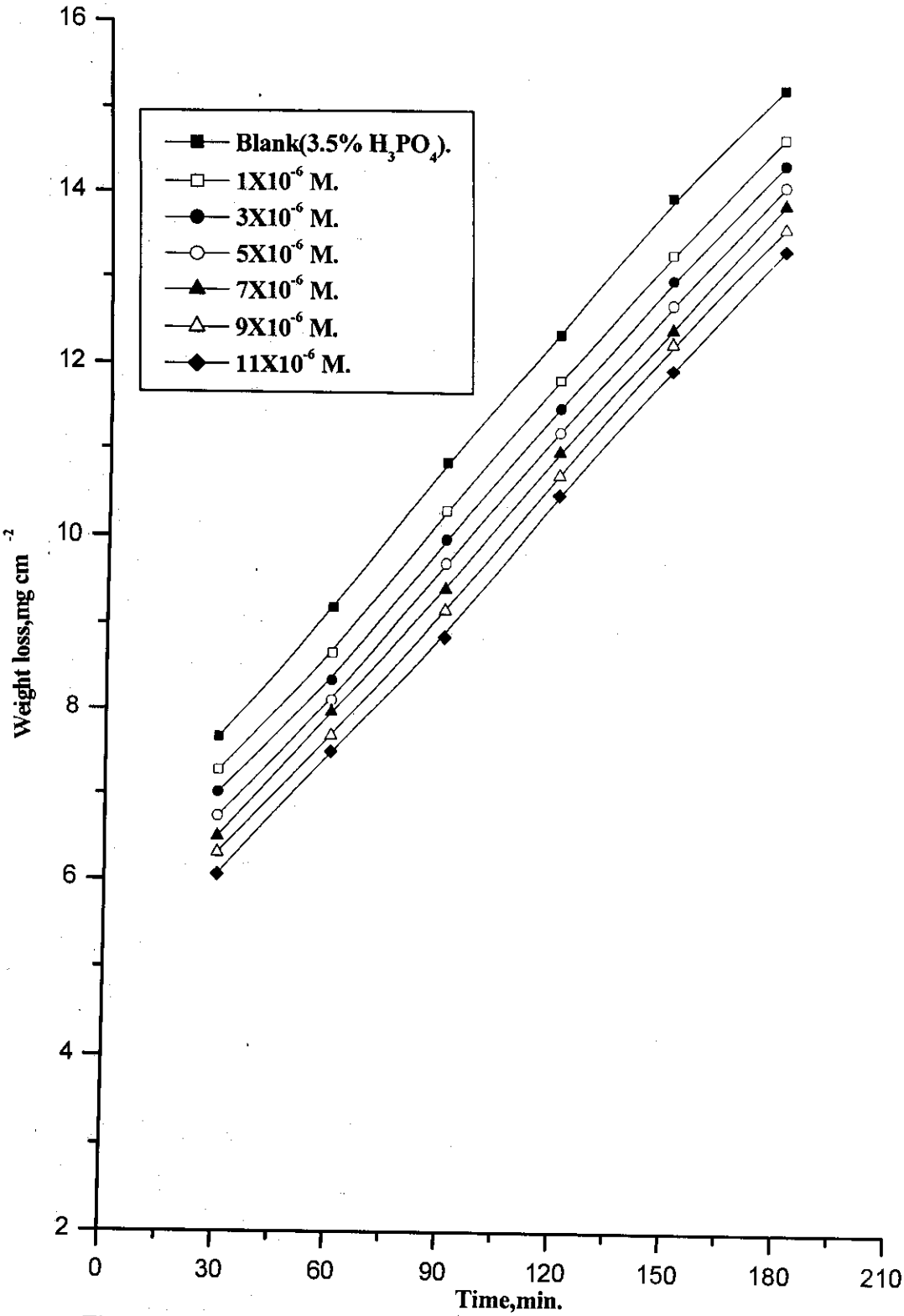


Fig: (3.84).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (III) at 50°C .

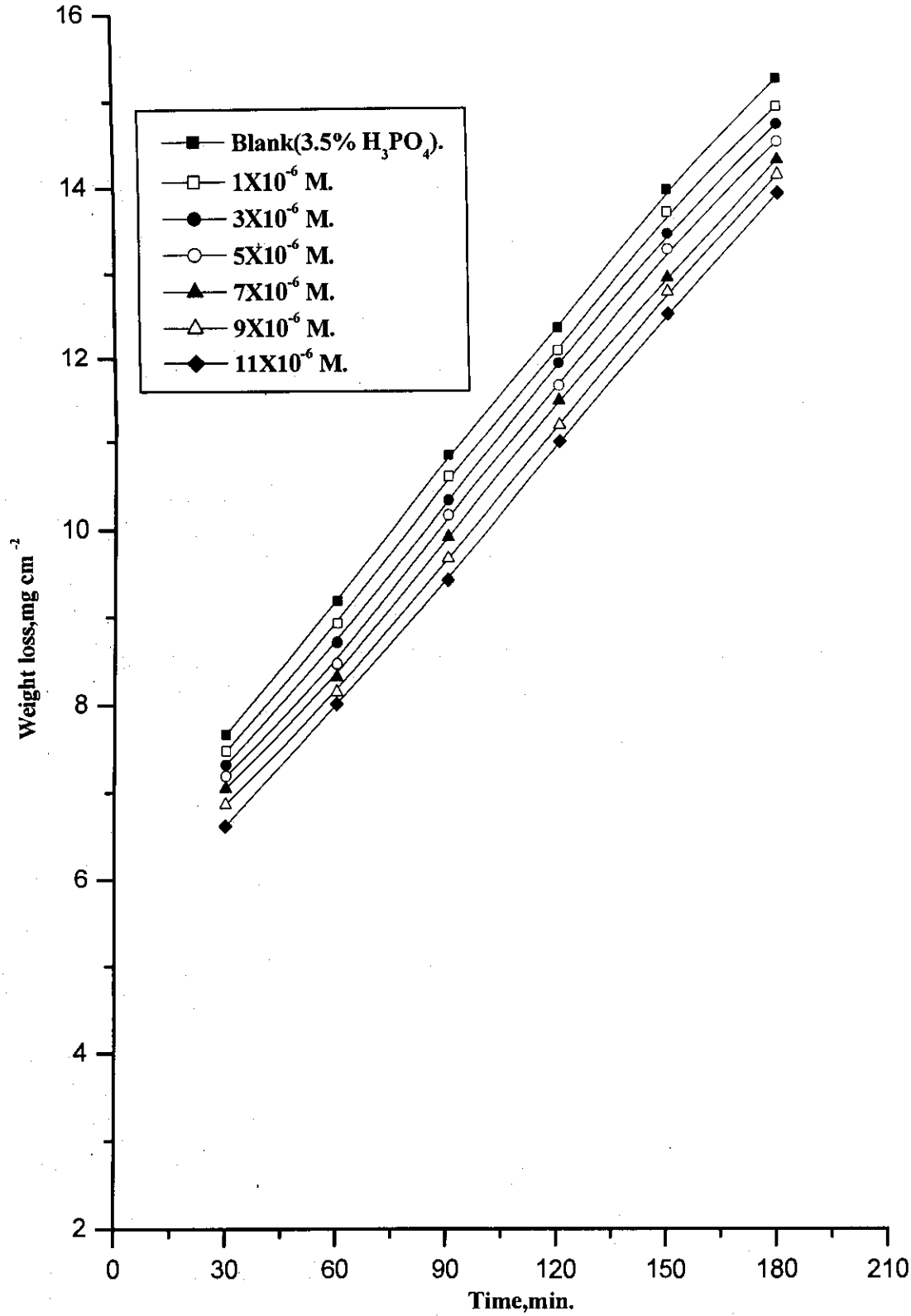


Fig: (3.85).Weight loss-time curves for the dissolution of iron in absence and presence of different concentrations of compound (IV) at 50°C .

Table(3.21): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of first group compounds at 50°C.

Concentration M	%Inhibition		
	(1)	(2)	(3)
$1X10^{-6}$	10.0	7.6	4.7
$3X10^{-6}$	11.7	8.7	7.0
$5X10^{-6}$	13.2	10.4	9.4
$7X10^{-6}$	15.6	13.7	11.2
$9X10^{-6}$	16.9	14.7	13.4
$11X10^{-6}$	18.9	16.0	14.9

Table(3.22): % Inhibition efficiency of iron dissolution at 120 min. immersion in 3.5% H_3PO_4 in presence of different concentrations of second group compounds at 50°C.

