PART II

DISCUSSION

Chapter3

Part II

Discussion

(A) The role of microstructure in corrosion behavior

Some pipes, which used in sanitary pipelines, are manufactured from reinforced concrete. In industrial area, wasters in these sanitary may be acidic in its effect. Then it absorbed and penetrate of the concrete layer to attack steel of reinforcement of concrete through the corrosion phenomena.

The famous method which used to protect these pipelines against corrosion is one in which the inhibitor mixed with fresh concrete during the process of manufacturing these pipelines.

In this study, the corrosion behavior of C.V.steel, L and M were studied in different concentration of HNO_3 as acidic media. Also, the effect of heat treatment on the above two samples were studied. There are three different methods of regimes, which are carried out, for the two samples under study. Therefore, we have four samples for L.C.V.steel (one as cast and the other three are heat treated). Also, we have four samples for M.C.V.steel.

The effect of HEAA, as inhibitor for the corrosion process, was studied for all specimens. The reflects that the HEAA regard as a good inhibitor for corrosion processes due to acidic media.

- Effect of heat treatment on mechanical properties and microstructure of vanadium steel

Two types of vanadium steel were selected for the present study. L and M.C.V.steel. Carbon is present in L and M vanadium steel as iron carbide and vanadium carbide in pearlitic phase lamina.

a) Microstructure of as-received (without heat treatment samples)

Microstructure of as-received L and M.C.V.steel samples was examined using optical microscope. Both polished and etched samples were examined. The micrographs of these samples are given in Fig(144-151). It is clear that the as-received L.C.V.steel (LA) consist wide ferritic area, and small one of pearlite as shown in Fig(144).

The as-received M.C.V.steel (MA) consist small area of ferrite, and wide one of pearlite in Fig(145). Ferrite phase is relatively pure bcc iron as shown in Fig.(7), while pearlite phase consist of alternate plates or lamellar structure (see Fig.8) of ferrite and cementite (carbide) which has formula, Fe_3C (see Fig.6).

b) Microstructure of heat treated samples

According to the method of heat treatment, which described in details in experimental section of this work, and the following samples are result of heat treatment of tow types of steel:

i) Normalized L.C.V.steel sample (LN)

Pearlite was transferred by normalizing regime to fine shape in ferritic matrix in small quantity as shown in Fig(146).

ii) Spheroidized L.C.V.steel sample (LS)

Cementite in pearlite was transferred to spherical ,particles in ferritic matrix by spheroidizing regime as shown in Fig(147).

iii) Quenched L.C.V.steel sample (LQ)

Matrix was transferred to martensitic one by used hardening regime as shown in Fig(148).

iv) Normalized M.C.V.steel sample (MN)

Pearlite was transferred to large quantity of fine pearlite which distributed in ferritic matrix, as shown in Fig(149).

v) Spheroidized M.C.V.steel sample (MS)

Cementite in pearlite was transferred to spherical ,particles in ferritic matrix as a large quantity, that is as shown in Fig(150).

vi) Quenched M.C.V.steel sample (MQ)

Martensite was produced by hardening regime as a large quantity, these is as shown in Fig(151).

Fig(144): Microstructure of as-received L.C.V.steel specimen with 2% nital.

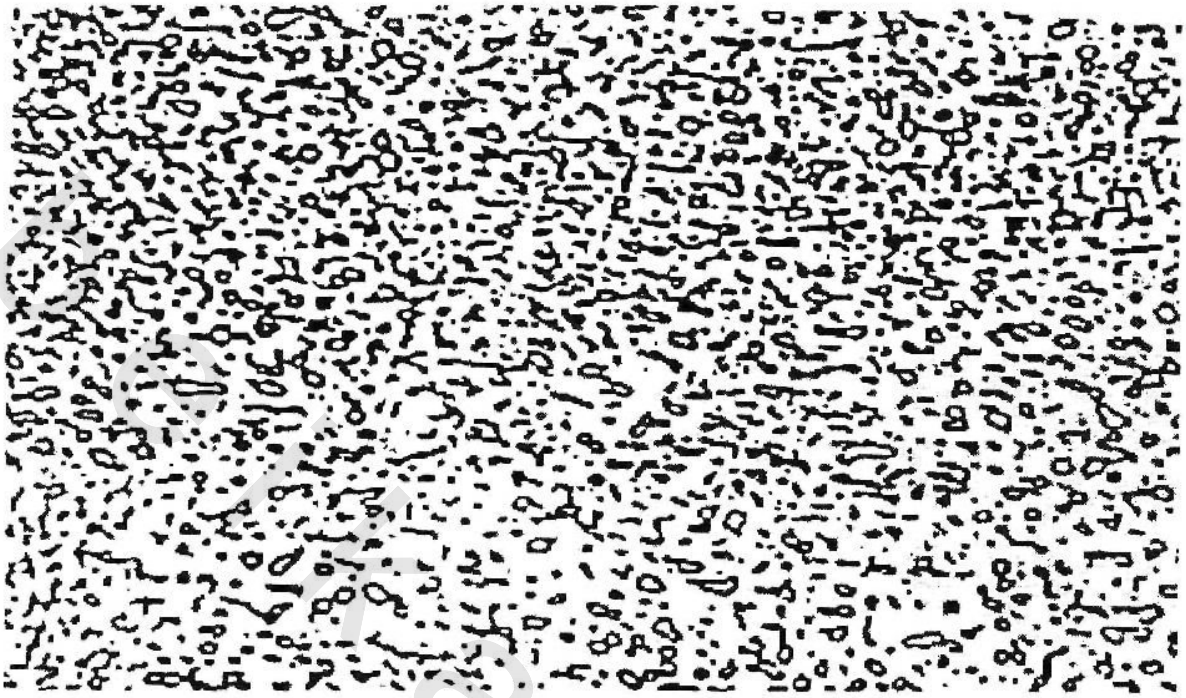
Fig(145): Microstructure of as-received M.C.V.steel specimen with 2% nital.

Fig(146): Microstructure of normalized L.C.V.steel specimen with 2% nital.

Fig(147): Microstructure of spheroidized L.C.V.steel specimen with 2% nital.

Fig(148): Microstructure of quenched L.C.V.steel specimen with 2% nital.

Fig(149): Microstructure of normalized M.C.V.steel specimen with 2% nital.



Fig(150):Microstructure of spheroidized M.C.V.steel specimen with 2% nital.

Fig(151): Microstructure of quenched M.C.V.steel specimen with 2% nital.

(B) Effect of concentration of HNO_3 on corrosion behavior

The corrosion behavior of all carbon vanadium (C.V) steel samples has been studied at 25,35,45 and 55 °C in 0.1,0.3 and 0.5 M HNO_3.

Inspection of the corrosion rate data in Tables (2-17), it is obvious that the corrosion rate increases as the concentration of HNO_3 increased i.e. in the order 0.1<0.3<0.5 M HNO_3 for all samples under study at different temperature. Such behavior can be discussed in view of increasing the hydrogen ion concentration (i.e. the cathodic. reactant) which accelerate the corrosion process.

(C) Effect of temperature on the corrosion behavior

The corrosion rate data in Tables(2-17) indicate that the rate of corrosion increases with increasing the temperature in the following order:
25°C < 35°C < 45°C < 55°C for all samples, indicating that the corrosion rate stimulated with increasing the temperature. The corrosion rate will increase with temperature as a result of decreasing the apparent activation energy E* of the charge transfer reaction(29-37):

Oxidation (anodic reaction): $Fe \longrightarrow Fe^{+2} + 2e$
Reduction (cathodic reaction): $2H^+ + 2e \longrightarrow H_2$

The increase in temperature will enhance the rate of H^+ diffusion to the metal surface as well as ionic mobility. At lower temperature, the adsorbed hydrogen atoms block the cathodic area, while the increase in the solution temperature causes desorption of hydrogen. Such hydrogen desorption leading to the increase of cathodic area and consequently increase the corrosion rate.

(D) Corrosion rate of low carbon vanadium steel samples

The corrosion rates were calculated for the studied samples in absence and presence 0f N,N dihydroxy ethyl acryl amide (HEAA)as anew inhibitor(117) in the corrosion media under the studied condition .

1- The Corrosion rate without inhibitor

From Tables(2-5), its obvious that the rate of corrosion decreases according the following order:

At 25 °C	$LA > LQ \geq LS \geq LN$
At 35 °C	$LA \geq LQ \geq LN \geq LS$
At 45 °C	$LA \geq LN \geq LQ \geq LS$
At 55 °C	$LA \geq LQ > LN > LS$

In general, it was found that the most predominant behavior for L.C.V. steel samples in the order:

$$LA > LQ > LN > LS$$

This order indicate that any heat treatment regime carried out in this study on L.C.V. steel samples increases the corrosion resistance.

2- The Corrosion rate in presence of HEAA (as an inhibitor)

The electrochemical method viz. polarization method used to study the inhibitory properties of HEAA on the corrosion behavior of LA, LN, LS, LQ, MA. MN, MS and MQ samples in 0.1 M HNO_3 solution in at five concentration (2, 4, 6, 8, 10) x10^{-5}M of HEAA.

Tables(6-9) represent the corrosion rates of L.C.V steel samples in 0.1 M HNO_3 in presence of different concentration of HEAA as a new corrosion inhibitor(117) .The corrosion rate in this case decreases in the following order:

At 25 ^{o}C LA > LQ > LS ≥ LN
At 35 ^{o}C LA > LQ > LN > LS
At 45 ^{o}C LQ ≥ LA > LN > LS
At 55 ^{o}C LN ≥ LA > LS > LQ

Although the high temperature(45 and 55 ^{o}C)have a sharp role in the corrosion of LQ and LN samples, respectively but it is possible to say that the most predominant order is:

LA>LQ>LN>LS

Another time, the heat treatment regime of L.C.V. steel samples decreases the rate of corrosion. These data show that the corrosion rate is inversely proportional with the concentration of HEAA indicating the inhibition of this new corrosion inhibitor.

(E) Corrosion rate of medium carbon vanadium steel samples

1- Corrosion rate in absence of HEAA inhibitor

The corrosion rates in Tables (10-13) at different concentration of HNO_3 (0.1,0.3, 0.5M) and at different temperatures (25,35,45 and 55 ^{o}C) can be ordered as follows:

At 25 ^{o}C MA > MQ > MN > MS
At 35 ^{o}C MA > MS > MN > MQ
At 45 ^{o}C MQ > MA > MS > MN
At 55 ^{o}C MQ > MA > MN > MS

The above behavior indicating that the corrosion rate of M.C.V. steel samples decreases in most predominant order as follow:

MA ≥ MQ > MN > MS

Here again, as mentioned in L.C.V. steel samples, that heat treatment of M.C.V.steel samples cause some inhibition for the corrosion processes.

2- Corrosion rate in presence of HEAA as an inhibitor

The corrosion rate of M.C.V.steel samples in 0.1 M HNO_3 in presence of different concentration of HEAA as an inhibitor were .tabulated in Tables(14-17). These data can be summarized in the following decreases:

At 25 °C MA > MQ ≥ MS ≥ MN
At 35 °C MA > MN ≥ MS ≥ MQ
At 45 °C MA ≥ MQ ≥ MN ≥ MS
At 55 °C MN > MA ≥ MQ ≥ MS

The above behavior illustrate that the corrosion rate for M.C.V.steel samples is decreased generally as follow:

MA > MQ > MS < MN

In general, all the previous corrosion rate data for L.C.V. and M.C.V. steel samples whether in absence or presence of HEAA as inhibitor show that the most predominant order in the corrosion rate decreases as follows:

A > Q > N > S

(with exception at 45 and 55 °C)

In the light of this general order, it was assure that any heat treatment regime alike the employed in these study resist in it selves the corrosion processes.

It worth-note that the corrosion rate of L.C.V.steel samples were much more higher than for M.C.V.steel samples whether in presence or absence of the inhibitor (with exception of very few cases at 45 and 55 °C) Then, in other word, one can say that M.C.V.steel resists the corrosion more than L.C.V.steel. This is may be interpreted from the lower percentage of ferrite phase in M.C.V.steel than that for L.C.V.steel.

(F) Inhibition efficiency of HEAA

The inhibition efficiency(P%) can be calculated from the following equation(117-118):

$$P\% = (r - r^{\cdot})/r \times 100$$

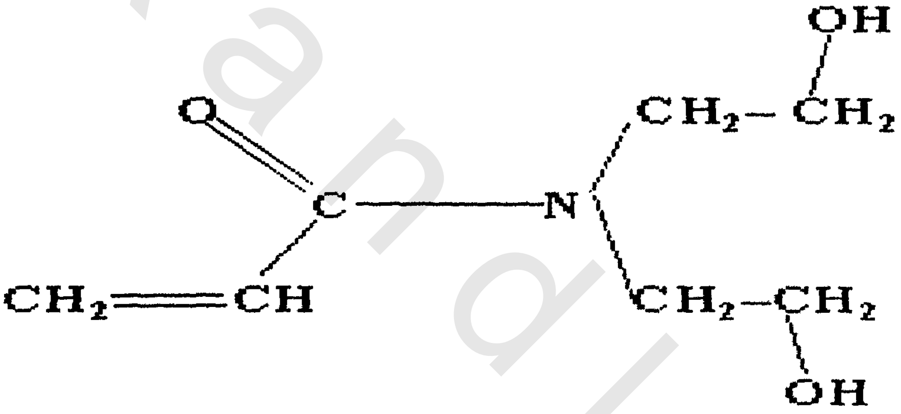
Where r and $r^{\cdot}$ are the corrosion rate in absence and presence of inhibitor.

Inspection the inhibition efficiency data in tables(18-25), it is obvious that this inhibition efficiency for all samples under study increases with increasing HEAA with concentration in the following order:

$$10^{-4} > 8x10^{-5} > 6x10^{-5} > 4x10^{-5} > 2x10^{-5} \text{ M HEAA}$$

Due to the adsorption of a more number of inhibitor molecules on the metal surface.

The study of N,Ndihydroxy ethyl acryl amide(HEAA) as a corrosion inhibitor is of significant interest because of its structure:



N,Ndihydroxy ethyl acryl amide(HEAA)

This organic structure has all the advantage of the efficiency inhibitor such as unsaturated bond, C=O group, nitrogen atom and tow alcoholic groups(117). These characteristic group of the inhibitor as well as the large molecule of this organic compound increase the property of adsorption and the surface coverage(117).

On the other hand the inhibition efficiency can be studied from both metal microstructure and temperature change point of view.

According to Tables(18-25), The higher inhibition efficiency was observed mostly in quenched heat treated. Then it was concluded that the martensitic surfaces (of L.C.V. or M.C.V.steel samples) are the best suitable surface using HEAA as inhibitor in 0.1 M HNO_3.In general, the inhibition efficiency decreases by increasing temperature in case of 25,45, and 55 ^{o}C

(taking account an abnormal of inhibition efficiency at 35 °C which has a lower values than those at the other temperature). This above behavior indicates that the inhibitor HEAA molecules controlled by inhibition mechanism and can be described as complex formation on the metal surface , but at high temperature(45, 55°C) this complex is decomposition.

Figures(152-159)represent the plot of the inhibition efficiency(P%) versus logarithm of concentration of HEAA (log [I]) in 0.1 M HNO_3 for all samples under study .

It is obvious that inhibition efficiency increases with increasing concentration of HEAA. These Figures exhibit a single S shape for all obtained curves. This means that the formation of one layer from HEAA molecules over the metal surfaces in all cases under study (where the number of S shapes is the best indication for the number of adsorbed layers the inhibition molecules).

(G)Activation energy (E*)(117-118).

The activation energy E* for the corrosion of eight C.V.steel samples under study in 0.1 M HNO_3 solution in absence and presence of different concentration of HEAA were calculated from Arrheniuse.equation(117-118):

$$\ln r = \ln A - E^*/RT \qquad (22)$$

where r = corrosion rate
A = Arrheniuse pre exponential factor
R = ideal gas constant
T = absolute temperature.
Plotting ln r vs. 1/T and E* would be deduced from slope =-E*/2.303R.

Values of E*for all samples in presence and absence of different concentrations of HEAA as cited in Tables (38-47). Indicating that:

1-In case of L.C.V.steel samples the activation energy values of the normalizing samples in presence and absence of the inhibitor are higher than those of the other samples. Also, the activation energy values of the normalizing sample in presence of the inhibitor are higher than those in absence of the inhibitor.

2-In case of M.C.V.steel samples, the activation energy values of the quenched sample is higher than those for other samples in absence of the inhibitor . While in case of presence of the inhibitor the activation energy values of the normalizing sample are higher than those of the other samples.

This attributed to that these heat treatments for these samples may be increase the energy barrier of the activation processes.

(H) Application of the thermodynamic models

Three models of surface chemistry were used to investigate corrosion inhibition mechanism of HEAA adsorption on the metal surfaces.

The above models which used in this work are Langmuir, Frumkin and El-Awady isotherm (119) .

Molecules of HEAA inhibit the corrosion process by adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitutional process in which an inhibitor molecule in the aqueous phase substitutes an (x) number of water molecules adsorbed on the metal surface as in the following equation(120):

$$I_{eq} + xH_2O_s \longrightarrow I_s + xH_2O_{eq}$$

Where (x) is know as the size ratio and simply equal to 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 and temperature.

1- Langmuir Isotherm(119)

Langmuir's equation is can be written as follows:

$$\theta/1-\theta = K[I]$$

Where K is equilibrium constant of the adsorption reaction,

[I] is concentration of HEAA in the bulk of the solution,

θ is the surface coverage, which can be calculated from the following equation(119):

$$\theta = 1 - (r^{'}/r)$$

Where $r^{\cdot}$ and r are the corrosion rate in the presence and absence of inhibitor respectively. K's values can be obtained by plotting $\theta/1-\theta$ against [I], and the are showing Figures (160-167), and data registered in Tables (38-47). All curves of Langmuir are straight lines, indicating to validity applying Langmuir model. Thermodynamic parameters of adsorption process were calculated from the following equation$^{(121)}$:

$$\Delta G^{\circ} = -2.303\ RT \log K \qquad (24)$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \qquad (25)$$

Where ΔG°, ΔH° and ΔS° are stander free energy, enthalpy and entropy changes respectively. Data of thermodynamic parameters using Langmuir model were collected in the Tables (42,47), . It is obviously described to obtain the standard enthalpy (ΔH°) by the study of the binding constant (K) over temperature range by applying a linear-least squares analysis according to the Van't Hoff's isochore$^{(121)}$.

$$\frac{d\,(\ln K)}{d\,(T^{-1})} = \frac{-\Delta H^{\circ}}{R} \qquad (26)$$

or

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S^{\circ}}{R} \qquad (27)$$

Where the values of log K are plotted versus T^{-1} giving a straight line with slope equal to ($-\Delta H^{\circ}/2.303\ R$)$^{(121)}$. Hence, the standard enthalpy changes ΔH° can be evaluated.

All ΔG° values for all samples under study are negative at different temperature indicating to spontaneously of adsorption process$^{(122)}$. But ΔH° values for all samples under study are positive referring to endothermicity of the adsorption processes. This behavior supported by the binding constant values which increases as the temperature increases indicating that the adsorption processes are endothermic ones which agree with the positive values of the standard enthalpy changes, ΔH°, as cited in Tables(38-47). Also, the spontaneity increases with increasing temperature as a result of the increasing the negativity ΔG° with increasing the temperature. The positive values of ΔS° indicate that these adsorption processes are entropy favored processes, where the positive ΔS° values are applicable with the negative ΔG°. This results indicate that the adsorption processes are mixed (physical and chemical) adsorption.

2-Frumkin isotherm(120)

The second thermo dynamic model is Frumkin's equation which could be written as follows(119):

$$\ln\{ \theta/1- \theta [I]\} = \ln K + 2a\, \theta$$

Where "a" = Lateral inter action term between adsorbed molecules describing the interaction in the adsorbed area and the measurement of steepness of the adsorption. Other terms in the equation are as mentioned above.