Concentration M	%Inhibition			
	(I)	(II)	(III)	(IV)
$1X10^{-6}$	12.4	7.3	4.4	2.2
$3X10^{-6}$	14.7	10.3	7.1	3.4
$5X10^{-6}$	17.1	12.7	9.3	5.6
$7X10^{-6}$	19.6	15.1	11.2	7.0
$9X10^{-6}$	22.5	17.0	13.3	9.4
$11X10^{-6}$	24.8	19.8	15.1	11.0

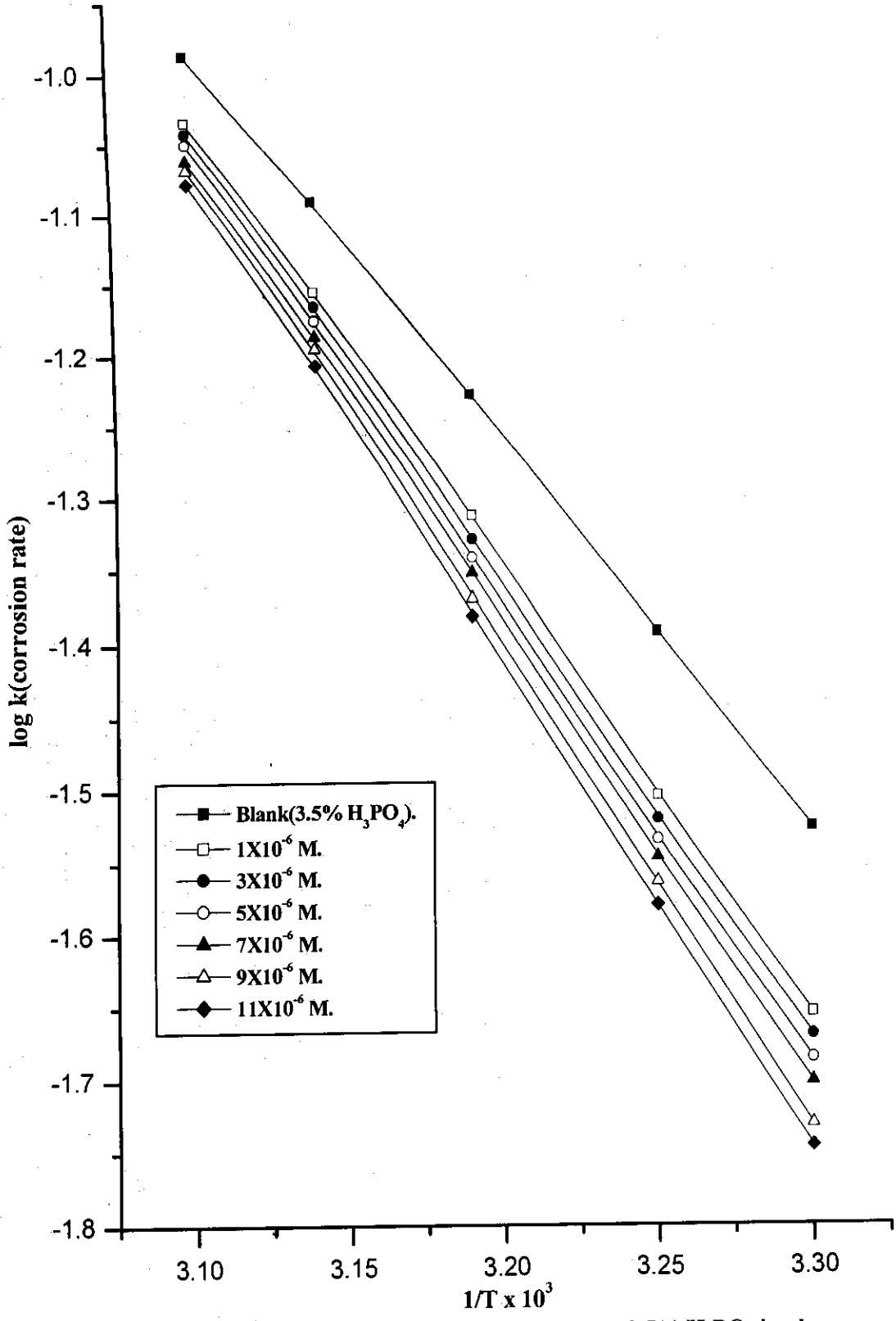


Fig.(3.86) :log k- 1/T curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(1).

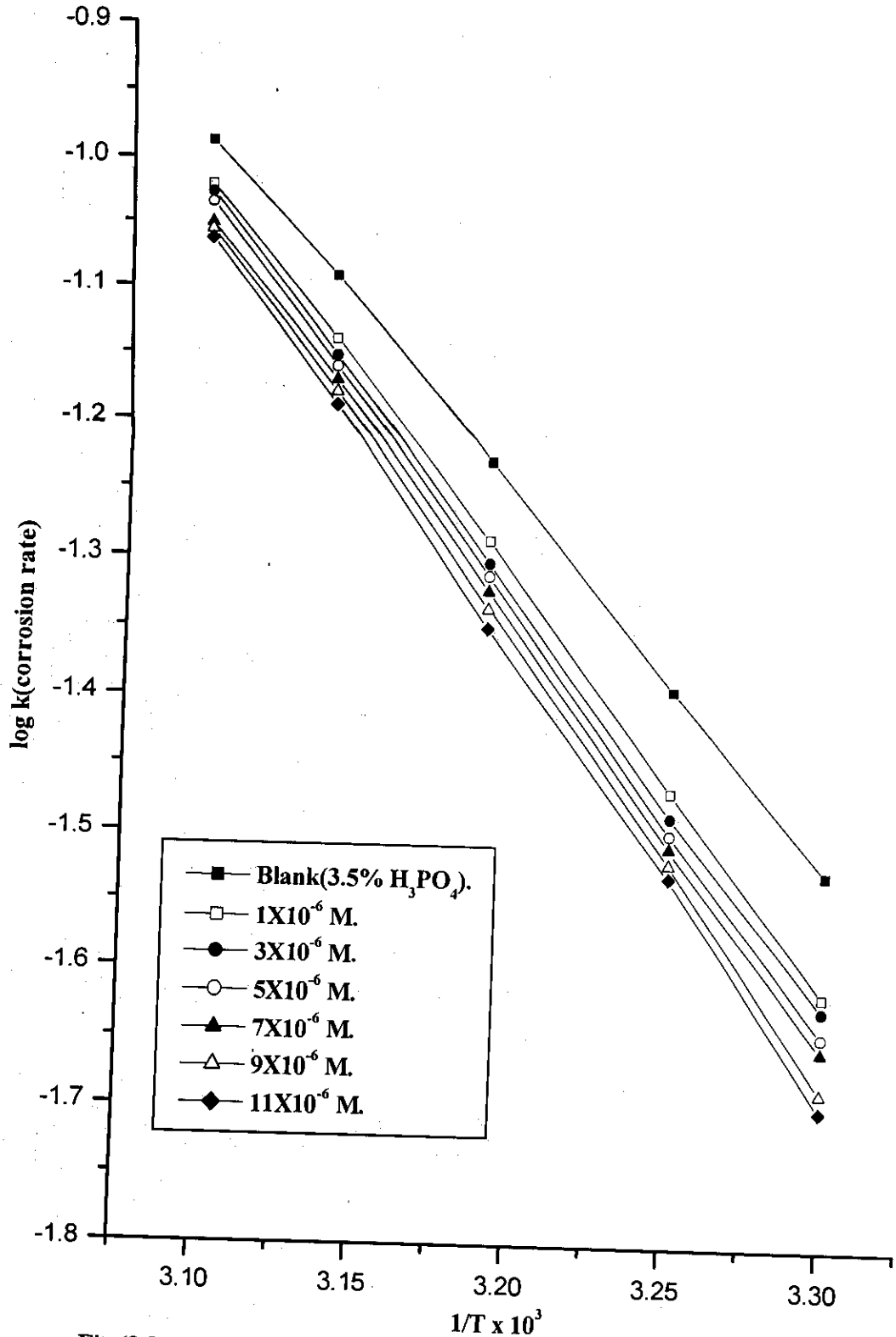


Fig.(3.87) :log k- 1/T curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(2).