Data of applying Frumkin equation are recorded in Tables(48-57). Most values of "a" are negative values or less than unity indicating a weak adsorption of HEAA molecules except in few cases, the values of "a" near or more than unity indicating strong adsorption of HEAA molecules in such few cases(120): As shown in Figures(168-176), A plot of $\ln\{ \theta/(1- \theta) [I]\}$ against θ gives a curvature relationship (not a straight line) indicating to Invalidity of Frumkin model. In this case, the values of K as well as (a) were calculated by using least square fit. Then, thermodynamic parameters of adsorption processes were calculated and reported in Tables(52,57). All ΔG° values are negative denoting that adsorption process proceeds spontaneously. In case of L.C.V.steel samples, all ΔH° values have negative values indicating to exothermcity of the adsorption processes of HEAA molecules, the negative values of ΔS° in this case indicating that these adsorption processes were enthalpy favored processes(121). Similar were observed in case of M.C.V.steel samples of MN and MS, while in case of MA and MQ samples the adsorption processes were entropy favored processes where ΔS° and ΔH° have a positive values. In these cases the adsorption processes for all samples are mixed (physical and chemical) adsorption.

3-El-Awady isotherm(119)

El-Awady equation was modified to the following one(119):

$$\log \theta/(1-\theta) = x \log K + 1/x \log [I]$$

Where "x" = Number of sites on the metal surface which can be replaced by one molecule of the inhibitor. Data of "x" and binding constant values (K) were collected in Tables(58-67), which contain "x" values are near or more than unity indicating a strong adsorption of inhibitor molecules on the metal surface. Straight lines of plotting log $\theta/(1-\theta)$ against log [I] in Figures(176-183)are indicating the validity of modified El-Awady isotherm. All ΔG° values are negative indicating to spontaneously of adsorption processes. ΔH° values are positive in most cases indicating to endothermicity of the adsorption processes, while negative in case of MS sample duo to exothermic nature of this adsorption process. Also, the K values increase as the temperature increases in most cases indicating that the adsorption processes are endothermic ones which agree with the positive values of the standard enthalpy changes, ΔH°, as reported in Tables (62,67).

The positive ΔS° values indicate the disordered adsorption processes of HEAA molecules over the metal surfaces. These positive values of ΔS° applicable with the negative ΔG° values indicate that the adsorption processes in these cases are entropy favored processes.

From values of K, ΔH°, ΔS° its obvious that the adsorption processes are mixed (physical and chemical) adsorption.

On comparison of the present data of the three models, it is obvious from Figures (160-167) and (176-183) the validity of the Langmuir isotherm and El-Awady isotherm due to their obtained straight lines, while the application of Frumkin thermodynamic model yields a curvature isotherm(119). This curvature isotherm as well as the negative "a" values indicating the invalidity of the Frumkin model if compared with Langmuir isotherm and El-Awady isotherm (119).

Although there is very good agreement between Langmuir isotherm and El-Awady model in the thermodynamic parameters and the binding constant behavior. It was conclude that the best applied thermodynamic model for the adsorption of HEAA molecules on various surface of the studied metal is Langmuir adsorption isotherm(119).

This final conclusion due to the excellent obtained straight line in application of Langmuir isotherm than that obtained from El-Awady isotherm as well as the ”x“ values were less than unity in some cases.

Table(18): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for as cast L.C.V. steel sample at various temperatures.

t °C	[I]x10^5 M	-log[I]	Efficiency %
25	2	4.69	35.04
	4	4.39	36.52
	6	4.22	38.83
	8	4.09	45.78
	10	4.00	48.83
35	2	4.69	14.98
	4	4.39	17.06
	6	4.22	23.35
	8	4.09	27.77
	10	4.00	31.70
45	2	4.69	14.20
	4	4.39	16.61
	6	4.22	24.89
	8	4.09	43.22
	10	4.00	48.58
55	2	4.69	3.24
	4	4.39	10.26
	6	4.22	24.96
	8	4.09	32.26
	10	4.00	34.59

Table(19): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for Normalized L.C.V. steel sample at various temperatures.

t °C	[I]x10^5 M	-log[I]	Efficiency %
25	2	4.69	31.82
	4	4.39	35.07
	6	4.22	42.50
	8	4.09	44.27
	10	4.00	47.61
35	2	4.69	18.17
	4	4.39	23.55
	6	4.22	28.31
	8	4.09	31.66
	10	4.00	41.59
45	2	4.69	10.57
	4	4.39	15.84
	6	4.22	34.51
	8	4.09	41.58
	10	4.00	42.53
55	2	4.69	16.90
	4	4.39	23.26
	6	4.22	26.00
	8	4.09	35.39
	10	4.00	38.13

Table(20): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for Spheroidized L.C.V. steel sample at various temperatures.

t °C	[I]x10^5 M	-log[I]	Efficiency %
25	2	4.69	37.82
	4	4.39	40.45
	6	4.22	43.43
	8	4.09	45.07
	10	4.00	47.98
35	2	4.69	5.58
	4	4.39	13.80
	6	4.22	18.16
	8	4.09	22.93
	10	4.00	27.32
45	2	4.69	28.85
	4	4.39	32.45
	6	4.22	34.44
	8	4.09	38.75
	10	4.00	39.70
55	2	4.69	1.97
	4	4.39	18.48
	6	4.22	29.49
	8	4.09	31.25
	10	4.00	38.03

Table(21): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for Quenched L.C.V. steel sample at various temperatures.

t °C	[I]x10^5 M	-log[I]	Efficiency %
25	2	4.69	38.14
	4	4.39	39.41
	6	4.22	42.77
	8	4.09	47.81
	10	4.00	48.78
35	2	4.69	5.65
	4	4.39	17.85
	6	4.22	27.16
	8	4.09	30.54
	10	4.00	33.22
45	2	4.69	4.21
	4	4.39	8.25
	6	4.22	33.04
	8	4.09	40.72
	10	4.00	41.43
55	2	4.69	21.13
	4	4.39	31.50
	6	4.22	40.75
	8	4.09	44.57
	10	4.00	49.35

Table(22): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for as cast M.C.V. steel sample at various temperatures.

t °C	$[I]\times10^5$ M	-log[I]	Efficiency %
25	2	4.69	38.48
	4	4.39	41.58
	6	4.22	46.22
	8	4.09	48.68
	10	4.00	54.73
35	2	4.69	8.08
	4	4.39	11.78
	6	4.22	27.61
	8	4.09	32.19
	10	4.00	37.41
45	2	4.69	36.32
	4	4.39	38.04
	6	4.22	42.97
	8	4.09	45.36
	10	4.00	49.42
55	2	4.69	21.60
	4	4.39	34.05
	6	4.22	39.30
	8	4.09	43.65
	10	4.00	45.95

Table(23): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for Normalized M.C.V. steel sample at various temperatures.

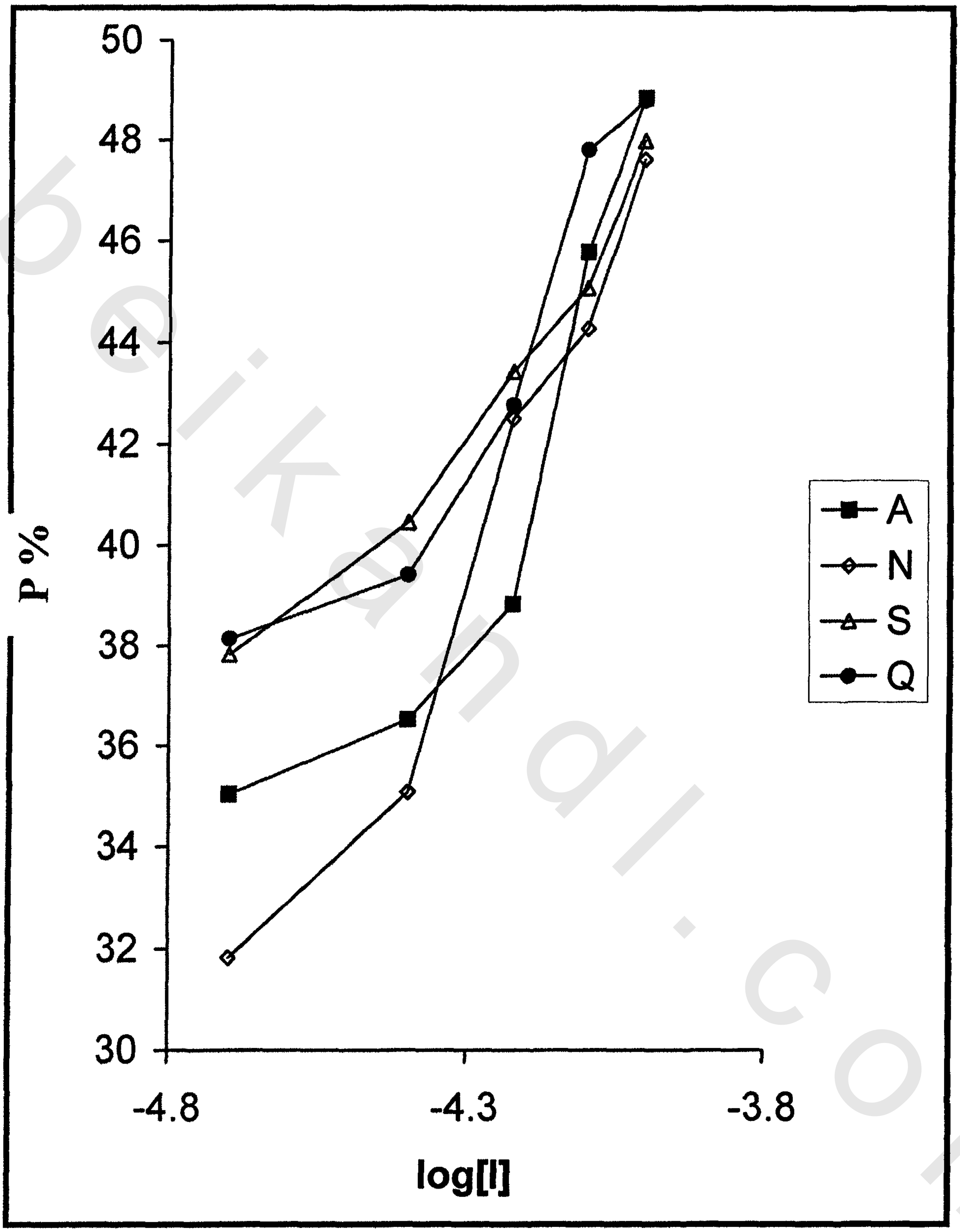
t °C	[I]x10^5 M	-log[I]	Efficiency %
25	2	4.69	28.92
	4	4.39	36.91
	6	4.22	39.10
	8	4.09	42.42
	10	4.00	49.61
35	2	4.69	7.54
	4	4.39	20.90
	6	4.22	21.62
	8	4.09	24.16
	10	4.00	27.21
45	2	4.69	8.39
	4	4.39	22.97
	6	4.22	28.00
	8	4.09	32.94
	10	4.00	38.18
55	2	4.69	18.02
	4	4.39	20.42
	6	4.22	26.51
	8	4.09	38.85
	10	4.00	40.32

Table(24): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for Spheroidized M.C.V. steel sample at various temperatures.

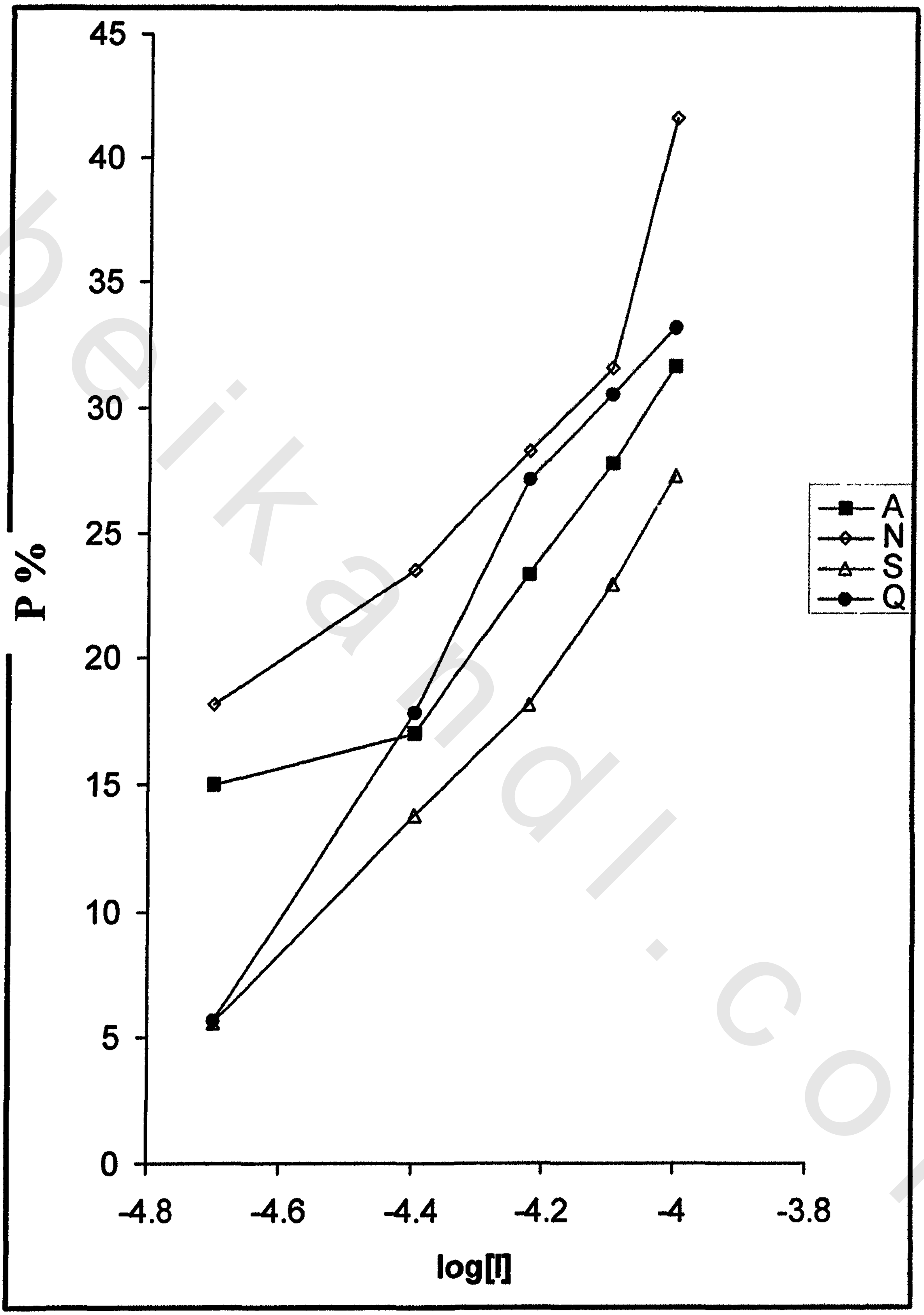
t °C	$[I]x10^5$ M	-log[I]	Efficiency %
25	2	4.69	28.83
	4	4.39	33.60
	6	4.22	37.72
	8	4.09	43.63
	10	4.00	48.54
35	2	4.69	7.67
	4	4.39	23.86
	6	4.22	27.09
	8	4.09	39.99
	10	4.00	42.14
45	2	4.69	24.57
	4	4.39	30.92
	6	4.22	40.03
	8	4.09	43.96
	10	4.00	50.29
55	2	4.69	12.73
	4	4.39	29.57
	6	4.22	33.09
	8	4.09	41.47
	10	4.00	46.34

Table(25): Inhibition efficiency of different concentrations of HEAA in 0.1M HNO_3 for Quenched M.C.V. steel sample at various temperatures.

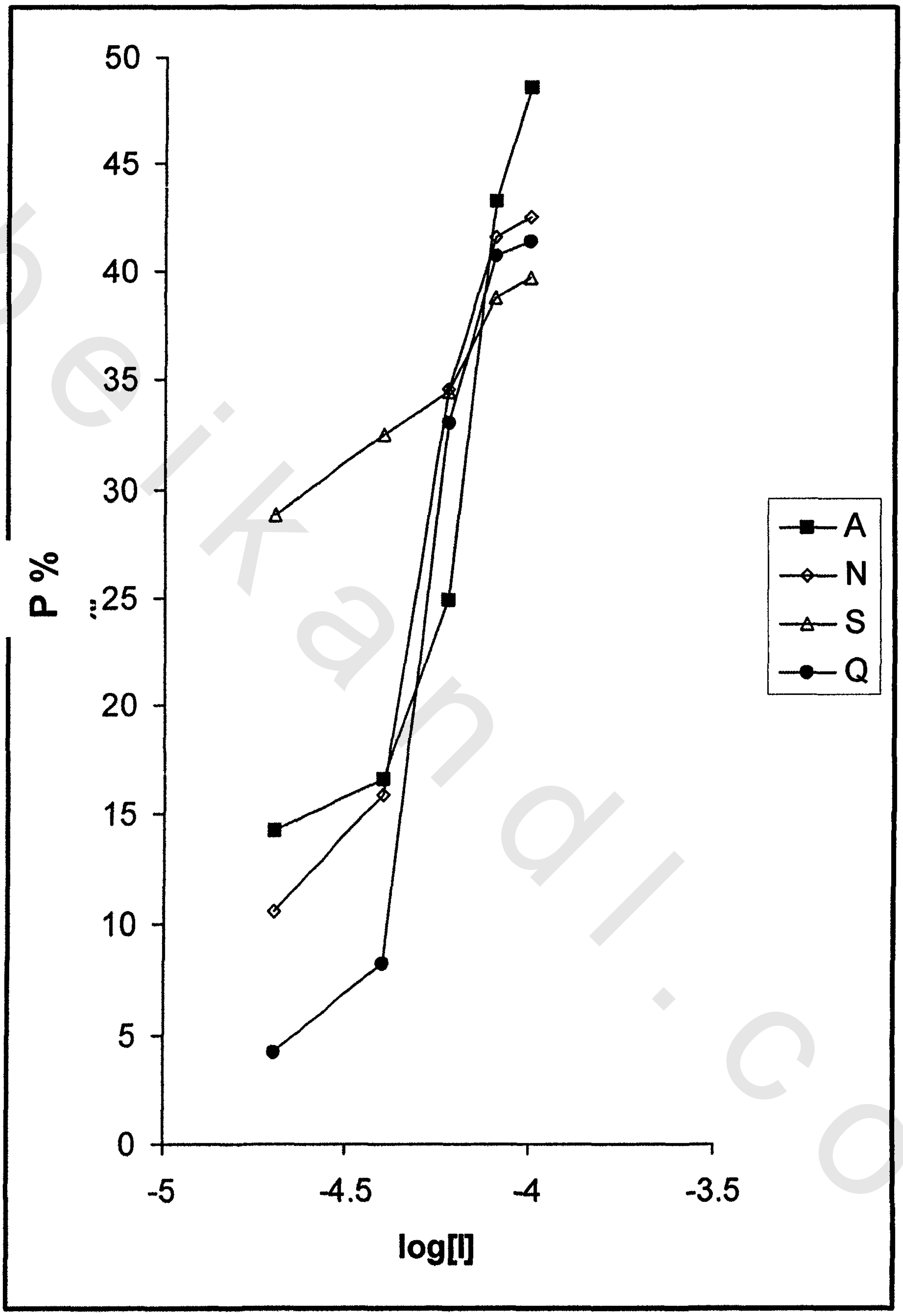
t °C	$[I]\times10^5$ M	-log[I]	Efficiency %
25	2	4.69	14.07
	4	4.39	19.99
	6	4.22	23.19
	8	4.09	28.97
	10	4.00	34.58
35	2	4.69	5.85
	4	4.39	14.68
	6	4.22	25.87
	8	4.09	27.55
	10	4.00	30.82
45	2	4.69	35.40
	4	4.39	38.80
	6	4.22	45.61
	8	4.09	48.83
	10	4.00	50.77
55	2	4.69	25.84
	4	4.39	43.14
	6	4.22	45.57
	8	4.09	49.69
	10	4.00	51.58