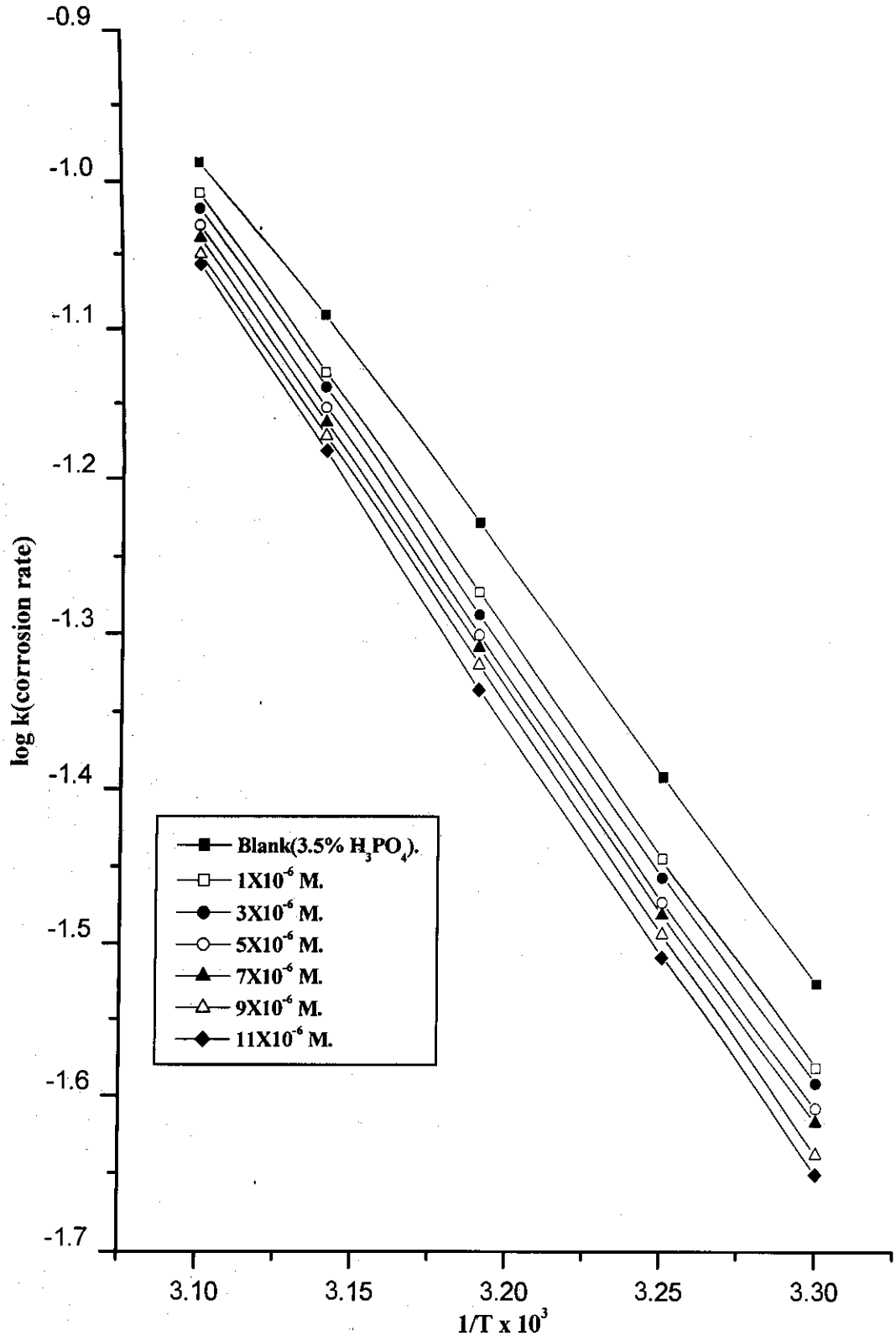


Fig.(3.88) :log k- 1/T curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(3).

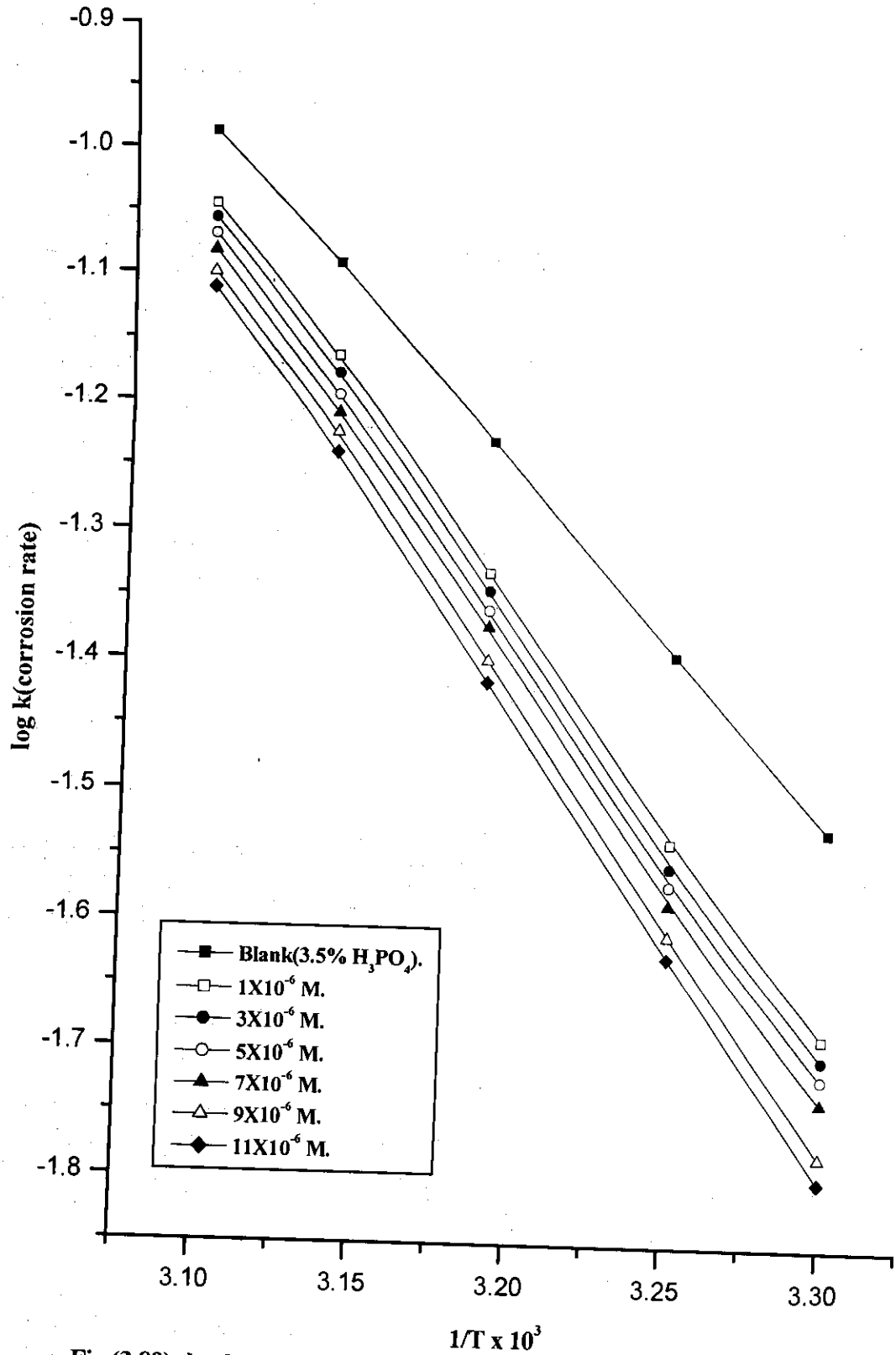


Fig.(3.89) :log k - 1/T curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(I).