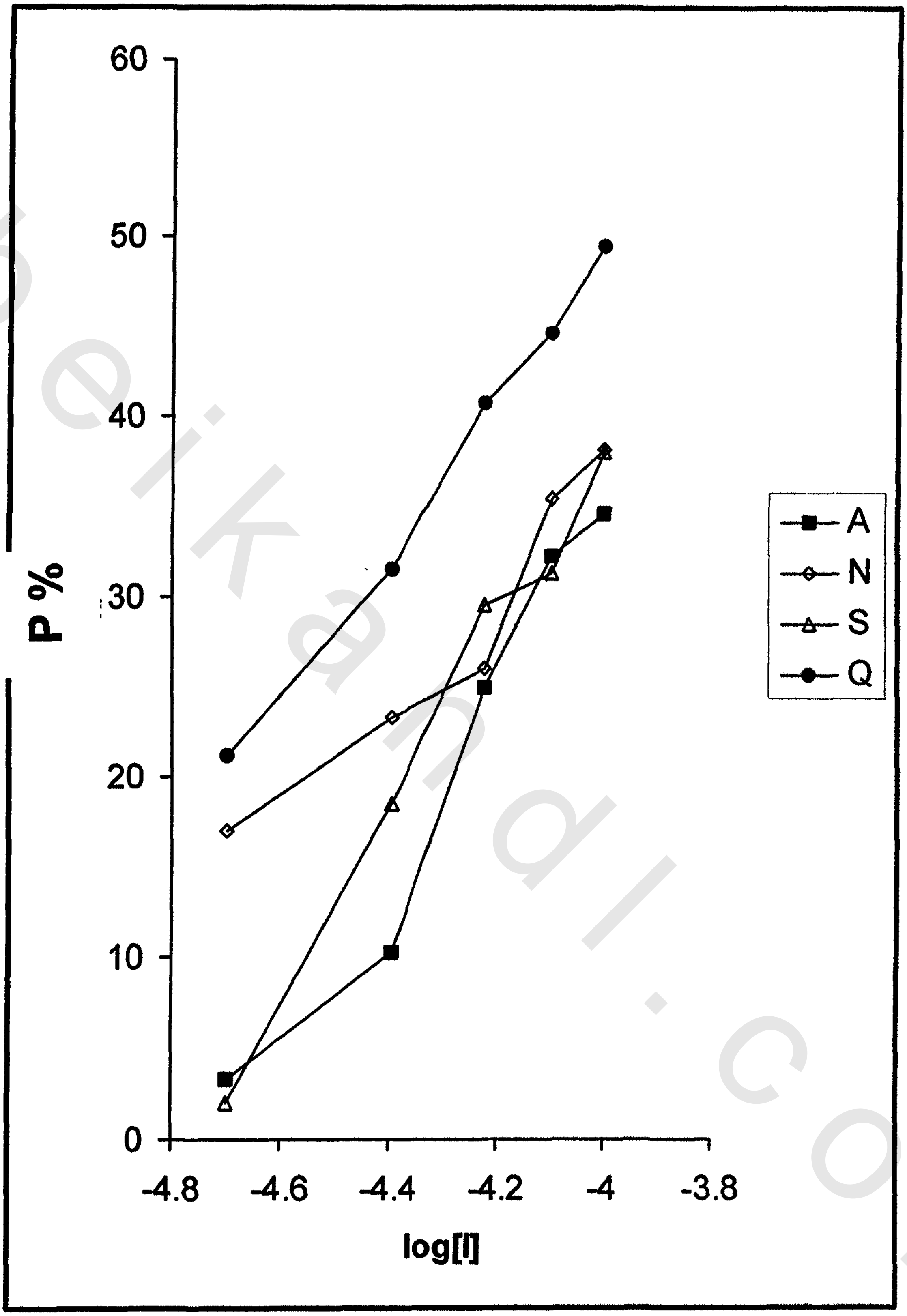
Fig(152):The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 25 °C for L.C.V. steel samples



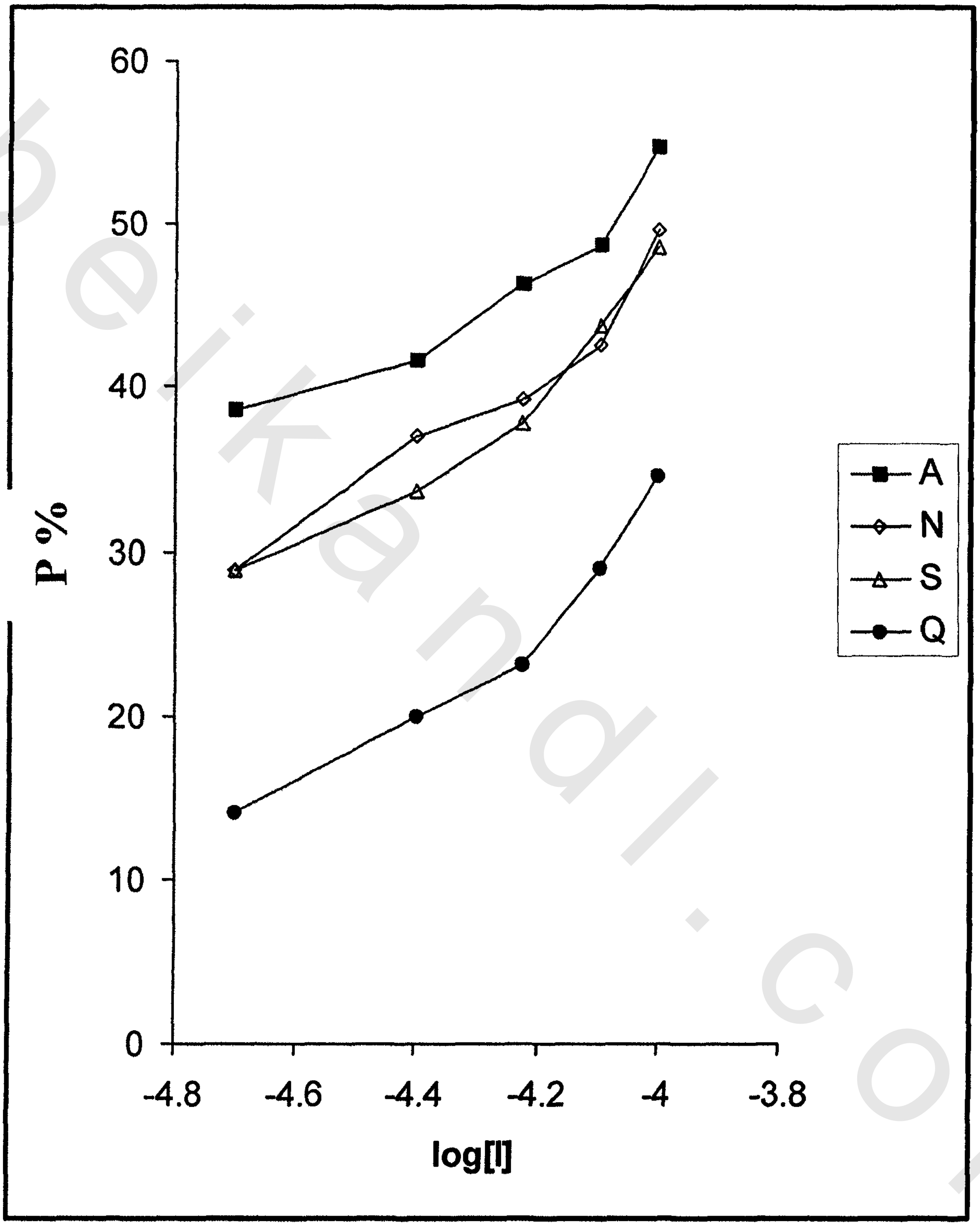
Fig(153): The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 35 °C for L.C.V. steel samples



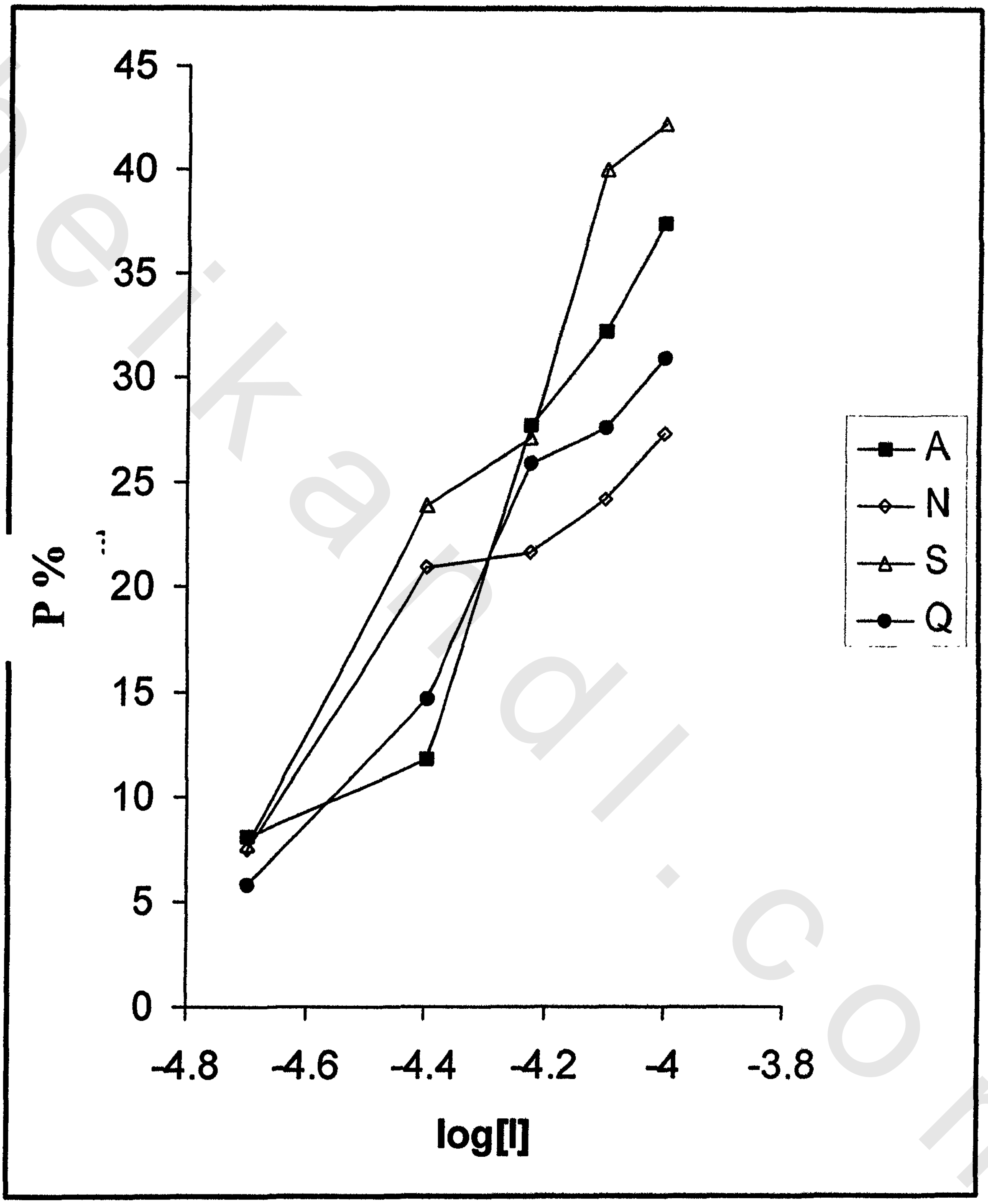
Fig(154): The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 45 °C for L.C.V. steel samples



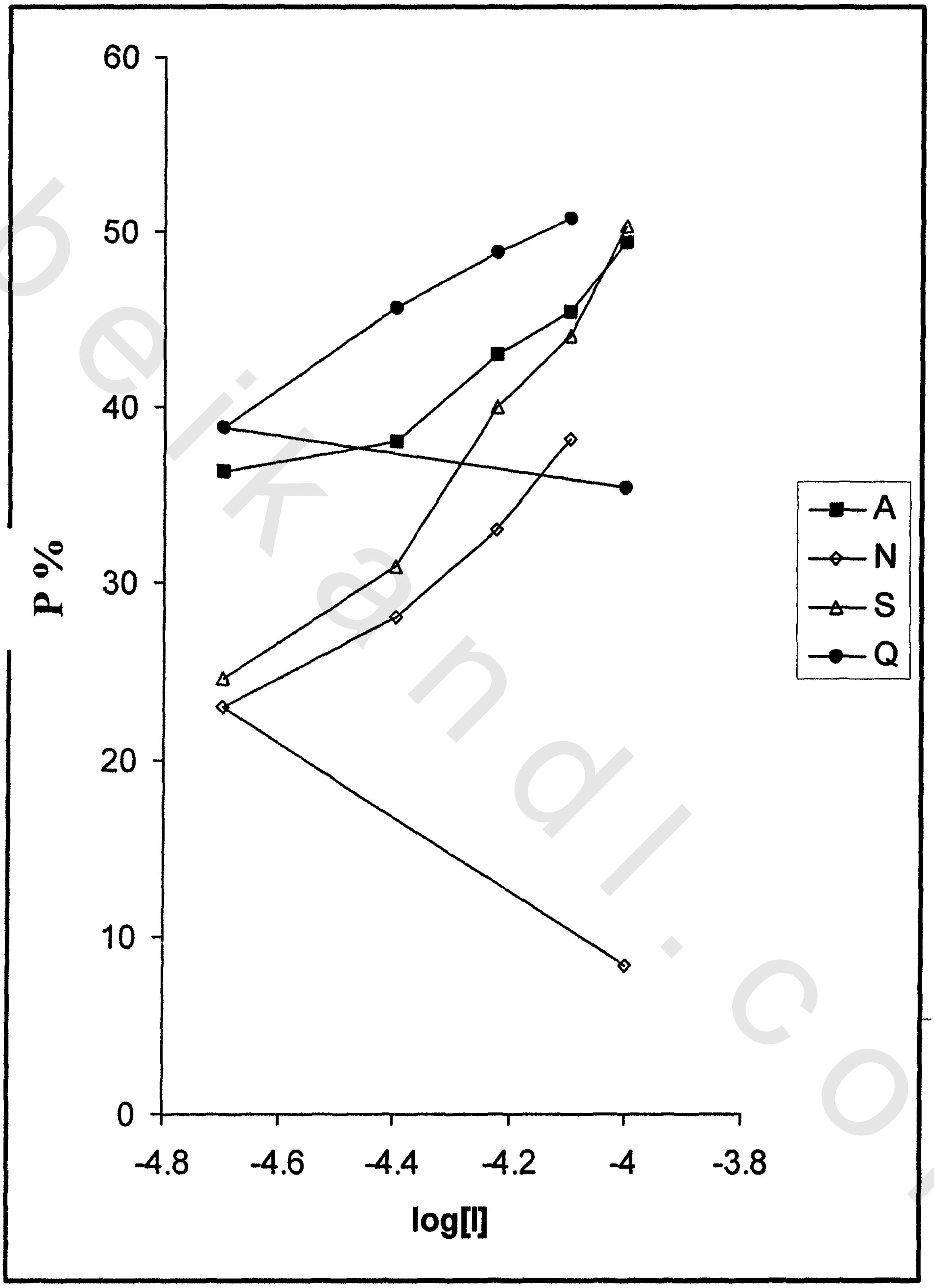
Fig(155): The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 55 °C for L.C.V. steel samples



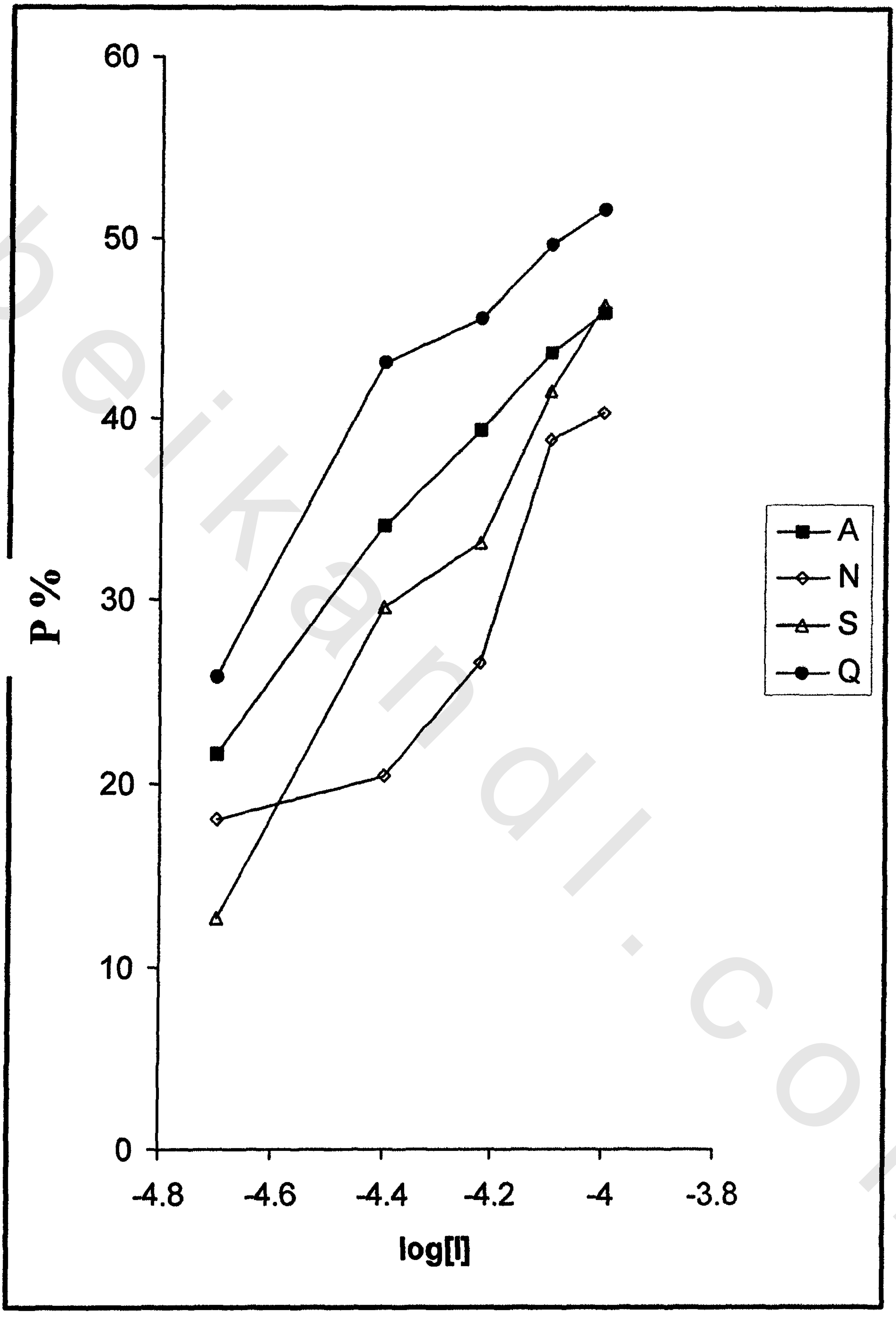
Fig(156): The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 25 °C for M.C.V. steel samples



Fig(157): The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 35 °C for M.C.V. steel samples



Fig(158): The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 45 °C for M.C.V. steel samples



Fig(159): The relation between inhibition efficiency and log [I] in 0.1M HNO_3 at 55 °C for M.C.V. steel samples

Table(26): Activation energy of L.C.V. steel samples in $0.1M$ HNO_3 and absence of inhibitor HEAA at various temperatures.

Sample	T°K	Log(C.R)	1/T x10^3	E* KJ/mol
As cast	298	1.92	3.35	6.19
	308	2.19	3.24	
	318	2.62	3.14	
	328	2.33	3.04	
Normalized	298	1.82	3.35	9.30
	308	2.23	3.24	
	318	2.52	3.14	
	328	2.55	3.04	
Spheroidized	298	1.85	3.35	5.51
	308	1.93	3.24	
	318	2.32	3.14	
	328	2.18	3.04	
Quenched	298	1.90	3.35	9.16
	308	2.11	3.24	
	318	2.45	3.14	
	328	2.63	3.04	

Table(27): Activation energy of L.C.V. steel samples in 0.1M HNO_3 in $2x10^{-5}$ M of inhibitor HEAA at various temperatures.

Sample	T°K	Log(C.R)	1/T x10^3	E* KJ/mol
As cast	298	1.44	3.35	12.44
	308	1.86	3.24	
	318	2.25	3.14	
	328	2.25	3.04	
Normalized	298	1.40	3.35	11.90
	308	1.82	3.24	
	318	2.25	3.14	
	328	2.12	3.04	
Spheroidized	298	1.34	3.35	10.59
	308	1.83	3.24	
	318	1.65	3.14	
	328	2.14	3.04	
Quenched	298	1.37	3.35	11.62
	308	1.99	3.24	
	318	2.35	3.14	
	328	2.07	3.04	

Table(28): Activation energy of L.C.V. steel samples in $0.1M\ HNO_3$ in 4×10^{-5} M of inhibitor HEAA at various temperatures.