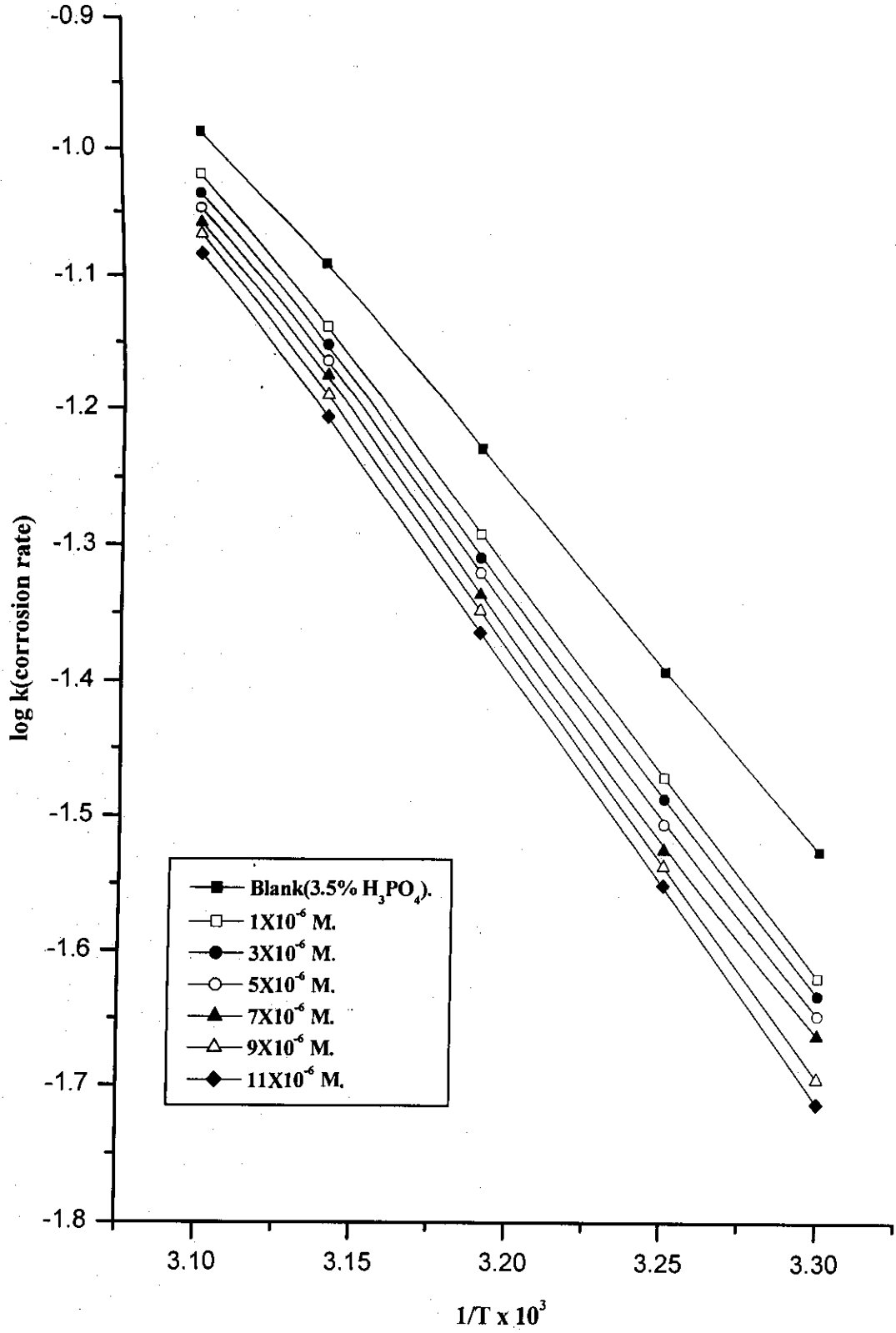


Fig.(3.90) :log k - 1/T curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(II).

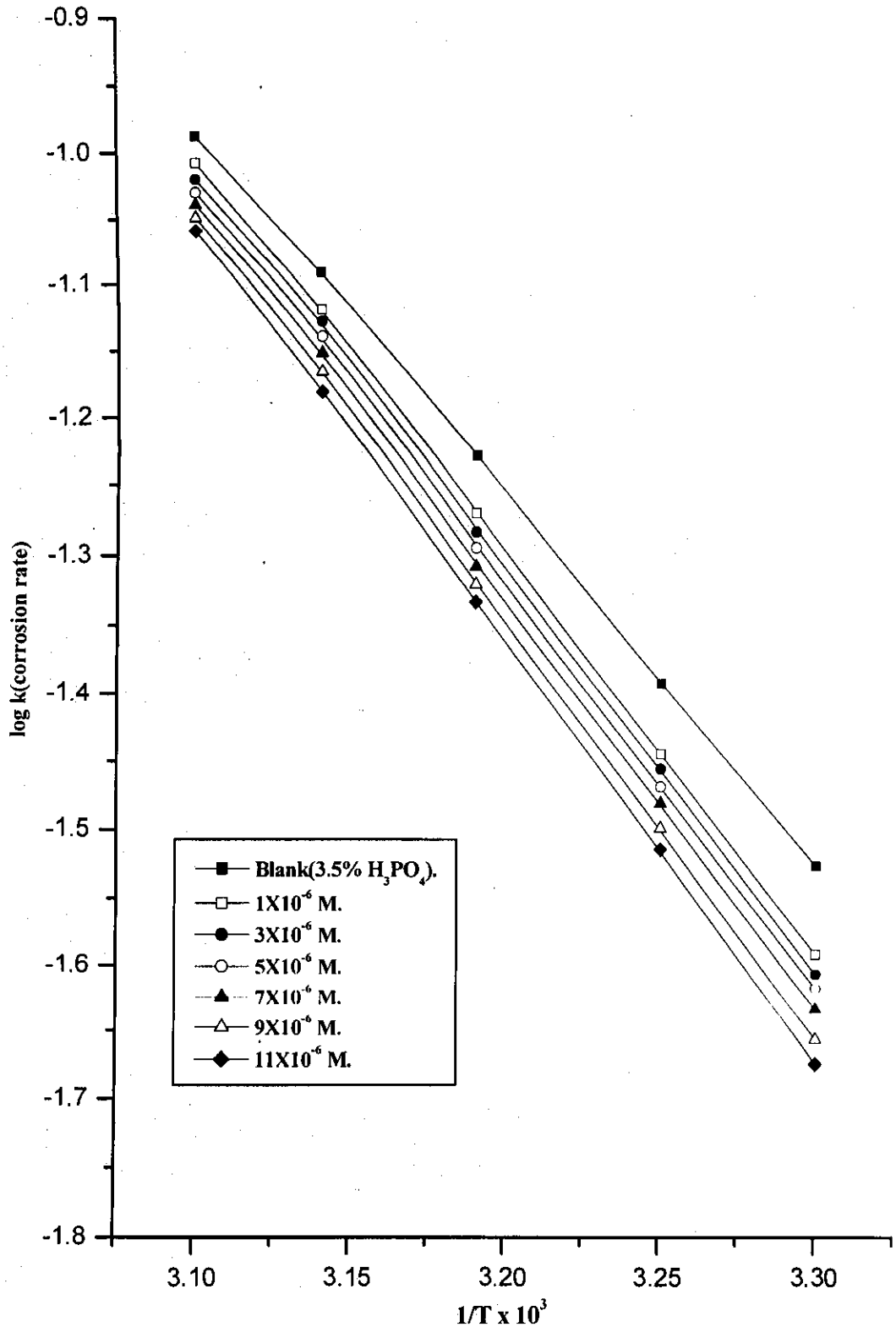


Fig.(3.91) :log k - 1/T curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(III).