Sample	T°K	Log(C.R)	$1/T \times 10^3$	E* KJ/mol
As cast	298	1.42	3.35	10.99
	308	1.82	3.24	
	318	2.18	3.14	
	328	2.09	3.04	
Normalized	298	1.35	3.35	10.87
	308	1.70	3.24	
	318	2.12	3.14	
	328	1.95	3.04	
Spheroidized	298	1.30	3.35	7.23
	308	1.67	3.24	
	318	1.57	3.14	
	328	1.78	3.04	
Quenched	298	1.35	3.35	9.31
	308	1.73	3.24	
	318	2.25	3.14	
	328	1.80	3.04	

Table(29): **Activation energy of L.C.V. steel samples in 0.1M HNO_3 in 6 x10^{-5} M of inhibitor HEAA at various temperatures.**

Sample	T°K	Log (C.R)	1/T x10^3	E* KJ/mol
As cast	298	1.38	3.35	7.09
	308	1.68	3.24	
	318	1.97	3.14	
	328	1.74	3.04	
Normalized	298	1.24	3.35	10.57
	308	1.60	3.24	
	318	1.65	3.14	
	328	1.88	3.04	
Spheroidized	298	1.25	3.35	4.85
	308	1.58	3.24	
	318	1.52	3.14	
	328	1.54	3.04	
Quenched	298	1.30	3.35	5.09
	308	1.53	3.24	
	318	1.64	3.14	
	328	1.56	3.04	

Table(30): Activation energy of L.C.V. steel samples in 0.1M HNO_3 in 8 x10^{-5} M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	1/T x10^3	E* KJ/mol
As cast	298	1.27	3.35	4.88
	308	1.58	3.24	
	318	1.48	3.14	
	328	1.57	3.04	
Normalized	298	1.21	3.35	7.30
	308	1.52	3.24	
	318	1.47	3.14	
	328	1.64	3.04	
Spheroidized	298	1.22	3.35	4.67
	308	1.49	3.24	
	318	1.42	3.14	
	328	1.50	3.04	
Quenched	298	1.21	3.35	4.53
	308	1.46	3.24	
	318	1.45	3.14	
	328	1.46	3.04	

Table(31): Activation energy of L.C.V. steel samples in 0.1M HNO_3 in 10^{-4} M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	1/T x10^3	E* KJ/mol
As cast	298	0.08	3.35	5.18
	308	0.17	3.24	
	318	0.15	3.14	
	328	0.18	3.04	
Normalized	298	0.06	3.35	8.49
	308	0.11	3.24	
	318	0.16	3.14	
	328	0.19	3.04	
Spheroidized	298	0.07	3.35	3.53
	308	0.14	3.24	
	318	0.15	3.14	
	328	0.13	3.04	
Quenched	298	0.07	3.35	2.93
	308	0.14	3.24	
	318	0.15	3.14	
	328	0.12	3.04	

Table(32): Activation energy of M.C.V. steel samples in 0.1M HNO_3 and absence M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	1/T x10^3	E* KJ/mol
As cast	298	0.28	3.35	11.27
	308	0.31	3.24	
	318	0.44	3.14	
	328	0.44	3.04	
Normalized	298	0.24	3.35	10.22
	308	0.30	3.24	
	318	0.34	3.14	
	328	0.41	3.04	
Spheroidized	298	0.24	3.35	10.40
	308	0.32	3.24	
	318	0.41	3.14	
	328	0.39	3.04	
Quenched	298	0.18	3.35	19.12
	308	0.29	3.24	
	318	0.45	3.14	
	328	0.46	3.04	

Table(33): Activation energy of M.C.V.steel samples in 0.1M HNO_3 in $2x10^{-5}$ M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	1/T $x10^3$	E* KJ/mol
As cast	298	0.14	3.35	10.32
	308	0.28	3.24	
	318	0.24	3.14	
	328	0.34	3.04	
Normalized	298	0.14	3.35	11.17
	308	0.26	3.24	
	318	0.30	3.14	
	328	0.32	3.04	
Spheroidized	298	0.13	3.35	11.17
	308	0.28	3.24	
	318	0.29	3.14	
	328	0.33	3.04	
Quenched	298	0.13	3.35	11.38
	308	0.26	3.24	
	318	0.27	3.14	
	328	0.33	3.04	

Table(34): Activation energy of M.C.V.steel samples in 0.1M HNO_3 in $4x10^{-5}$ M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	1/T $x10^3$	E* KJ/mol
As cast	298	0.12	3.35	7.20
	308	0.26	3.24	
	318	0.23	3.14	
	328	0.26	3.04	
Normalized	298	0.10	3.35	12.33
	308	0.20	3.24	
	318	0.22	3.14	
	328	0.31	3.04	
Spheroidized	298	0.11	3.35	8.03
	308	0.19	3.24	
	318	0.25	3.14	
	328	0.24	3.04	
Quenched	298	0.10	3.35	6.63
	308	0.22	3.24	
	318	0.24	3.14	
	328	0.22	3.04	

Table(35): Activation energy of M.C.V.steel samples in 0.1M HNO_3 in 6 x10^{-5}M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	1/T x10^3	E* KJ/mol
As cast	298	0.10	3.35	7.54
	308	0.17	3.24	
	318	0.19	3.14	
	328	0.23	3.04	
Normalized	298	0.09	3.35	10.58
	308	0.19	3.24	
	318	0.19	3.14	
	328	0.29	3.04	
Spheroidized	298	0.09	3.35	7.09
	308	0.17	3.24	
	318	0.19	3.14	
	328	0.22	3.04	
Quenched	298	0.10	3.35	6.40
	308	0.16	3.24	
	318	0.19	3.14	
	328	0.20	3.04	

Table(36): Activation energy of M.C.V. steel samples in 0.1M HNO_3 in $8x10^{-5}$ M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	1/T $x10^3$	E* KJ/mol
As cast	298	0.10	3.35	6.77
	308	0.15	3.24	
	318	0.18	3.14	
	328	0.19	3.04	
Normalized	298	0.07	3.35	6.89
	308	0.18	3.24	
	318	0.16	3.14	
	328	0.20	3.04	
Spheroidized	298	0.06	3.35	6.69
	308	0.10	3.24	
	318	0.15	3.14	
	328	0.16	3.04	
Quenched	298	0.07	3.35	5.65
	308	0.15	3.24	
	318	0.17	3.14	
	328	0.16	3.04	

Table(37): Activation energy of M.C.V. steel samples in 0.1M HNO_3 in 10^{-4} M of inhibitor HEAA at various temperatures.

Sample	T°K	Log (C.R)	$1/T \times 10^3$	E* KJ/mol
As cast	298	0.04	3.35	8.12
	308	0.11	3.24	
	318	0.14	3.14	
	328	0.17	3.04	
Normalized	298	0.03	3.35	8.50
	308	0.16	3.24	
	318	0.13	3.14	
	328	0.19	3.04	
Spheroidized	298	0.03	3.35	5.63
	308	0.07	3.24	
	318	0.10	3.14	
	328	0.12	3.04	
Quenched	298	0.04	3.35	6.34
	308	0.13	3.24	
	318	0.14	3.14	
	328	0.15	3.04	

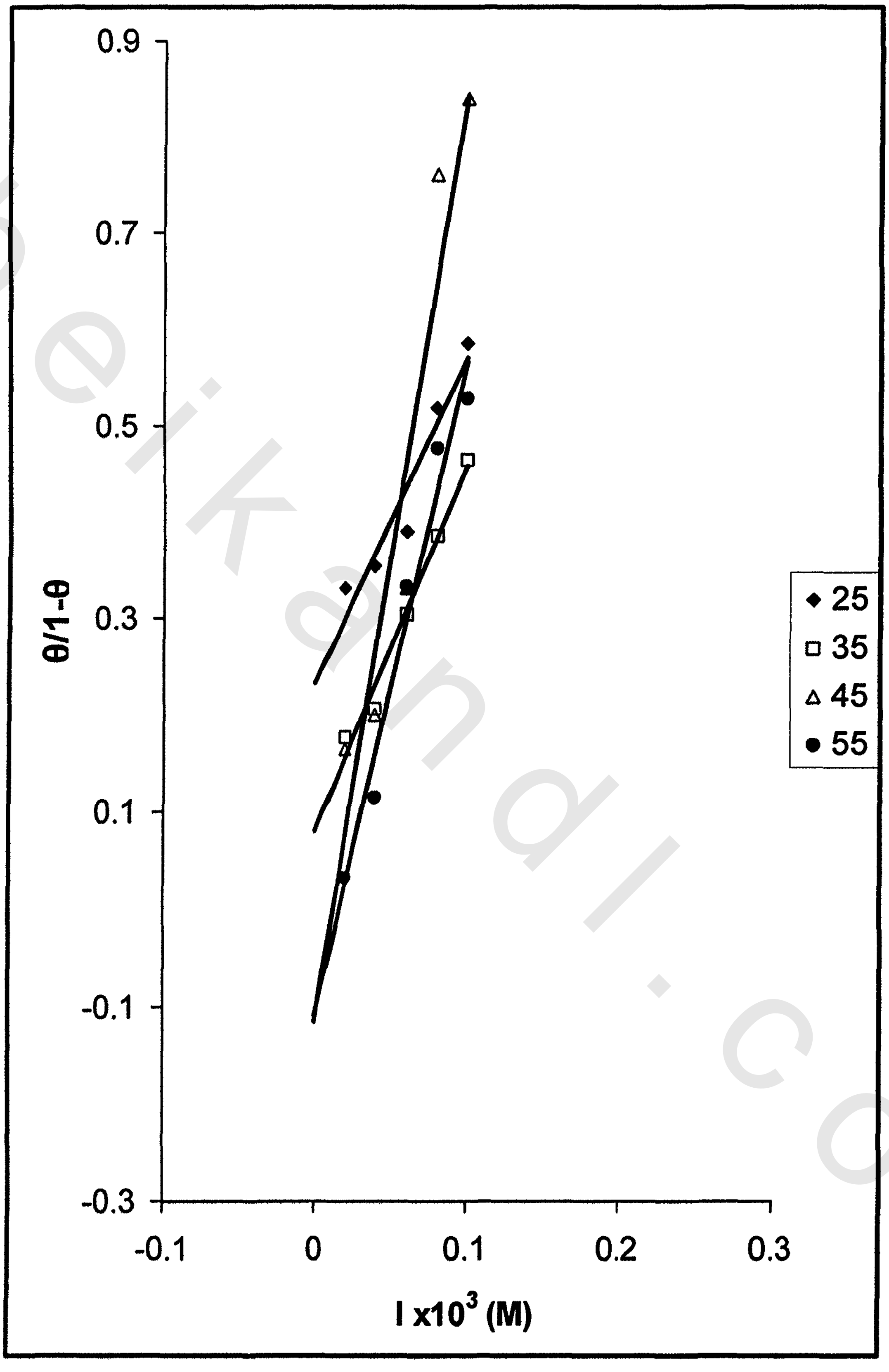


Fig (160):The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for As cast L.C.V. steel sample at various temperatures.

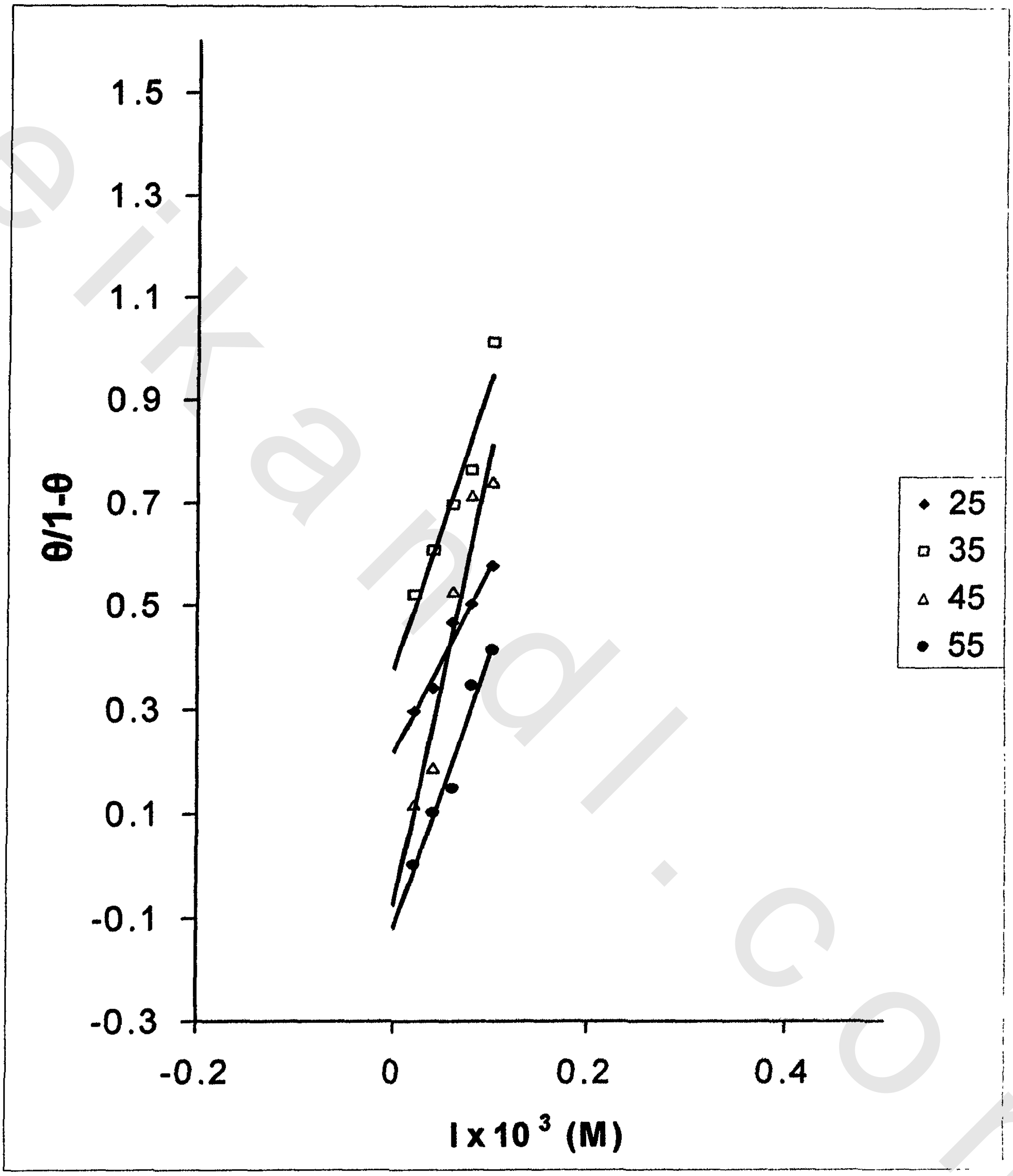


Fig (161): The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for normalized L.C.V. steel sample at various temperatures.

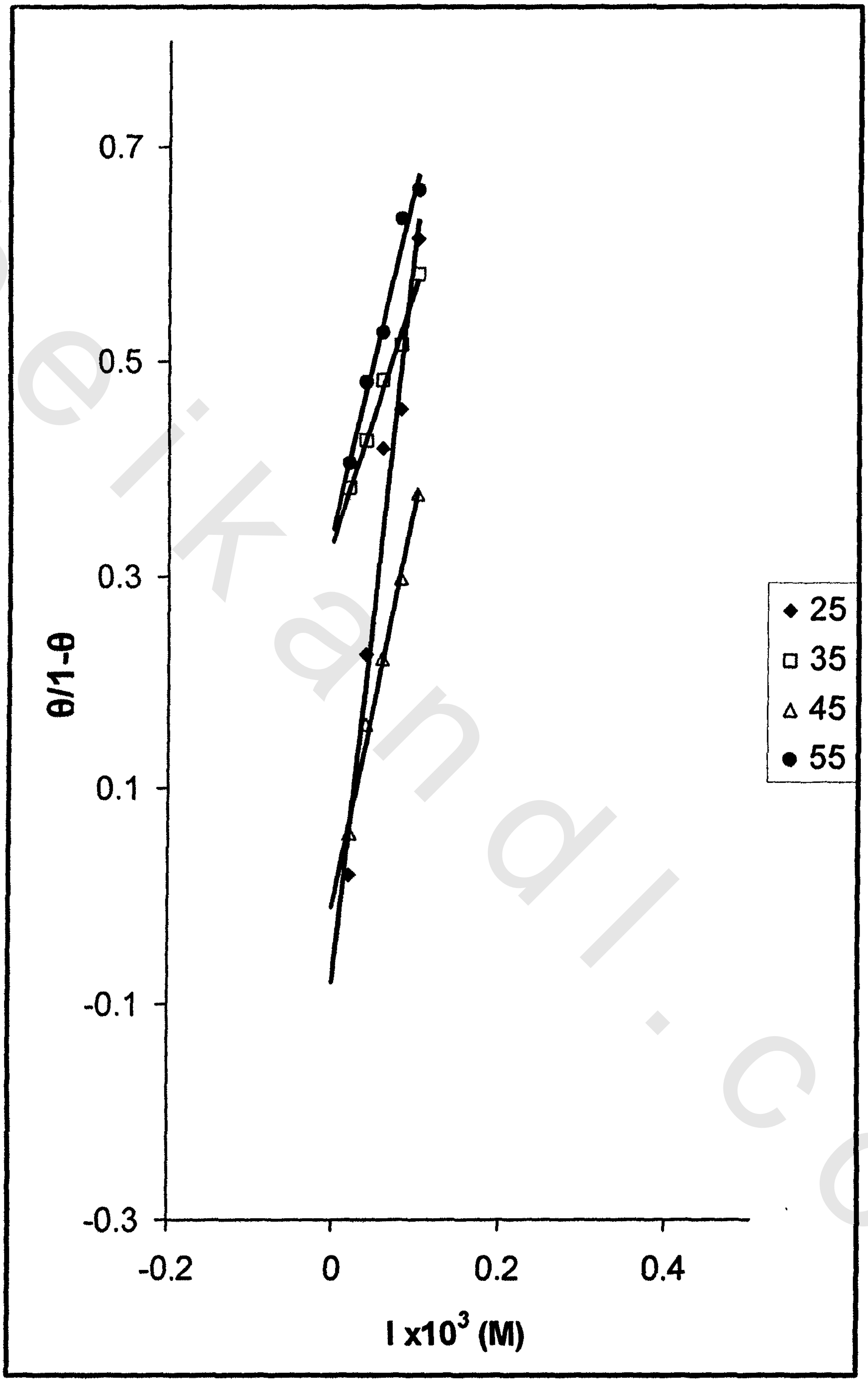


Fig (162): The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for spheroidized L.C.V. steel sample at various temperatures.

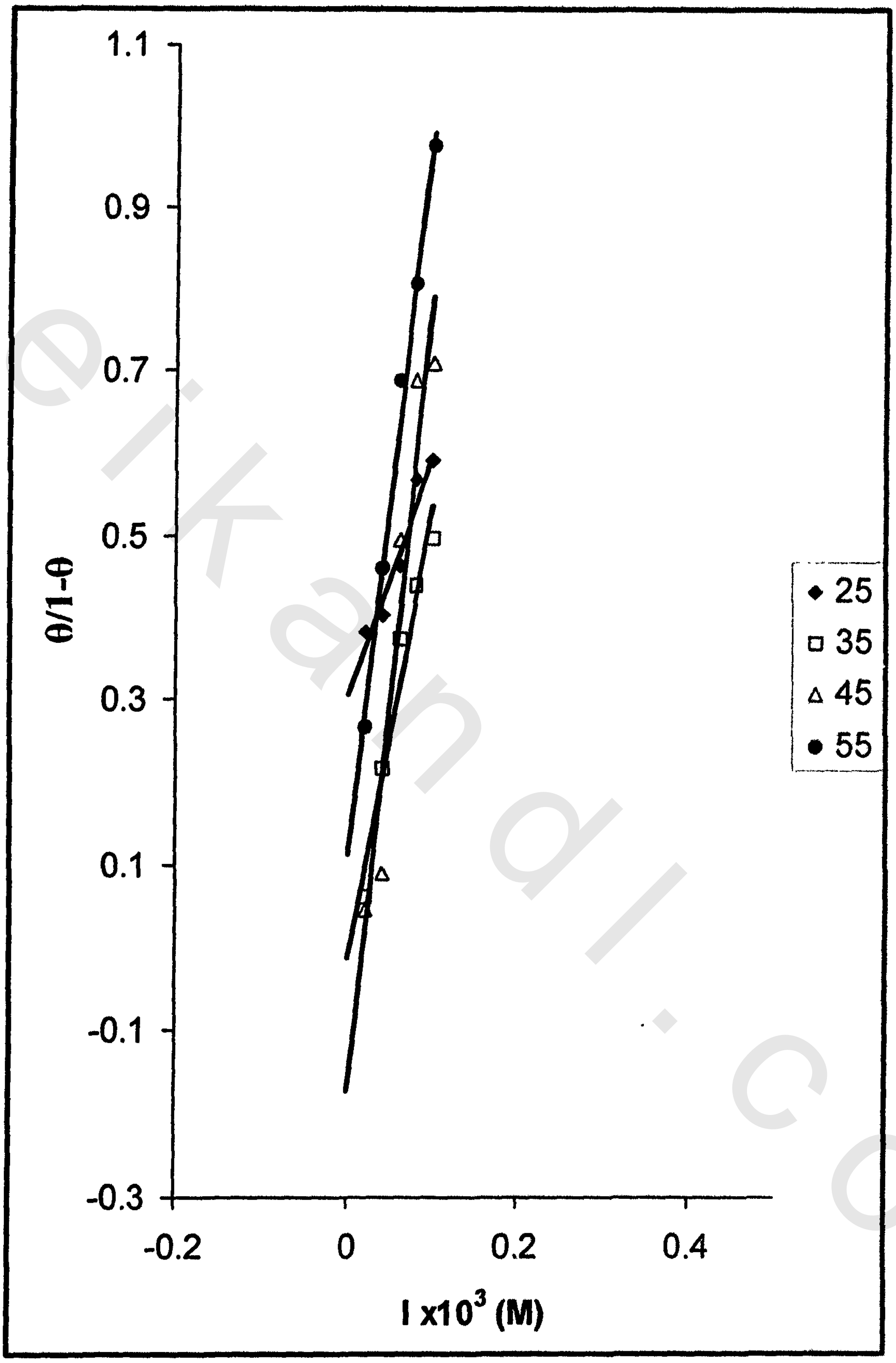


Fig (163): The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for quenched L.C.V. steel sample at various temperatures.

Table(38): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for As cast L.C.V. steel sample at various temperatures

t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.33	3.53
	4	0.35	
	6	0.39	
	8	0.52	
	10	0.58	
35	2	0.17	3.58
	4	0.21	
	6	0.30	
	8	0.38	
	10	0.46	
45	2	0.16	3.98
	4	0.19	
	6	0.33	
	8	0.76	
	10	0.84	
55	2	0.03	3.83
	4	0.11	
	6	0.33	
	8	0.47	
	10	0.53	

Table(39): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for Normalized L.C.V. steel sample at various temperatures

t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.29	3.56
	4	0.34	
	6	0.46	
	8	0.50	
	10	0.57	
35	2	0.22	3.75
	4	0.30	
	6	0.39	
	8	0.46	
	10	0.71	
45	2	0.11	3.95
	4	0.18	
	6	0.52	
	8	0.71	
	10	0.74	
55	2	0.20	3.73
	4	0.30	
	6	0.35	
	8	0.54	
	10	0.61	

Table(40): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for Spheroidized L.C.V. steel sample at various Temperatures

t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.38	3.38
	4	0.42	
	6	0.48	
	8	0.51	
	10	0.57	
35	2	0.06	3.59
	4	0.16	
	6	0.22	
	8	0.29	
	10	0.37	
45	2	0.40	3.52
	4	0.48	
	6	0.52	
	8	0.63	
	10	0.65	
55	2	0.02	3.85
	4	0.22	
	6	0.41	
	8	0.45	
	10	0.61	

Table(41): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for Quenched L.C.V. steel sample at various temperatures

t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.38	3.46
	4	0.40	
	6	0.46	
	8	0.56	
	10	0.58	
35	2	0.06	3.74
	4	0.21	
	6	0.37	
	8	0.43	
	10	0.49	
45	2	0.04	3.98
	4	0.08	
	6	0.49	
	8	0.68	
	10	0.70	
55	2	0.26	3.94
	4	0.45	
	6	0.68	
	8	0.80	
	10	0.97	

Table(42):Thermodynamic parameters of adsorption-desorption process for L.C.V. steel samples in 0.1M HNO_3 in presence of different concentrations of HEAA Calculated from equilibrium constant of langmuir equation.

Sample	t °C	log K	$-\Delta G^\circ$ KJ/mol	ΔH° KJ/mol	ΔS° J/mol.K
A	25	3.53	20.13	24.71	150.47
	35	3.58	21.10	24.71	148.70
	45	3.98	24.23	24.71	153.91
	55	3.83	24.05	24.71	148.66
N	25	3.56	20.30	13.64	113.90
	35	3.75	22.14	13.64	116.16
	45	3.95	24.03	13.64	118.45
	55	3.73	23.42	13.64	112.97
S	25	3.38	19.31	24.73	147.77
	35	3.59	21.15	24.73	148.96
	45	3.52	21.42	24.73	145.11
	55	3.85	24.18	24.73	149.11
Q	25	3.46	19.76	31.92	173.42
	35	3.74	22.05	31.92	175.24
	45	3.98	24.25	31.92	176.65
	55	3.94	24.77	31.92	172.84

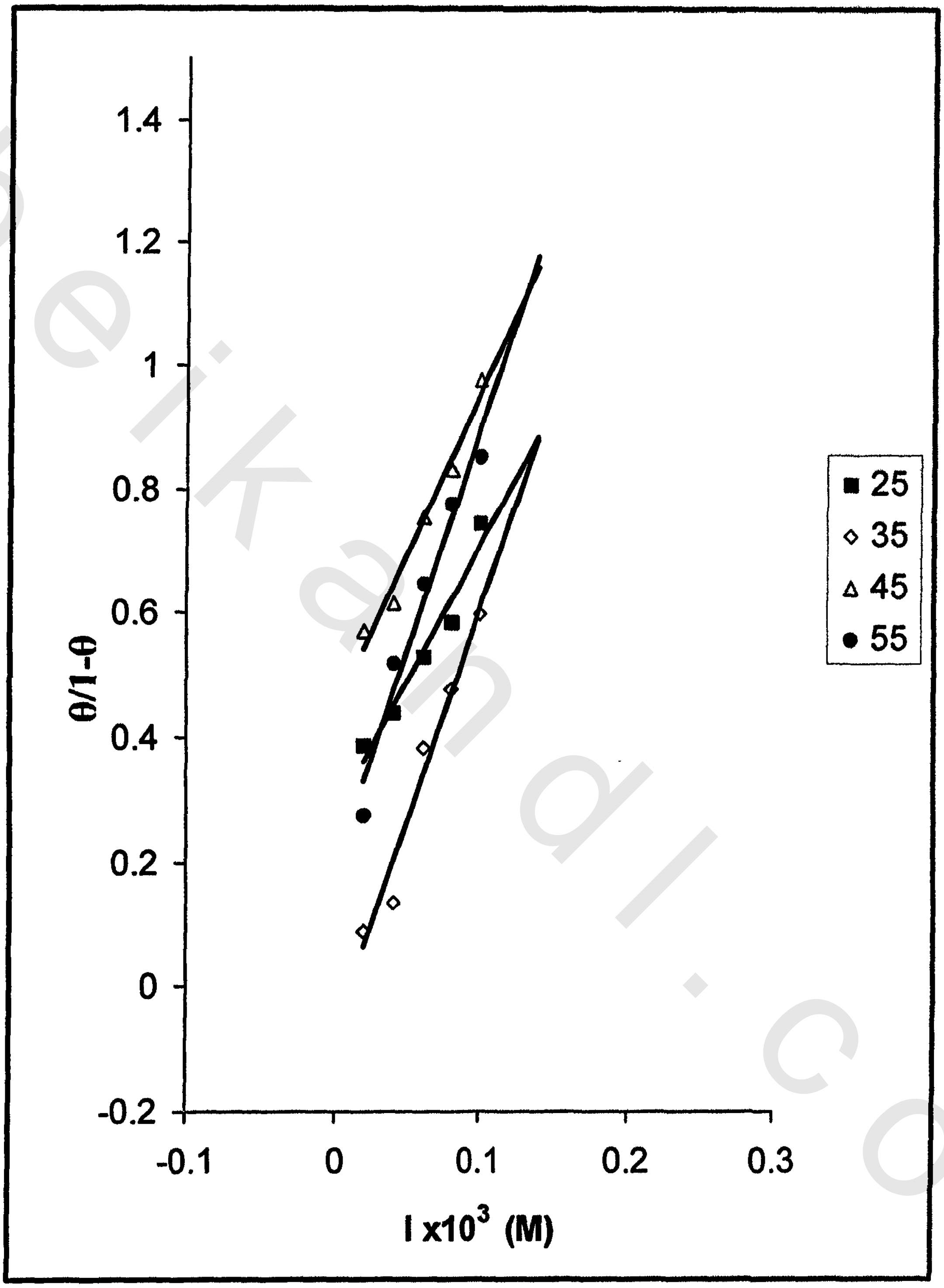


Fig (164): The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for as cast M.C.V. steel sample at various temperatures.

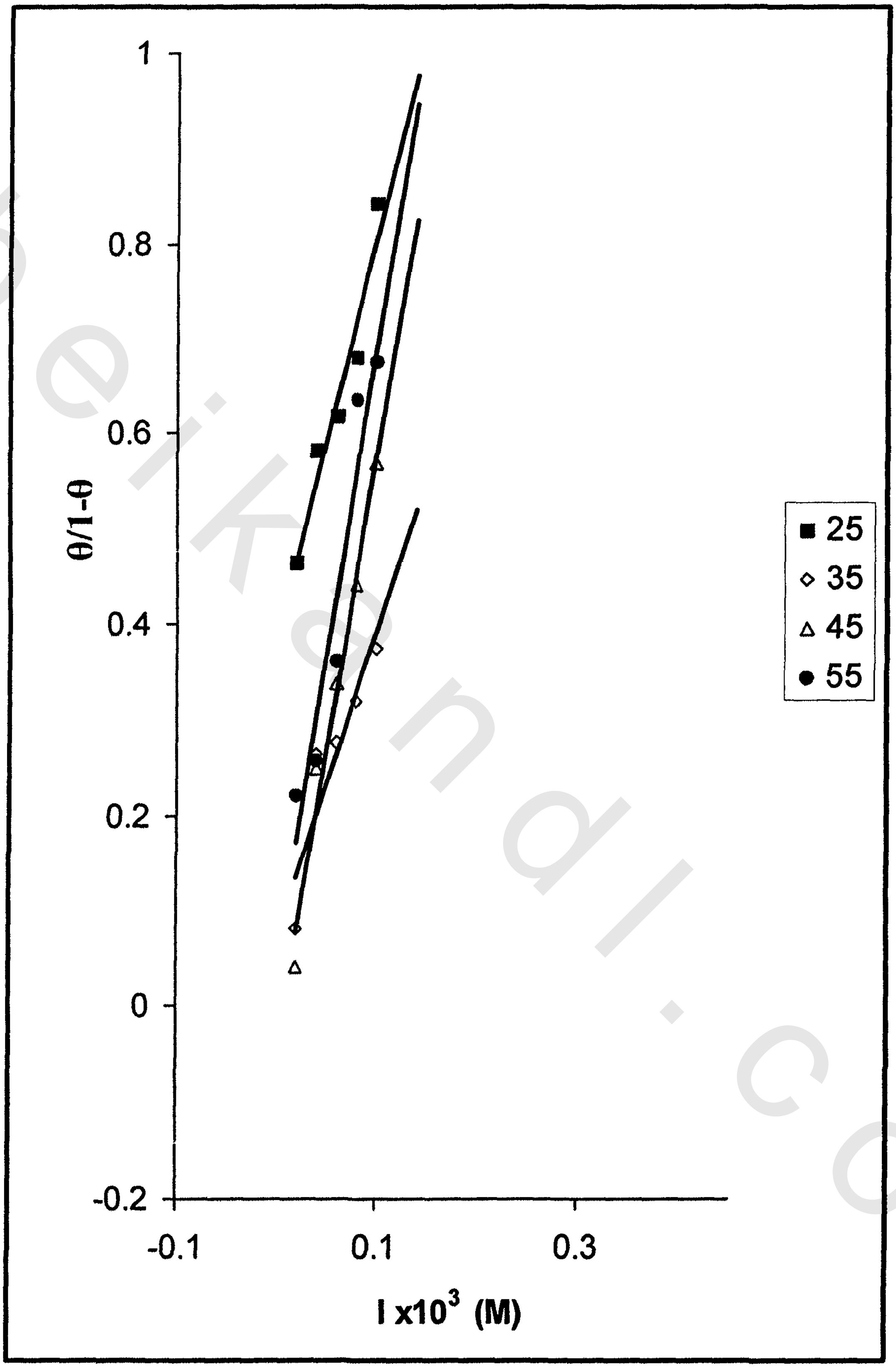


Fig (165): The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for normalized M.C.V. steel sample at various temperatures.

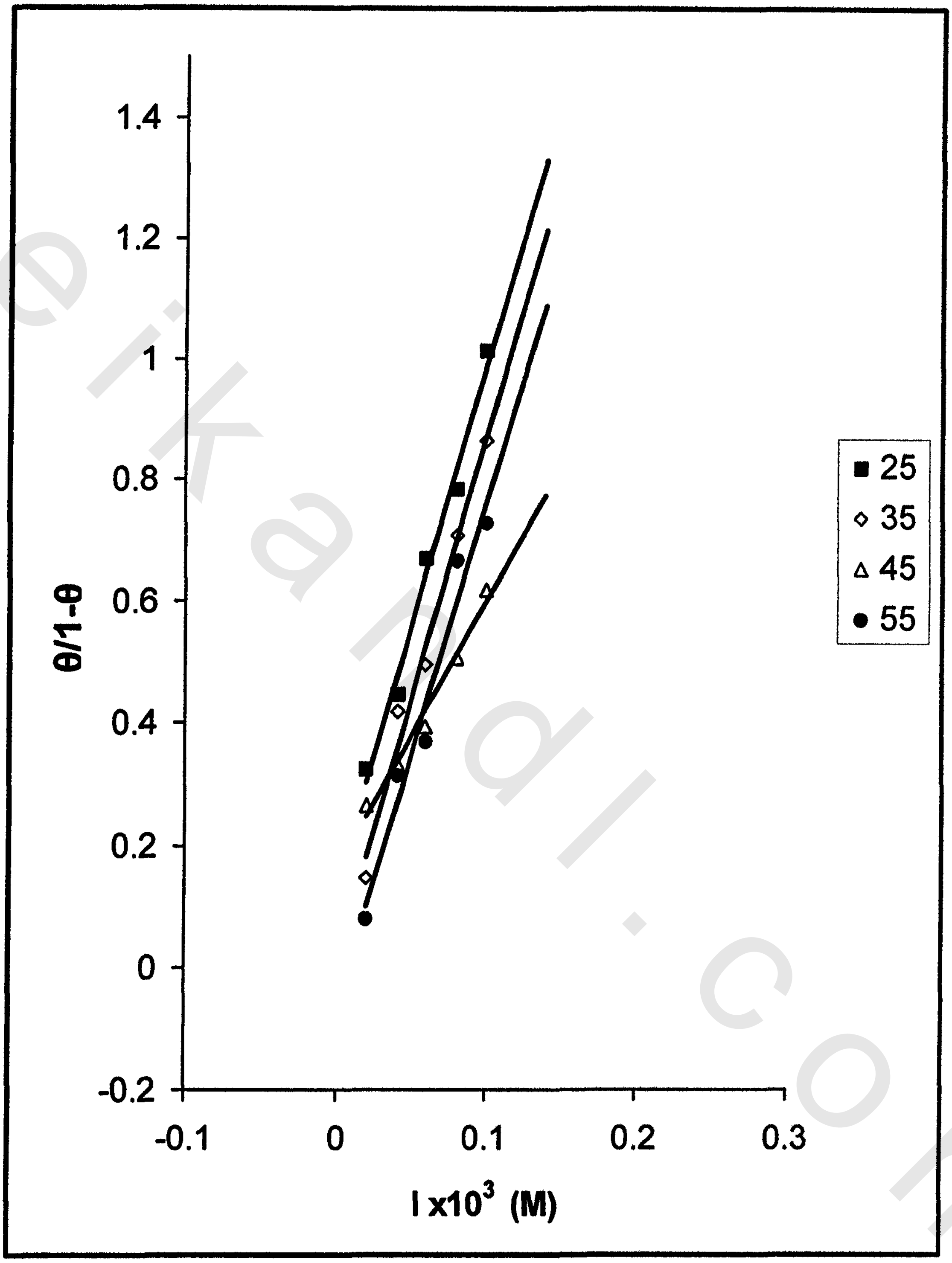


Fig (166): The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for spheroidized M.C.V. steel sample at various temperatures.

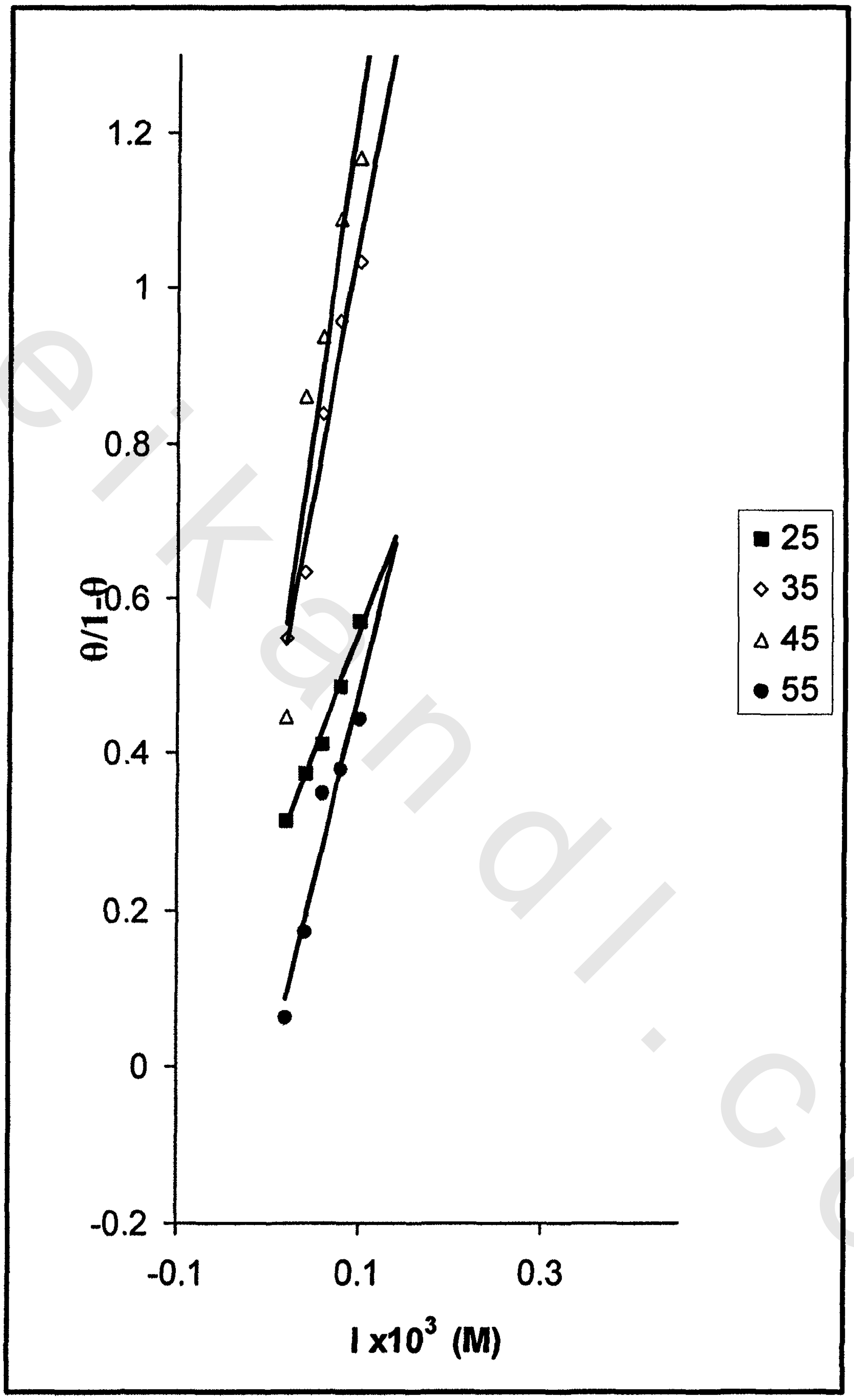


Fig (167): The relation between θ/1-θ and concentration of inhibitor [I] in 0.1M HNO_3 for quenched M.C.V. steel sample at various temperatures.