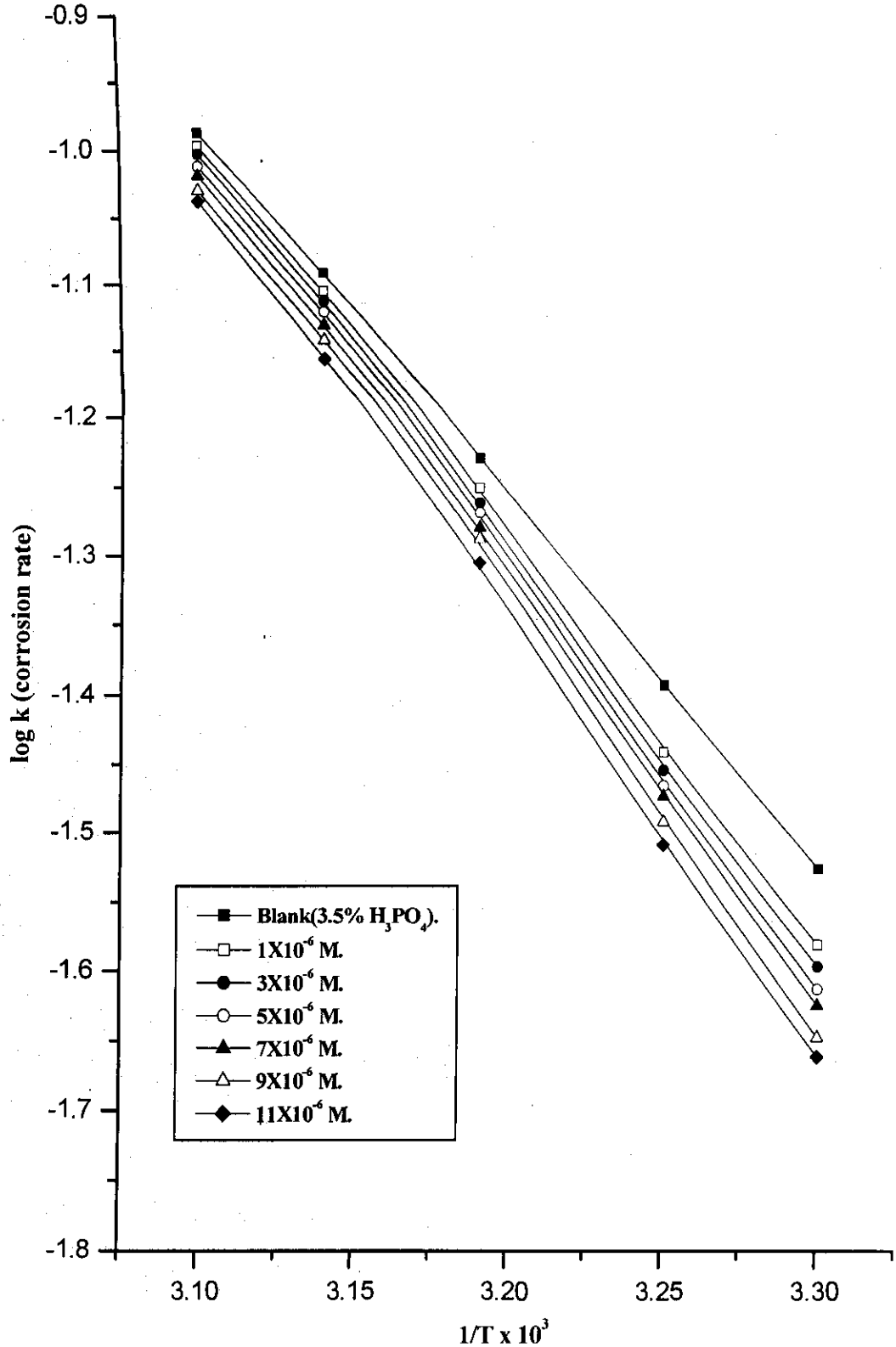


Fig.(3.92) :log k - 1/T curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(IV).

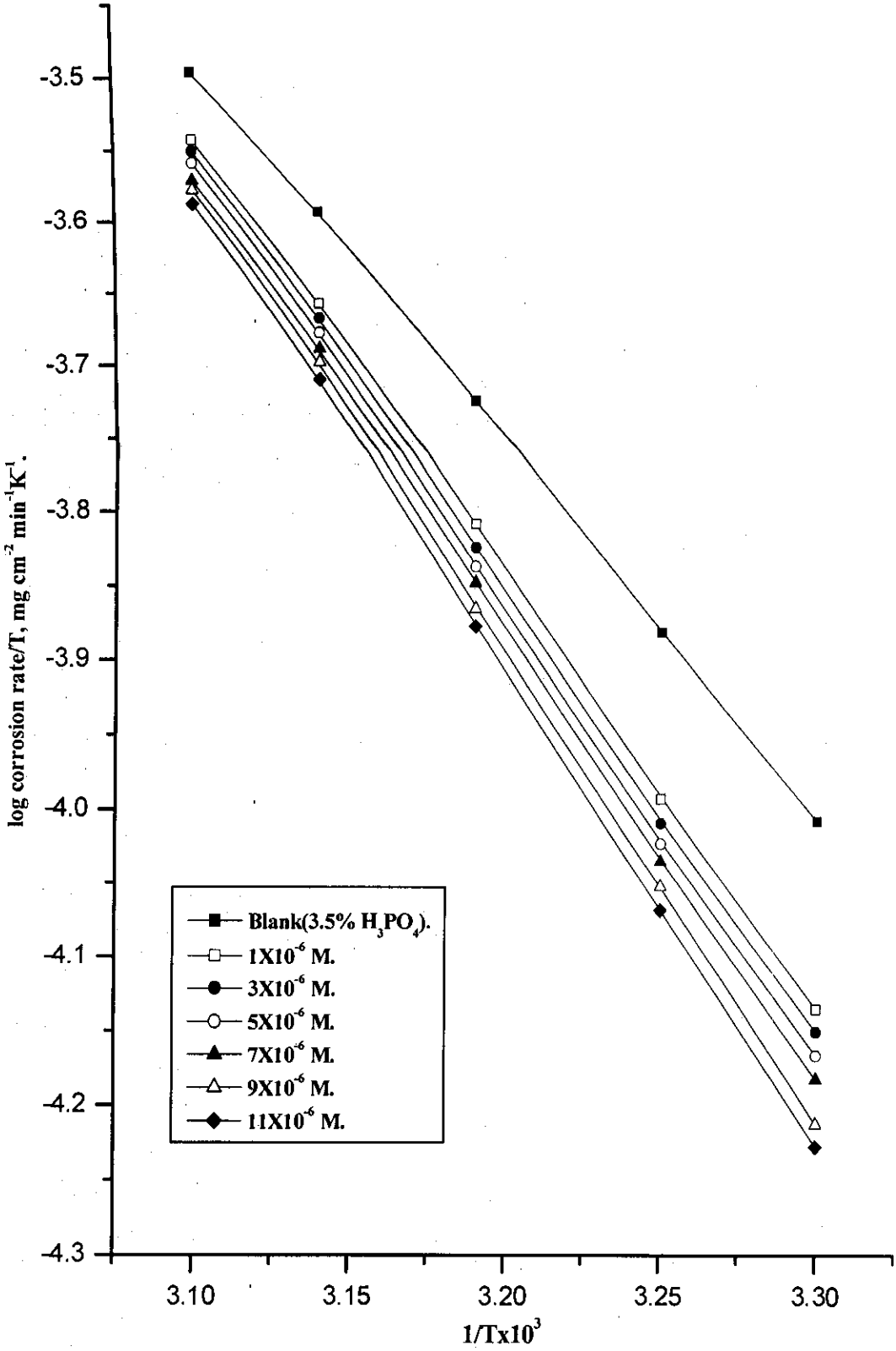


Fig.(3.93) :log (corrosion rate/T) -(1/T) curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(1).

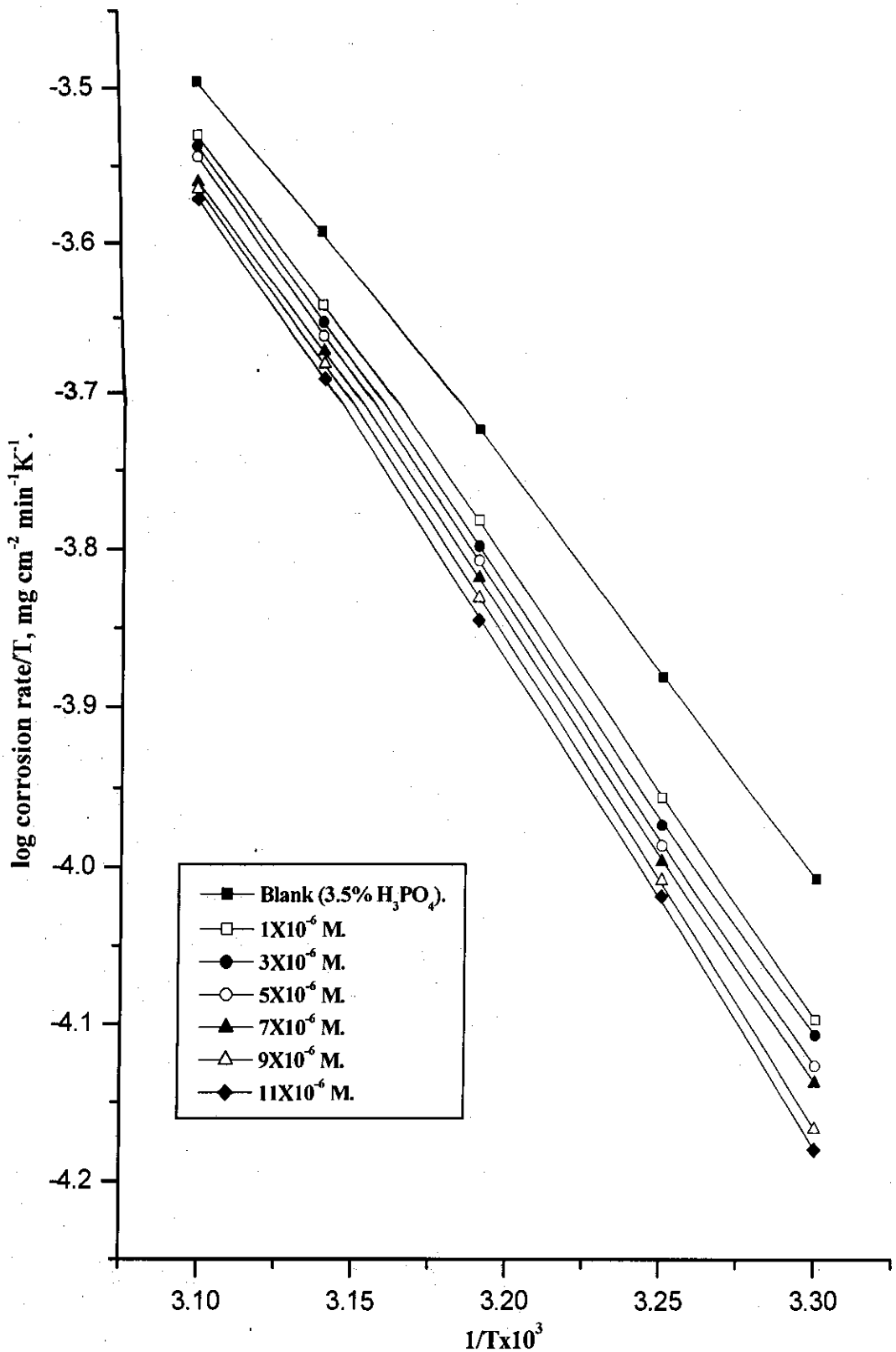


Fig.(3.94) :log (corrosion rate/T) -(1/T) curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(2).

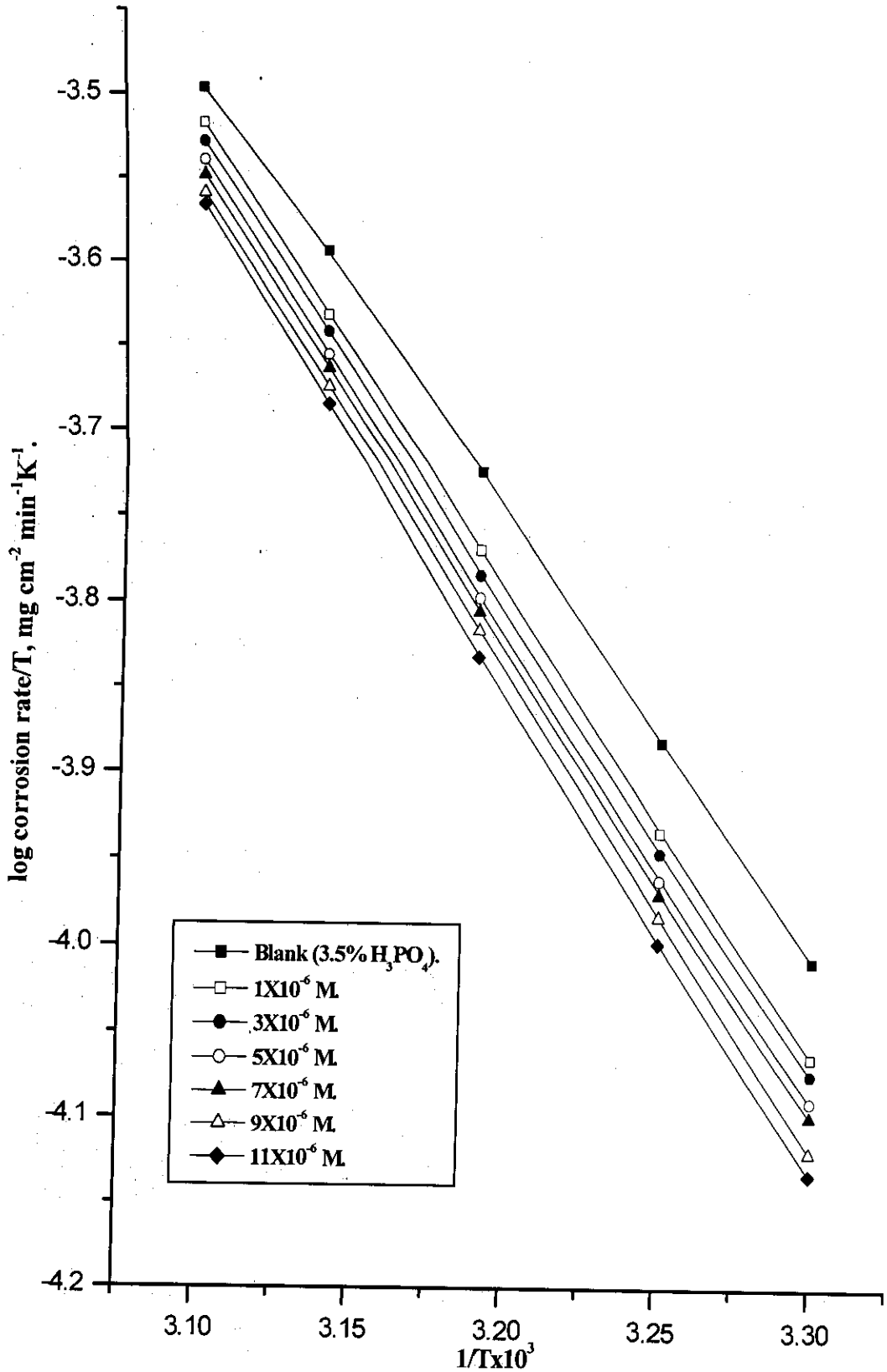


Fig.(3.95) :log (corrosion rate/T) -(1/T) curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(3).

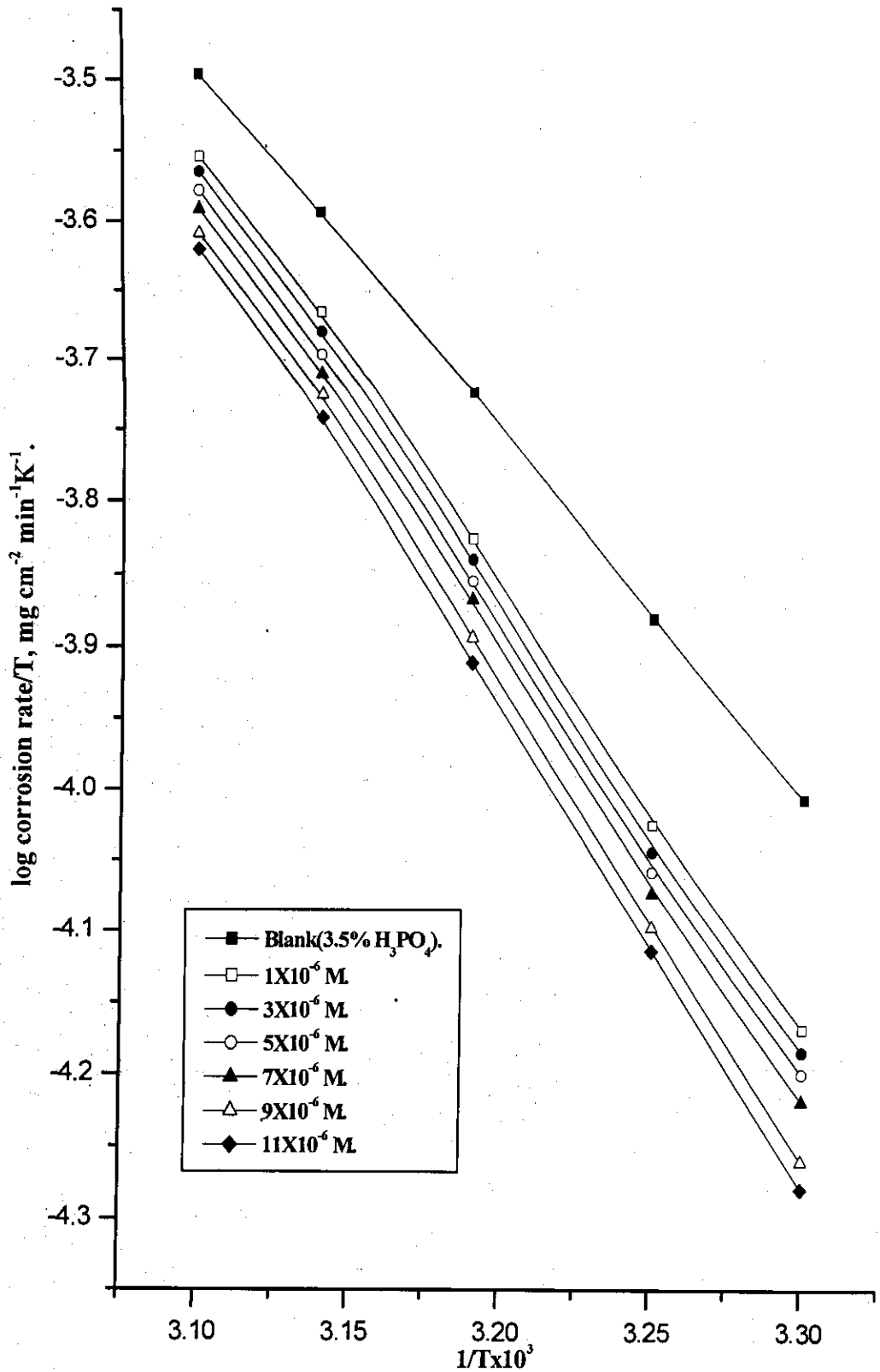


Fig.(3.96) :log (corrosion rate/T) -(1/T) curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(I).