Table(43): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for As cast M.C.V. steel sample at various temperatures

t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.38	3.63
	4	0.43	
	6	0.52	
	8	0.58	
	10	0.74	
35	2	0.08	3.83
	4	0.13	
	6	0.38	
	8	0.47	
	10	0.59	
45	2	0.57	3.71
	4	0.61	
	6	0.75	
	8	0.83	
	10	0.97	
55	2	0.27	3.85
	4	0.51	
	6	0.64	
	8	0.77	
	10	0.85	

Table(44): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for normalized M.C.V. steel sample at various temperatures

t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.26	3.63
	4	0.38	
	6	0.42	
	8	0.47	
	10	0.64	
35	2	0.08	3.50
	4	0.26	
	6	0.27	
	8	0.31	
	10	0.37	
45	2	0.09	3.79
	4	0.29	
	6	0.38	
	8	0.49	
	10	0.61	
55	2	0.21	3.81
	4	0.25	
	6	0.36	
	8	0.63	
	10	0.67	

Table(45): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for spheroidized M.C.V. steel sample at various temperatures

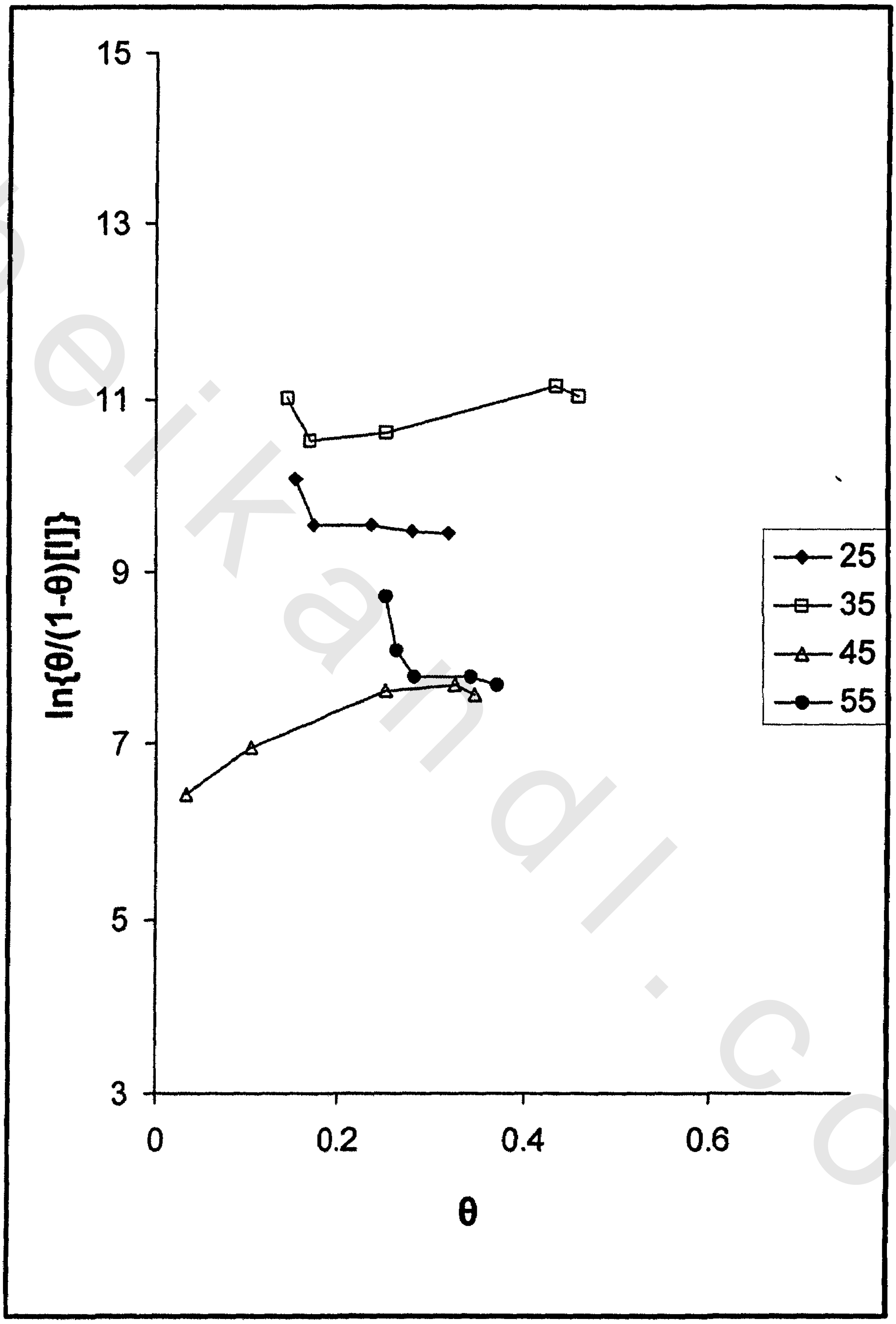
t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.26	3.64
	4	0.33	
	6	0.39	
	8	0.50	
	10	0.61	
35	2	0.08	3.91
	4	0.31	
	6	0.37	
	8	0.66	
	10	0.72	
45	2	0.32	3.93
	4	0.44	
	6	0.66	
	8	0.78	
	10	1.01	
55	2	0.14	3.94
	4	0.41	
	6	0.49	
	8	0.71	
	10	0.86	

Table(46): Calculation of binding constant (K) of HEAA in langmuir equation in 0.1M HNO_3 for quenched M.C.V. steel sample at various temperatures

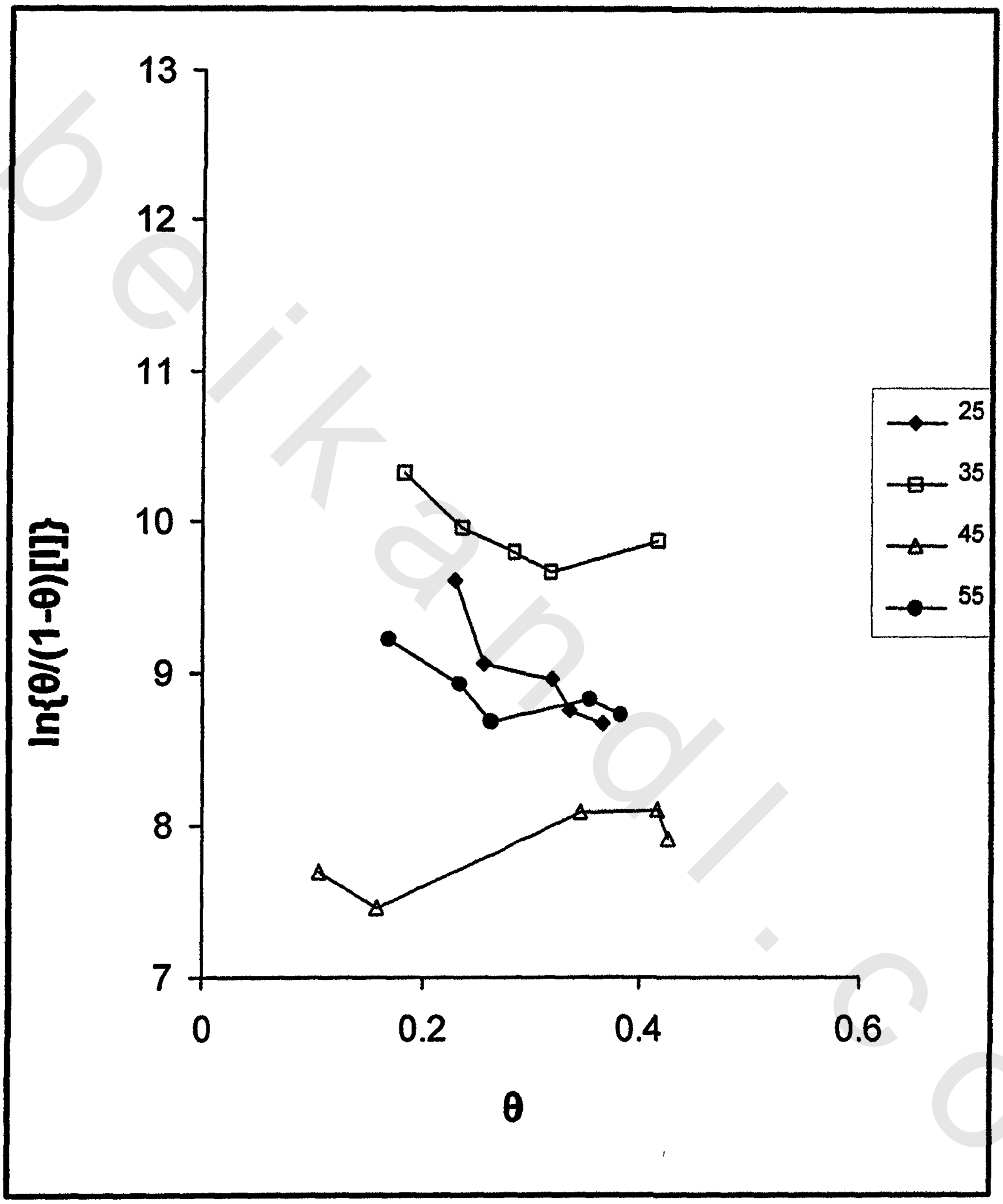
t °C	Conc. of inhibitor[I] M x(10^5)	θ/1-θ	Log k
25	2	0.11	3.49
	4	0.17	
	6	0.21	
	8	0.28	
	10	0.36	
35	2	0.06	3.69
	4	0.17	
	6	0.34	
	8	0.38	
	10	0.44	
45	2	0.54	3.81
	4	0.63	
	6	0.83	
	8	0.95	
	10	1.03	
55	2	0.34	3.92
	4	0.75	
	6	0.83	
	8	0.98	
	10	1.06	

Table(47): Thermodynamic parameters of adsorption-desorption process for M.C.V. steel samples in 0.1M HNO_3 in presence of different concentrations of HEAA Calculated from equilibrium constant of langmuir equation.

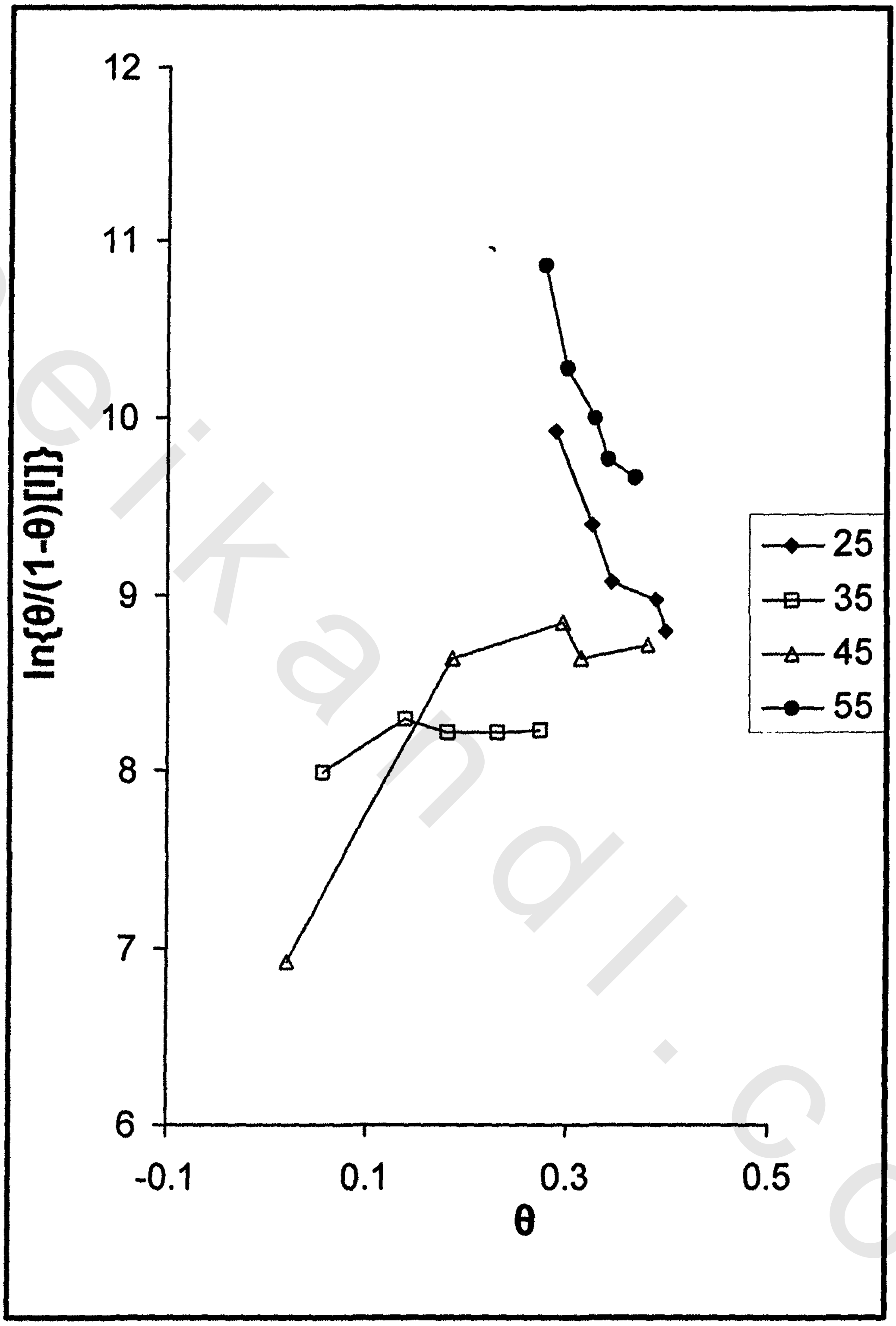
Sample	t °C	log K	-ΔG° KJ/mol	ΔH° KJ/mol	ΔS° J/mol.K
A	25	3.63	20.75	9.69	102.13
	35	3.83	22.60	9.69	104.84
	45	3.71	22.60	9.69	101.53
	55	3.85	24.16	9.69	103.20
N	25	3.63	20.71	15.38	121.10
	35	3.50	20.67	15.38	117.05
	45	3.79	23.10	15.38	121.02
	55	3.81	23.93	15.38	119.84
S	25	3.64	20.79	17.07	127.03
	35	3.91	23.09	17.07	130.38
	45	3.93	23.94	17.07	128.96
	55	3.94	24.72	17.07	127.40
Q	25	3.49	19.92	26.36	155.32
	35	3.69	21.75	26.36	156.20
	45	3.81	23.19	26.36	155.82
	55	3.92	24.62	26.36	155.42



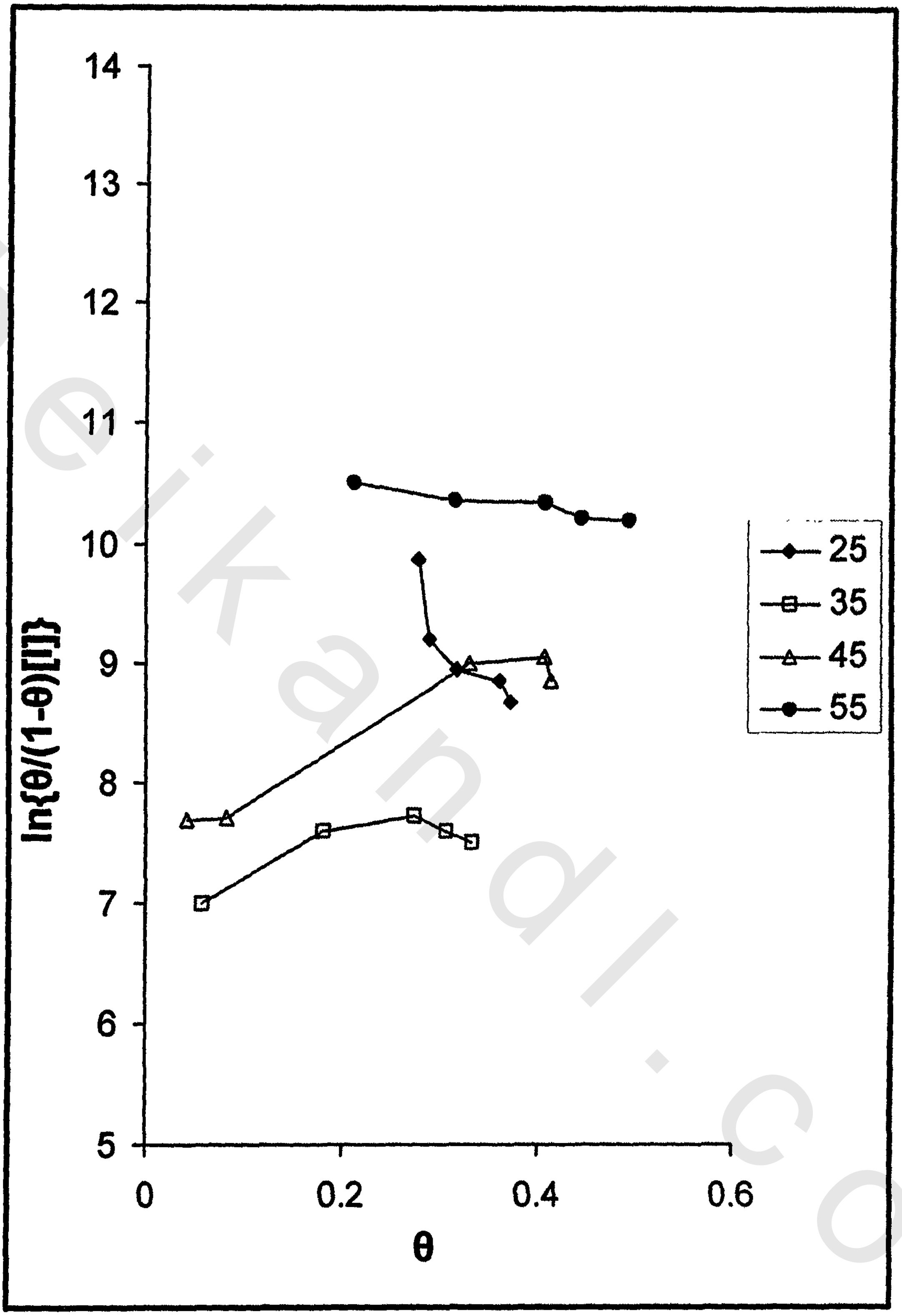
Fig(168): **The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for as cast L.C.V. steel sample at various temperatures.**



Fig(169): The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for Normalized L.C.V. steel sample at various temperatures .



Fig(170): The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for Spheroidized L.C.V. steel sample at various temperatures .



Fig(171): The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for Quenched L.C.V. steel sample at various temperatures .