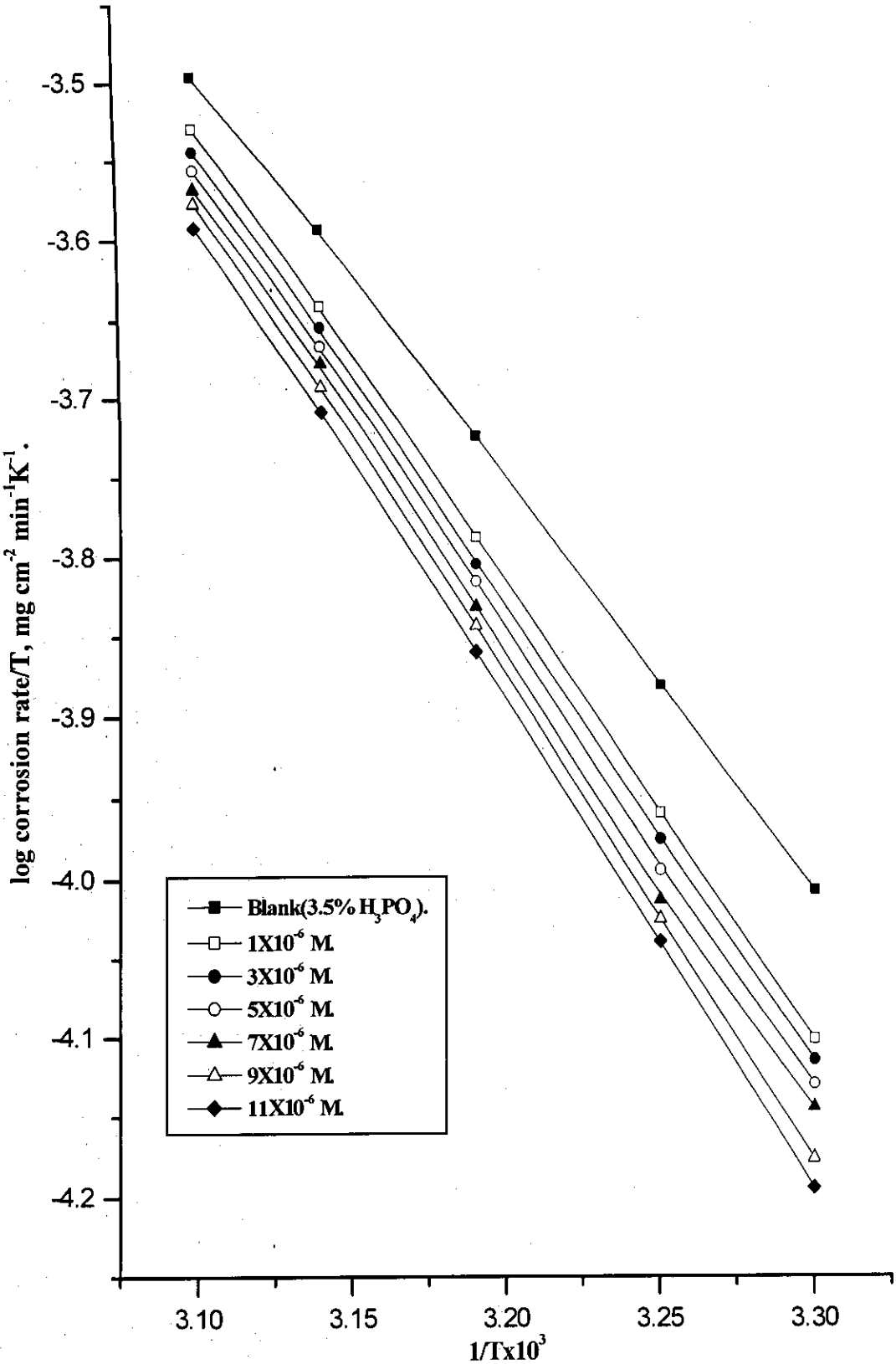


Fig.(3.97) :log (corrosion rate/T) -(1/T) curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(II).

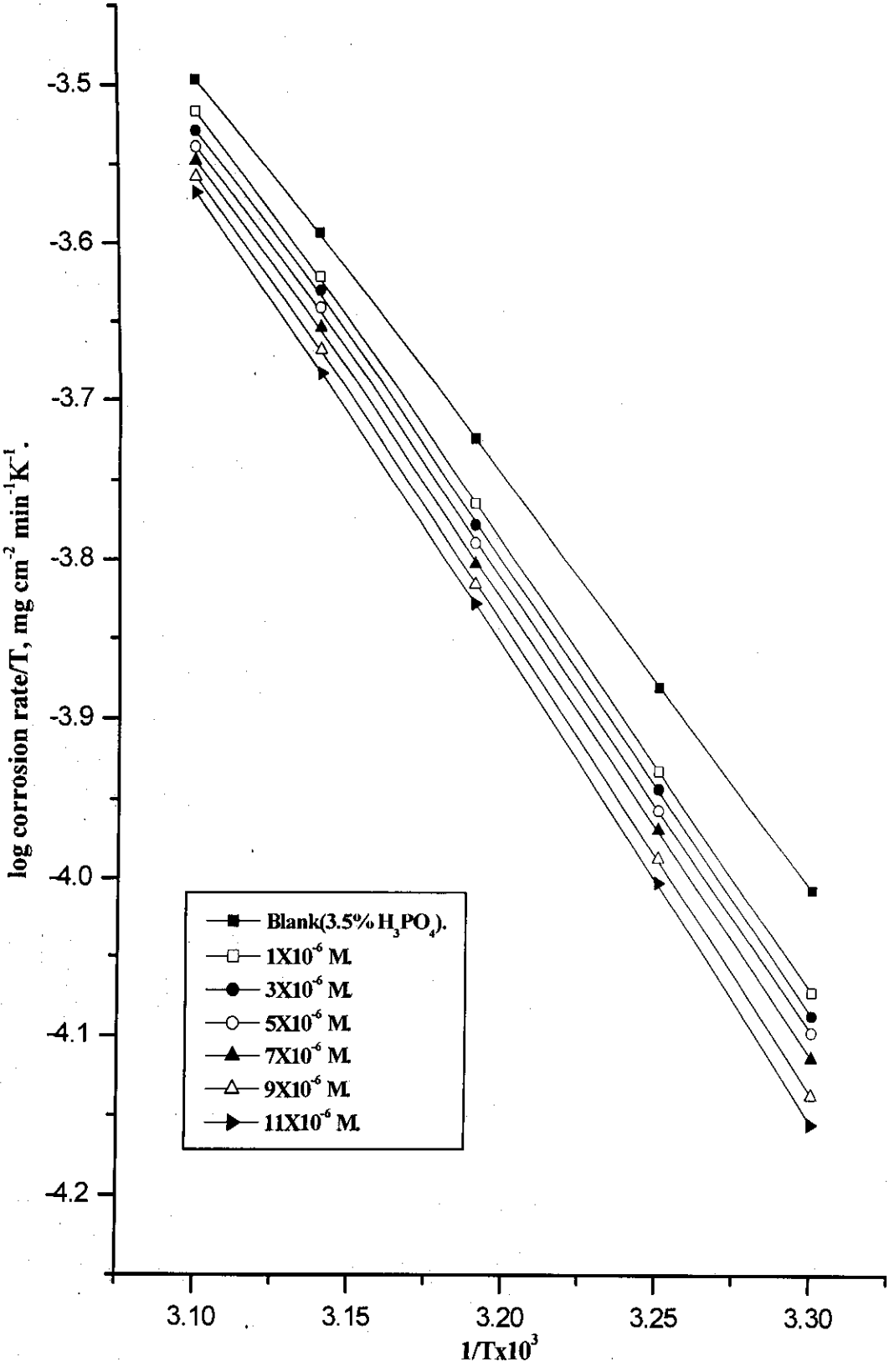


Fig.(3.98) :log (corrosion rate/T) -(1/T) curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(III).

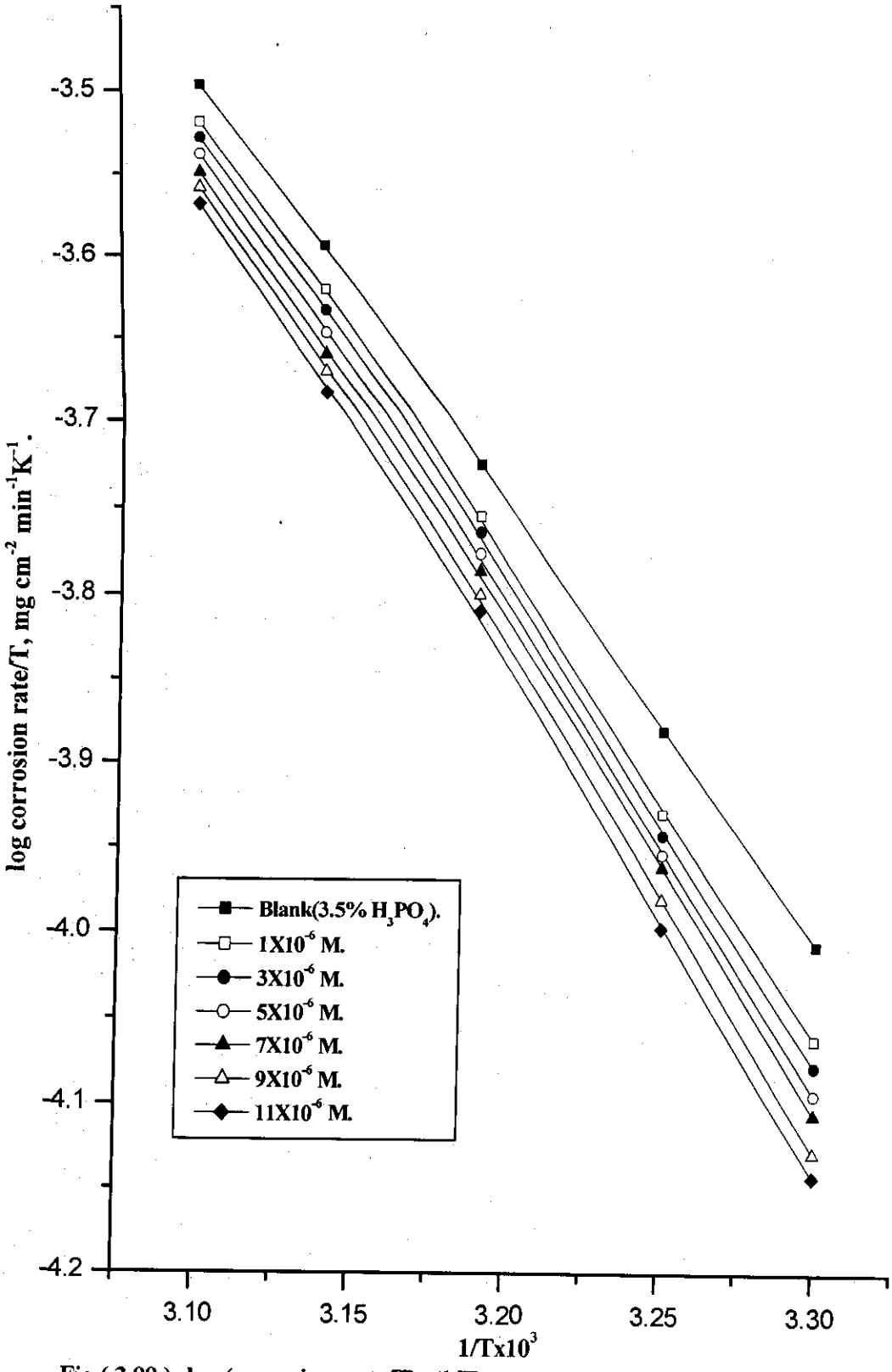


Fig.(3.99) :log (corrosion rate/T) -(1/T) curves for iron dissolusion in 3.5% H_3PO_4 in absence and presence of different concentrations of inhibitor(IV).

Table (3.23): Effect of concentrations of first group compounds on the activation energy of iron dissolution in 3.5% H_3PO_4 .

Concentration M	Activation energy, E_a^*, KJ mol^{-1}		
	(1)	(2)	(3)
0.0	51.8		
$1x10^{-6}$	59.7	57.0	54.2
$3x10^{-6}$	60.4	57.4	54.4
$5x10^{-6}$	61.2	58.5	54.9
$7x10^{-6}$	61.5	58.8	54.9
$9x10^{-6}$	63.6	60.1	56.1
$11x10^{-6}$	64.1	60.5	56.5

Table (3.24): Effect of concentrations of second group compounds on . the activation energy of iron dissolution in 3.5% H_3PO_4

Concentration M	Activation energy, E_a^*, KJ mol^{-1}			
	(I)	(II)	(III)	(IV)
0.0	51. 8			
$1x10^{-6}$	62.3	57.8	56.1	55.0
$3x10^{-6}$	62.9	57.9	56.4	55.5
$5x10^{-6}$	62.9	58.0	56.5	55.9
$7x10^{-6}$	63.4	58.5	57.0	56.0
$9x10^{-6}$	65.8	59.8	58.2	57.7
$11x10^{-6}$	66.6	60.1	58.7	57.9

Table (3.25): Effect of concentrations of first group compounds on the activation enthalpy of iron dissolution in 3.5% H_3PO_4.

Concentration M	Activation enthalpy , ΔH^*, KJ mol^{-1}		
	(1)	(2)	(3)
0.0	49.2		
$1x10^{-6}$	57.1	54.4	52.3
$3x10^{-6}$	57.9	54.8	52.5
$5x10^{-6}$	58.6	55.5	52.8
$7x10^{-6}$	59.0	55.9	52.9
$9x10^{-6}$	61.0	57.5	53.6
$11x10^{-6}$	61.5	57.9	54.2

Table(3.26):Effect of concentrations of second group compounds on the activation enthalpy of iron dissolution in 3.5% H_3PO_4.

Concentration M	Activation enthalpy , ΔH^*, KJ mol^{-1}			
	(I)	(II)	(III)	(IV)
0.0	49.2			
$1x10^{-6}$	59.7	54.9	53.5	52.5
$3x10^{-6}$	60.3	55.2	53.8	53.0
$5x10^{-6}$	60.3	55.4	53.9	53.4
$7x10^{-6}$	60.8	55.9	54.4	53.5
$9x10^{-6}$	63.0	57.5	55.6	54.6
$11x10^{-6}$	63.5	57.7	56.2	55.0

Table (3.27): Effect of concentrations of first group compounds on the activation entropy of iron dissolution in 3.5% H_3PO_4.

Concentration M	Activation entropy , $-\Delta S^*$, KJ mol^{-1}		
	(1)	(2)	(3)
0.0	111.9		
$1x10^{-6}$	88.2	96.5	102.9
$3x10^{-6}$	86.1	95.3	102.7
$5x10^{-6}$	84.0	92.0	101.8
$7x10^{-6}$	83.1	89.8	101.4
$9x10^{-6}$	76.9	87.5	99.5
$11x10^{-6}$	75.4	86.3	97.8

Table (3.28): Effect of concentrations of first group compounds on the activation entropy of iron dissolution in 3.5% H_3PO_4.

Concentration M	Activation entropy , $-\Delta S^*$, KJ mol^{-1}			
	(I)	(II)	(III)	(IV)
0.0	111.9			
$1x10^{-6}$	80.3	94.9	98.9	102.1
$3x10^{-6}$	78.8	94.5	98.3	100.7
$5x10^{-6}$	78.1	93.9	98.0	99.7
$7x10^{-6}$	77.7	92.5	96.6	97.7
$9x10^{-6}$	71.2	87.6	93.3	96.3
$11x10^{-6}$	69.8	87.5	91.7	95.1