Table(48):Calculation of binding constant (K) of HEAA in frumkin equation in 0.1M HNO_3 for as cast L.C.V. steel sample at various temperatures

t °C	$[I]\times10^5$ M	θ	ln{θ/(1-θ)[I]}	lnK	a
25	2	0.25	9.71	10.83	-3.04
	4	0.26	9.08		
	6	0.28	8.78		
	8	0.34	8.77		
	10	0.37	8.67		
35	2	0.15	9.08	9.26	-1.39
	4	0.17	8.54		
	6	0.23	8.53		
	8	0.28	8.48		
	10	0.32	8.44		
45	2	0.14	9.02	8.07	0.58
	4	0.17	8.51		
	6	0.25	8.62		
	8	0.43	9.16		
	10	0.45	9.03		
55	2	0.03	7.42	7.46	1.89
	4	0.10	7.96		
	6	0.25	8.62		
	8	0.32	8.69		
	10	0.34	8.57		

Table(49):Calculation of binding constant (K) of HEAA in frumkin equation in 0.1M HNO_3 for Normalized L.C.V. steel sample at various temperatures

t °C	$[I]\times10^5$ M	θ	$\ln\{\theta/(1-\theta)[I]\}$	lnK	a
25	2	0.23	9.60	10.79	-2.97
	4	0.25	9.05		
	6	0.32	8.96		
	8	0.33	8.75		
	10	0.37	8.66		
35	2	0.18	9.31	9.44	-0.90
	4	0.23	8.95		
	6	0.28	8.79		
	8	0.31	8.66		
	10	0.42	8.87		
45	2	0.10	8.68	8.41	0.75
	4	0.16	8.45		
	6	0.34	9.08		
	8	0.42	9.09		
	10	0.42	8.91		
55	2	0.17	9.23	9.39	-0.92
	4	0.23	8.93		
	6	0.26	8.67		
	8	0.35	8.83		
	10	0.38	8.73		

Table(50): Calculation of binding constant (K) of HEAA in frumkin equation in 0.1M HNO_3 for Spheroidized L.C.V.steel sample at various temperatures

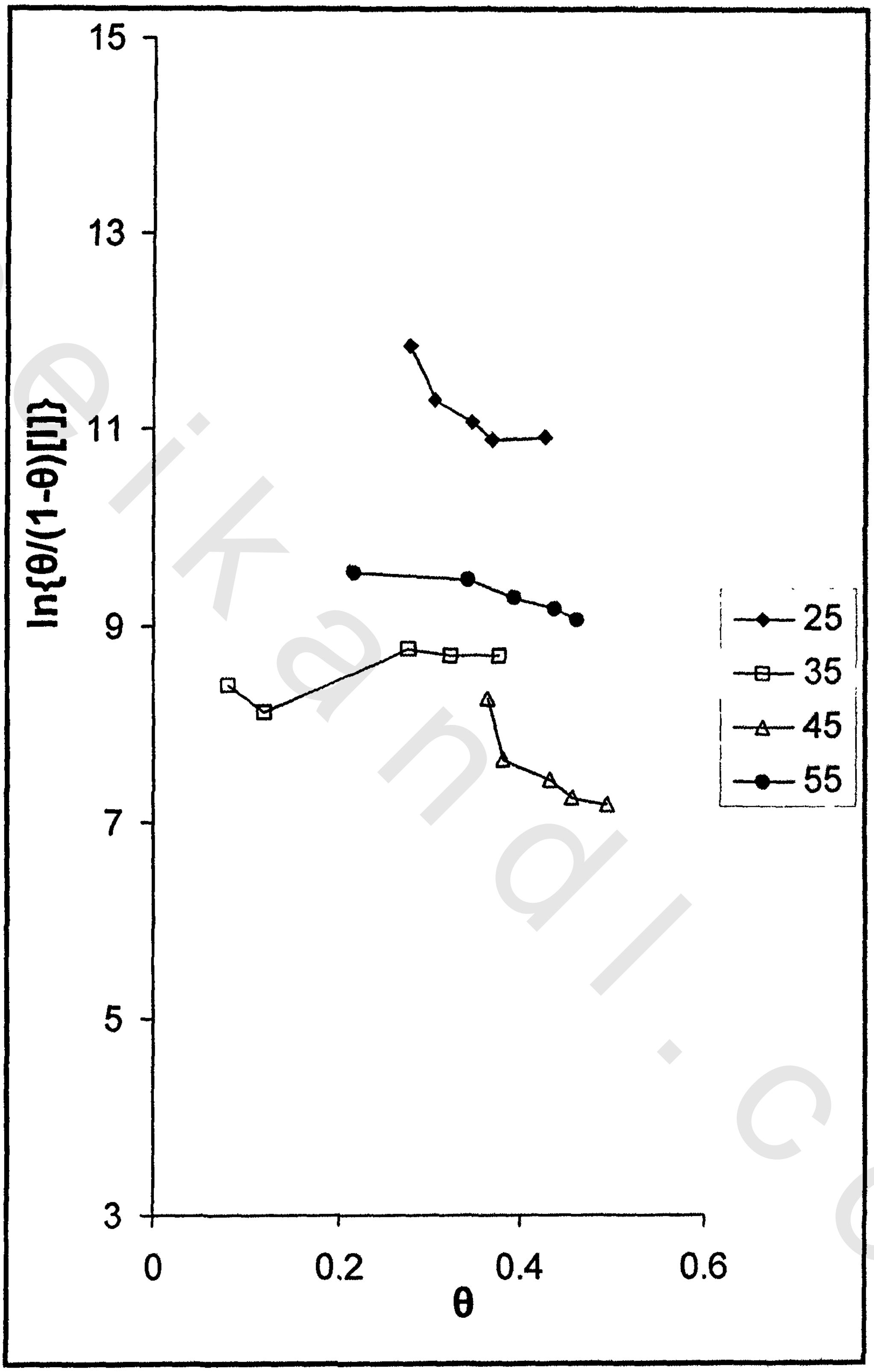
t °C	$[I]\times10^5$ M	θ	$\ln\{\theta/(1-\theta)[I]\}$	lnK	a
25	2	0.27	9.89	13.29	-6.49
	4	0.30	9.27		
	6	0.32	8.99		
	8	0.34	8.77		
	10	0.37	8.66		
35	2	0.05	7.99	8.03	0.45
	4	0.14	8.29		
	6	0.18	8.21		
	8	0.23	8.22		
	10	0.27	8.23		
45	2	0.29	9.92	12.50	-4.69
	4	0.32	9.39		
	6	0.34	9.08		
	8	0.39	8.97		
	10	0.40	8.79		
55	2	0.02	6.91	7.15	2.52
	4	0.18	8.64		
	6	0.29	8.85		
	8	0.31	8.64		
	10	0.38	8.72		

Table(51):Calculation of binding constant (K)of HEAA in frumkin equation in 0.1M HNO_3 for Quenched L.C.V. steel sample at various temperatures

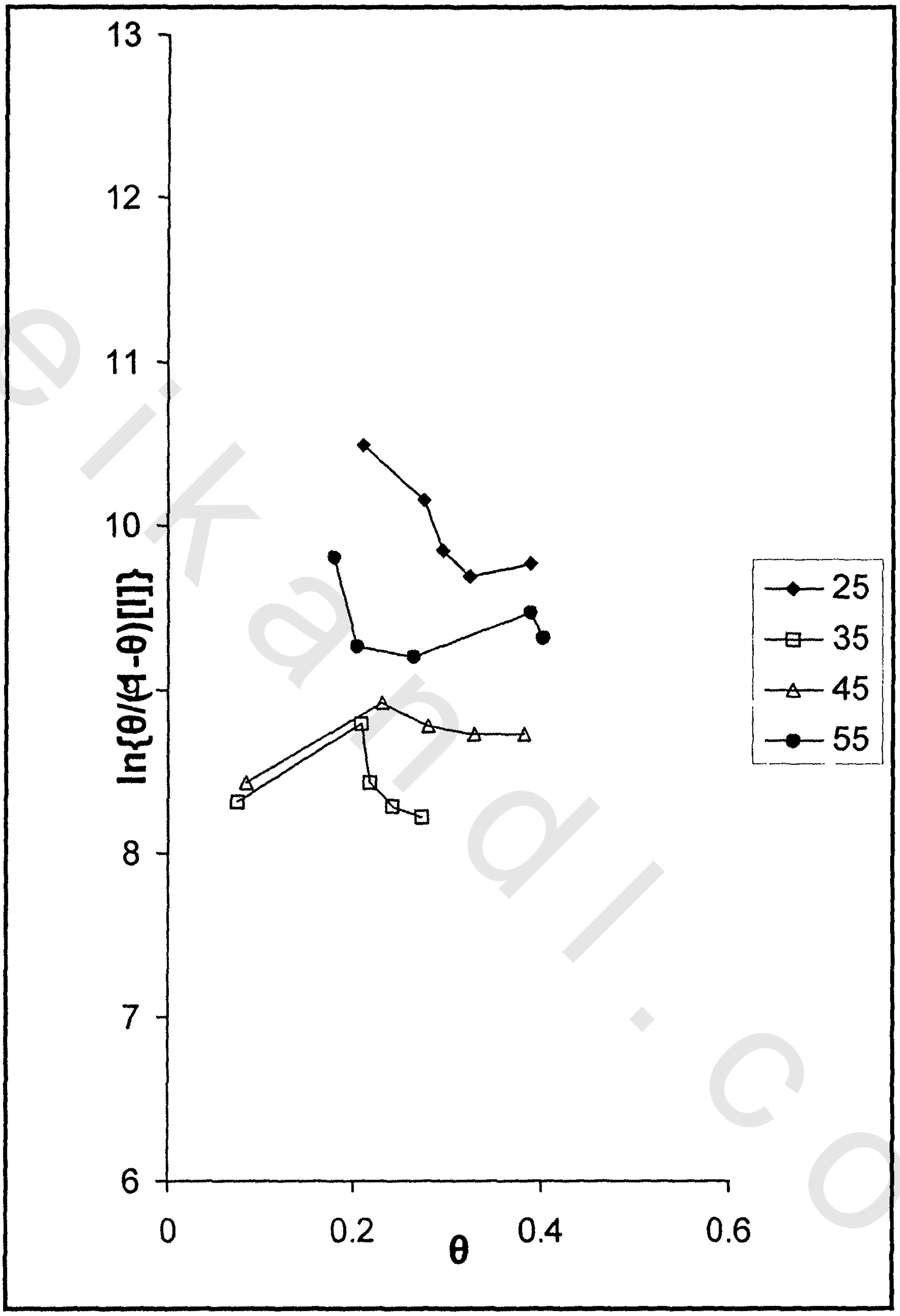
t °C	$[I]\times10^5$ M	θ	ln{θ/(1-θ)[I]}	lnK	a
25	2	0.28	9.86	12.09	-4.62
	4	0.29	9.22		
	6	0.32	8.95		
	8	0.36	8.87		
	10	0.37	8.68		
35	2	0.05	8.01	8.04	0.99
	4	0.18	8.60		
	6	0.27	8.73		
	8	0.30	8.61		
	10	0.33	8.51		
45	2	0.04	7.69	7.51	1.89
	4	0.08	7.72		
	6	0.33	9.01		
	8	0.41	9.06		
	10	0.41	8.86		
55	2	0.21	9.50	9.72	-0.54
	4	0.32	9.35		
	6	0.41	9.34		
	8	0.44	9.22		
	10	0.49	9.18		

Table(52): **Thermodynamic parameters of adsorption-desorption process for L.C.V. steel samples in 0.1M HNO_3 in presence of different concentrations of HEAA Calculated from equilibrium constant of frumkin equation.**

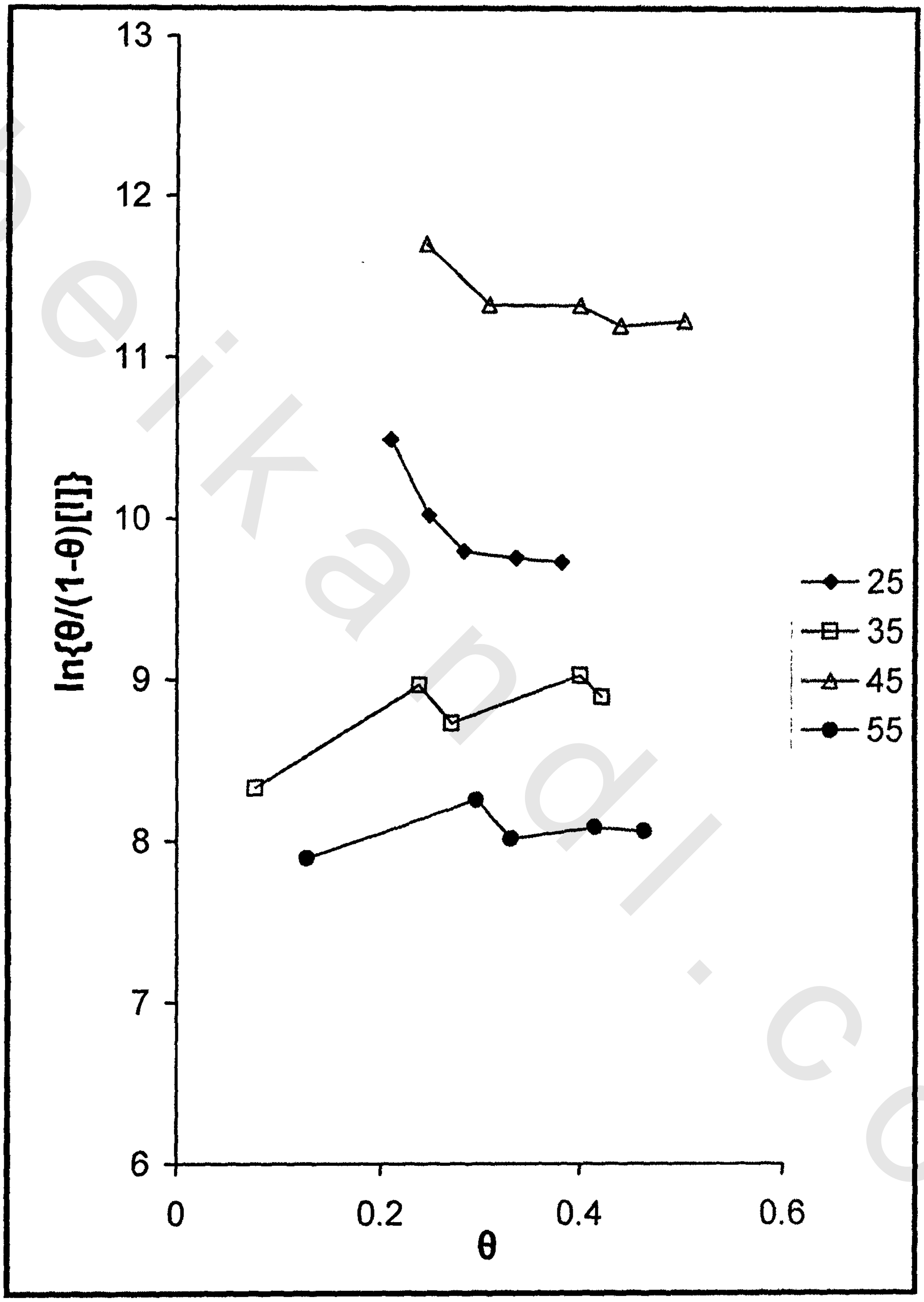
Sample	t °C	ln K	$-\Delta G^{\circ}$ KJ/mol	ΔH° KJ/mol	ΔS° J/mol.K
A	25	10.83	26.85	-203.64	-593.28
	35	9.26	23.71	-203.64	-584.21
	45	8.07	22.56	-203.64	-569.44
	55	7.46	20.34	-203.64	-558.85
N	25	10.79	26.75	-101.01	-249.19
	35	9.44	24.16	-101.01	-249.51
	45	8.41	22.23	-101.01	-247.75
	55	9.39	25.61	-101.01	-229.89
S	25	13.29	32.93	-261.21	-766.02
	35	8.03	20.57	-261.21	-781.30
	45	12.50	33.05	-261.21	-717.48
	55	7.15	19.50	-261.21	-736.919
Q	25	12.09	29.96	-150.53	-404.57
	35	8.04	20.59	-150.53	-421.87
	45	7.51	19.85	-150.53	-410.94
	55	9.72	26.51	-150.53	-378.08



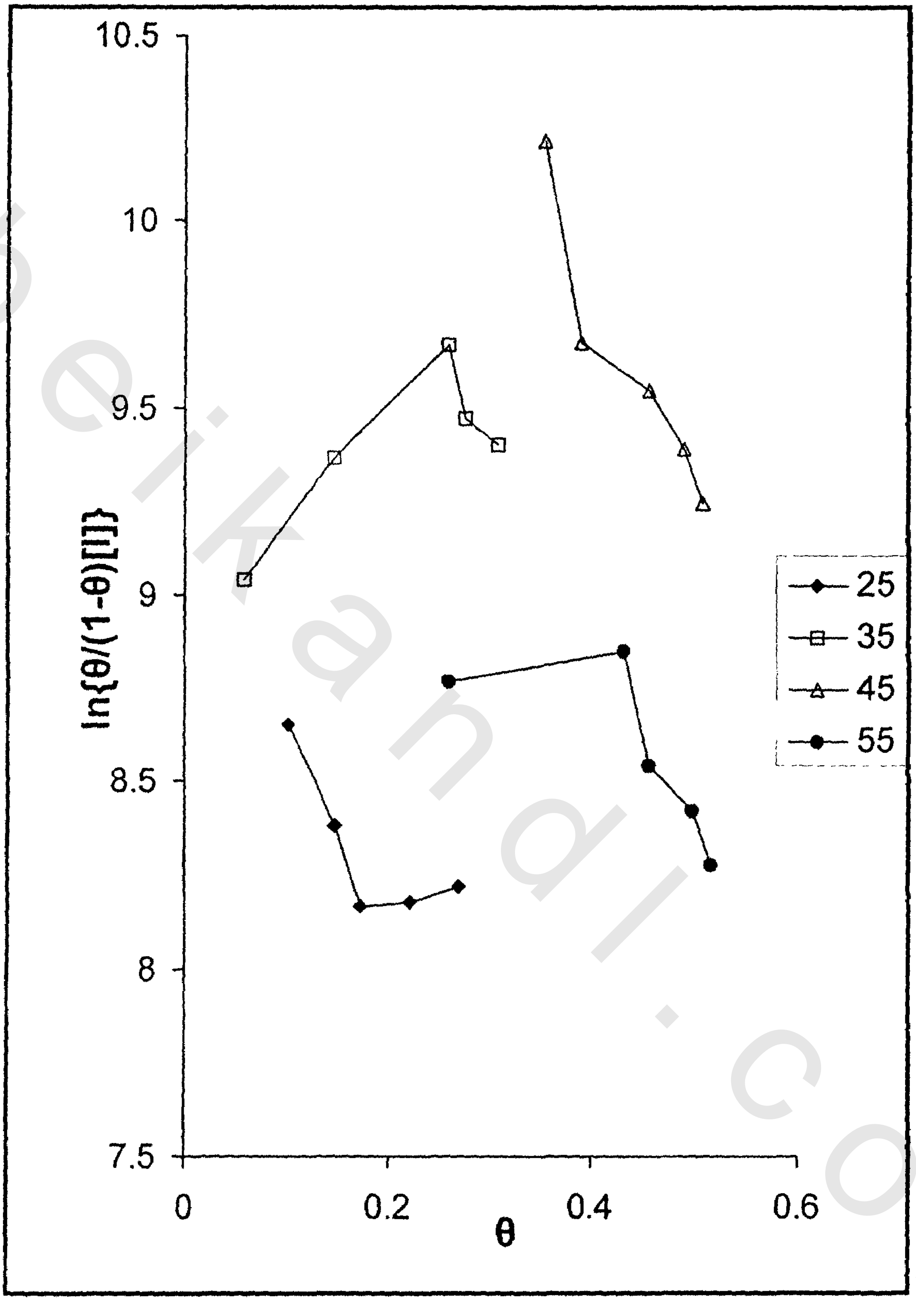
Fig(172): The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for As cast M.C.V. steel sample at various temperatures.



Fig(173): The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for Normalized M.C.V. steel sample at various temperatures.



Fig(174): The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for Spheroidized M.C.V. steel sample at various temperatures.



Fig(175): The relation between ln{θ/(1-θ)[I]} and (θ) in .1M HNO_3 in presence of different concentration of HEAA for Quenched M.C.V. steel sample at various temperatures.

Table(53):Calculation of binding constant (K)of HEAA in frumkin equation in 0.1M HNO_3 for As cast M.C.V. steel sample at various temperatures

t °C	[I]x10^5 M	θ	ln{θ/(1-θ)[I]}	lnK	a
25	2	0.28	9.86	11.26	-2.97
	4	0.30	9.30		
	6	0.35	9.08		
	8	0.37	8.89		
	10	0.43	8.91		
35	2	0.08	8.39	8.11	0.88
	4	0.12	8.11		
	6	0.28	8.76		
	8	0.32	8.69		
	10	0.37	8.69		
45	2	0.36	10.26	12.59	-3.58
	4	0.38	9.64		
	6	0.43	9.40		
	8	0.45	9.25		
	10	0.49	9.19		
55	2	0.22	9.53	10.00	-0.95
	4	0.34	9.46		
	6	0.39	9.29		
	8	0.44	9.18		
	10	0.46	9.05		

Table(54):Calculation of binding constant (K)of HEAA in frumkin equation in 0.1M HNO_3 for Normalized M.C.V. steel sample at various temperatures

t °C	$[I]\times10^5$ M	θ	ln{θ/(1-θ)[I]}	lnK	a
25	2	0.21	9.49	10.29	-2.16
	4	0.27	9.16		
	6	0.29	8.85		
	8	0.32	8.70		
	10	0.39	8.76		
35	2	0.07	8.31	8.43	-0.05
	4	0.21	8.79		
	6	0.22	8.43		
	8	0.24	8.29		
	10	0.27	8.23		
45	2	0.08	8.43	8.47	0.46
	4	0.23	8.92		
	6	0.28	8.78		
	8	0.33	8.72		
	10	0.38	8.73		
55	2	0.18	9.30	9.11	-0.36
	4	0.20	8.77		
	6	0.26	8.70		
	8	0.39	8.98		
	10	0.40	8.82		

Table(55):Calculation of binding constant (K)of HEAA in frumkin equation in 0.1M HNO_3 for Spheroidized M.C.V. steel sample at various temperatures

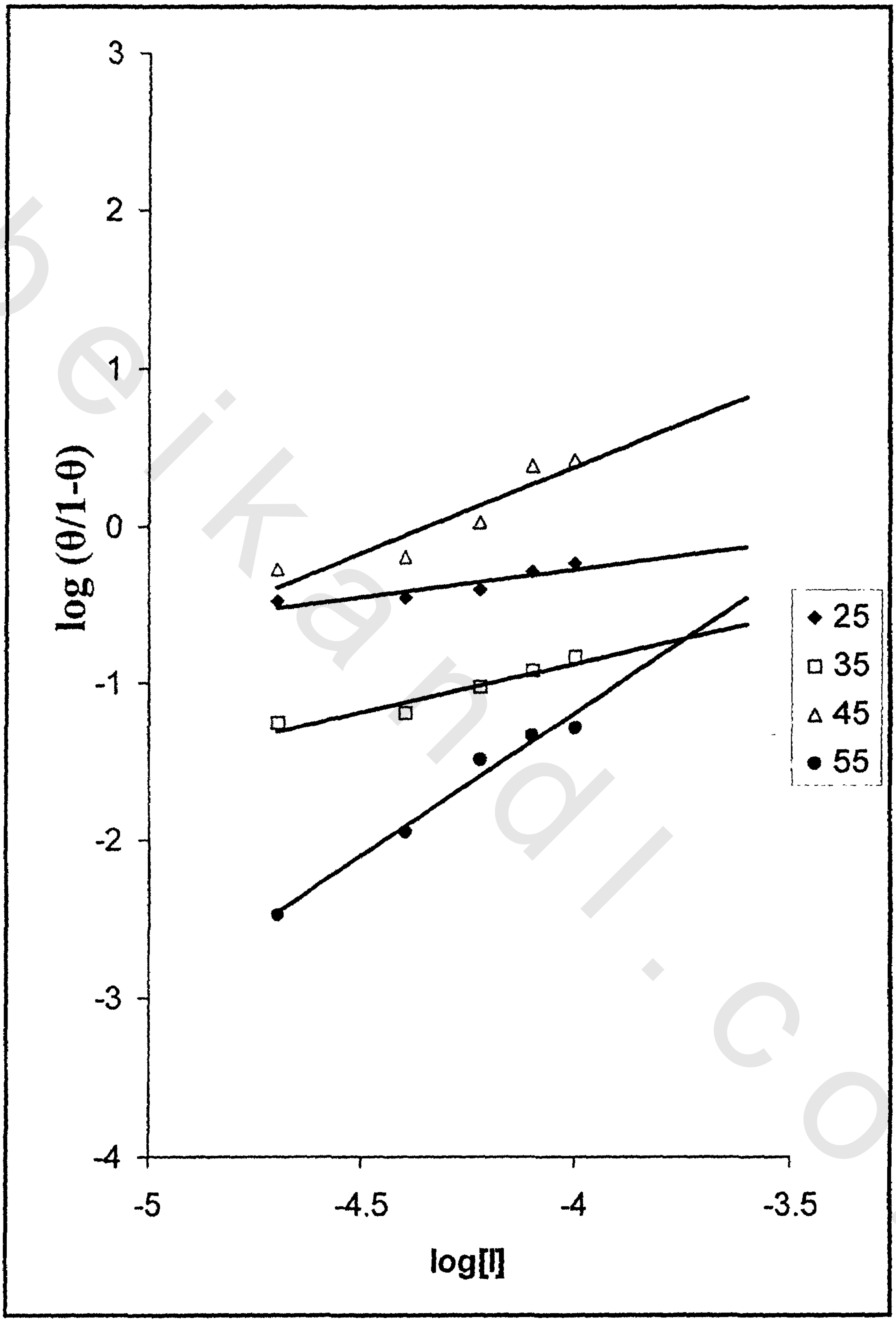
t °C	[I]x10^5 M	θ	ln{θ/(1-θ)[I]}	lnK	a
25	2	0.21	9.49	10.13	-2.00
	4	0.25	9.02		
	6	0.28	8.79		
	8	0.34	8.75		
	10	0.38	8.73		
35	2	0.08	8.33	8.32	0.83
	4	0.24	8.97		
	6	0.27	8.73		
	8	0.40	9.03		
	10	0.42	8.89		
45	2	0.24	9.70	9.99	-0.84
	4	0.31	9.32		
	6	0.40	9.31		
	8	0.44	9.19		
	10	0.50	9.22		
55	2	0.13	8.89	8.92	0.22
	4	0.30	9.26		
	6	0.33	9.02		
	8	0.41	9.09		
	10	0.46	9.06		

Table(56):Calculation of binding constant (K)of HEAA in frumkin equation in 0.1M HNO_3 for Quenched M.C.V. steel sample at various temperatures

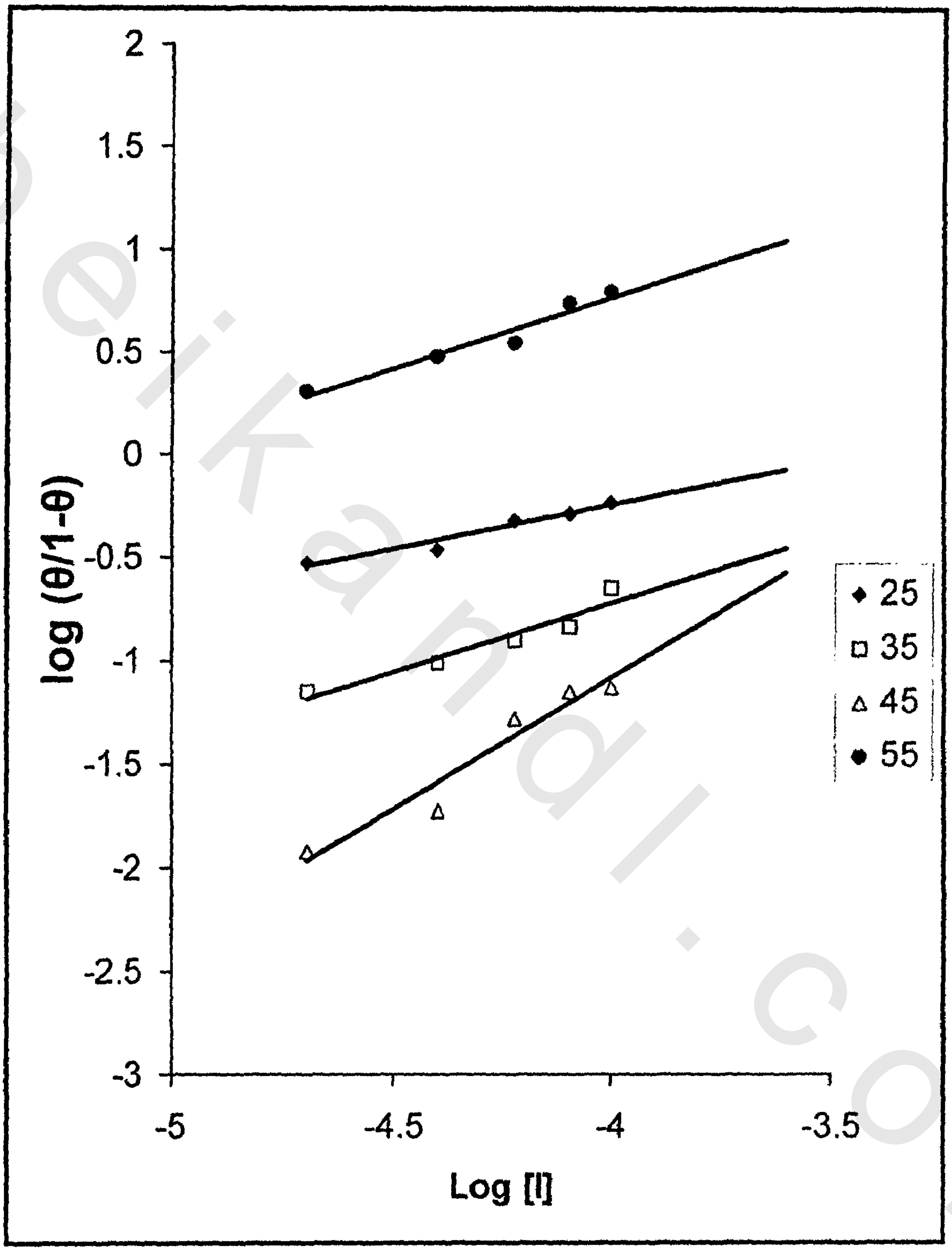
t °C	$[I]\times10^5$ M	θ	$\ln\{\theta/(1-\theta)[I]\}$	lnK	a
25	2	0.10	8.65	8.78	-1.25
	4	0.15	8.38		
	6	0.17	8.17		
	8	0.22	8.18		
	10	0.27	8.21		
35	2	0.06	8.04	8.03	0.86
	4	0.15	8.37		
	6	0.26	8.67		
	8	0.27	8.47		
	10	0.31	8.40		
45	2	0.35	10.22	11.95	-2.67
	4	0.39	9.67		
	6	0.46	9.54		
	8	0.49	9.39		
	10	0.51	9.24		
55	2	0.26	9.76	10.28	-0.82
	4	0.43	9.85		
	6	0.46	9.54		
	8	0.50	9.42		
	10	0.52	9.27		

Table(57):Thermodynamic parameters of adsorption-desorption process for M.C.V. steel samples in 0.1M HNO_3 in presence of different concentrations of HEAA Calculated from equilibrium constant of frumkin equation.

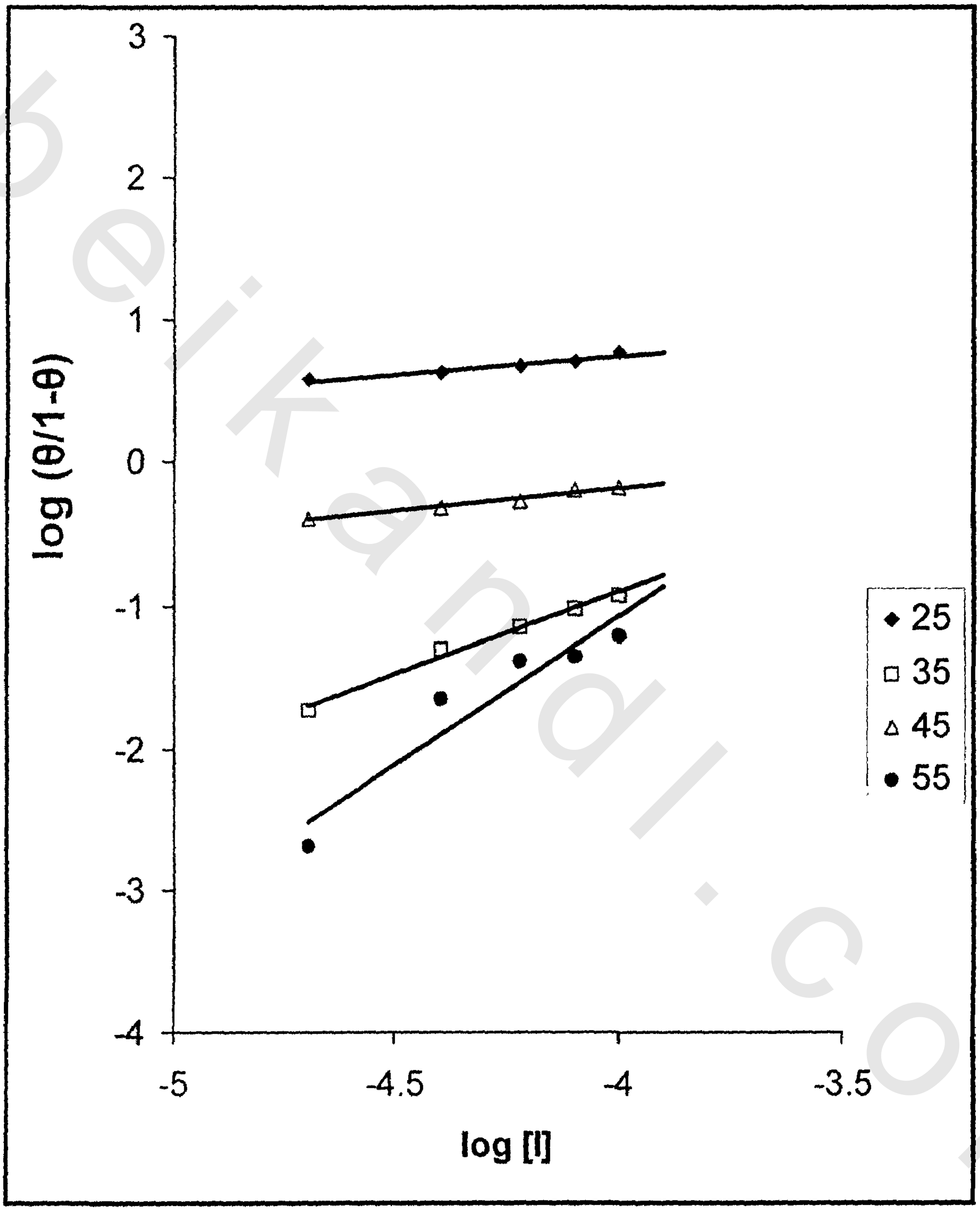
Sample	t °C	ln K	-ΔG° KJ/mol	ΔH° KJ/mol	ΔS° J/mol.K
A	25	11.26	27.89	12.58	135.84
	35	8.11	20.78	12.58	108.33
	45	12.59	33.30	12.58	144.31
	55	10.00	27.28	12.58	121.54
N	25	10.29	25.48	-67.98	-142.60
	35	8.43	21.59	-67.98	-150.59
	45	8.47	22.41	-67.98	-143.29
	55	9.11	24.85	-67.98	-131.48
S	25	10.13	25.09	-37.53	-41.73
	35	8.32	21.31	-37.53	-52.67
	45	9.99	26.41	-37.53	-34.98
	55	8.92	24.33	-37.53	-40.25
Q	25	8.78	21.75	158.80	605.89
	35	8.03	20.56	158.80	582.36
	45	11.95	31.61	158.80	598.79
	55	10.28	28.04	158.80	569.65



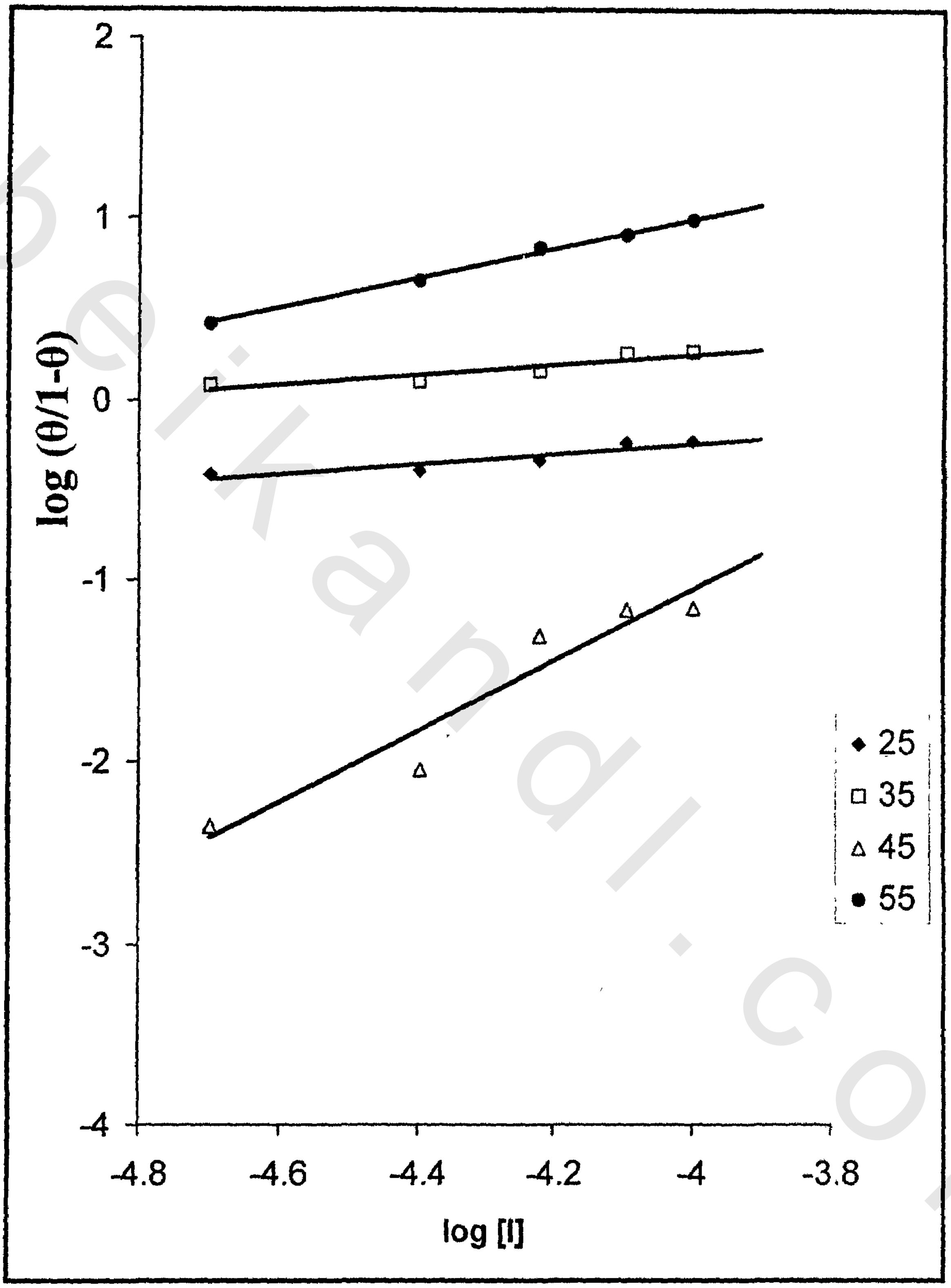
Fig(176):The relation between log (θ/1-θ) and log [I] in 0.1M HNO_3 for as cast L.C.V. steel sample at various temperatures.



Fig(177): The relation between log ($\theta/1-\theta$) and log [I]in 0.1M HNO_3 for normalized L.C.V. steel sample at various temperatures.



Fig(178):The relation between log (θ/1-θ) and log [I]in 0.1M HNO_3 for Spheroidized L.C.V. steel sample at various temperatures.



Fig(179):The relation between log (θ/1-θ) and log [I]in 0.1M HNO_3 for Quenched L.C.V. steel sample at various temperatures.

Table(58):Data of El-Awady thermodynamic model application for as cast L.C.V.steel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

t ^{0}C	[I]x10^5 M	-log [I]	-log(θ/1-θ)	log K	X
25	2	4.69	0.27	3.23	2.83
	4	4.39	0.48		
	6	4.22	0.45		
	8	4.09	0.41		
	10	4.00	0.28		
35	2	4.69	0.75	3.41	1.61
	4	4.39	0.68		
	6	4.22	0.51		
	8	4.09	0.41		
	10	4.00	0.33		
45	2	4.69	0.78	3.88	0.91
	4	4.39	0.70		
	6	4.22	0.48		
	8	4.09	0.12		
	10	4.00	0.07		
55	2	4.69	1.47	3.89	0.55
	4	4.39	0.94		
	6	4.22	0.48		
	8	4.09	0.32		
	10	4.00	0.27		

Table(59):Data of El-Awady thermodynamic model application for Normalized L.C.V. steel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

t^0C	$[I]x10^5$ M	-log [I]	-log (θ/1-θ)	log K	X
25	2	4.69	0.52	3.41	2.34
	4	4.39	0.46		
	6	4.22	0.33		
	8	4.09	0.29		
	10	4.00	0.24		
35	2	4.69	0.65	3.66	1.51
	4	4.39	0.51		
	6	4.22	0.40		
	8	4.09	0.33		
	10	4.00	0.15		
45	2	4.69	0.92	3.93	0.78
	4	4.39	0.72		
	6	4.22	0.28		
	8	4.09	0.14		
	10	4.00	0.13		
55	2	4.69	0.69	3.67	1.44
	4	4.39	0.51		
	6	4.22	0.45		
	8	4.09	0.26		
	10	4.00	0.21		

Table(60):Data of El-Awady thermodynamic model application for Spheroidized L.C.V. steel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

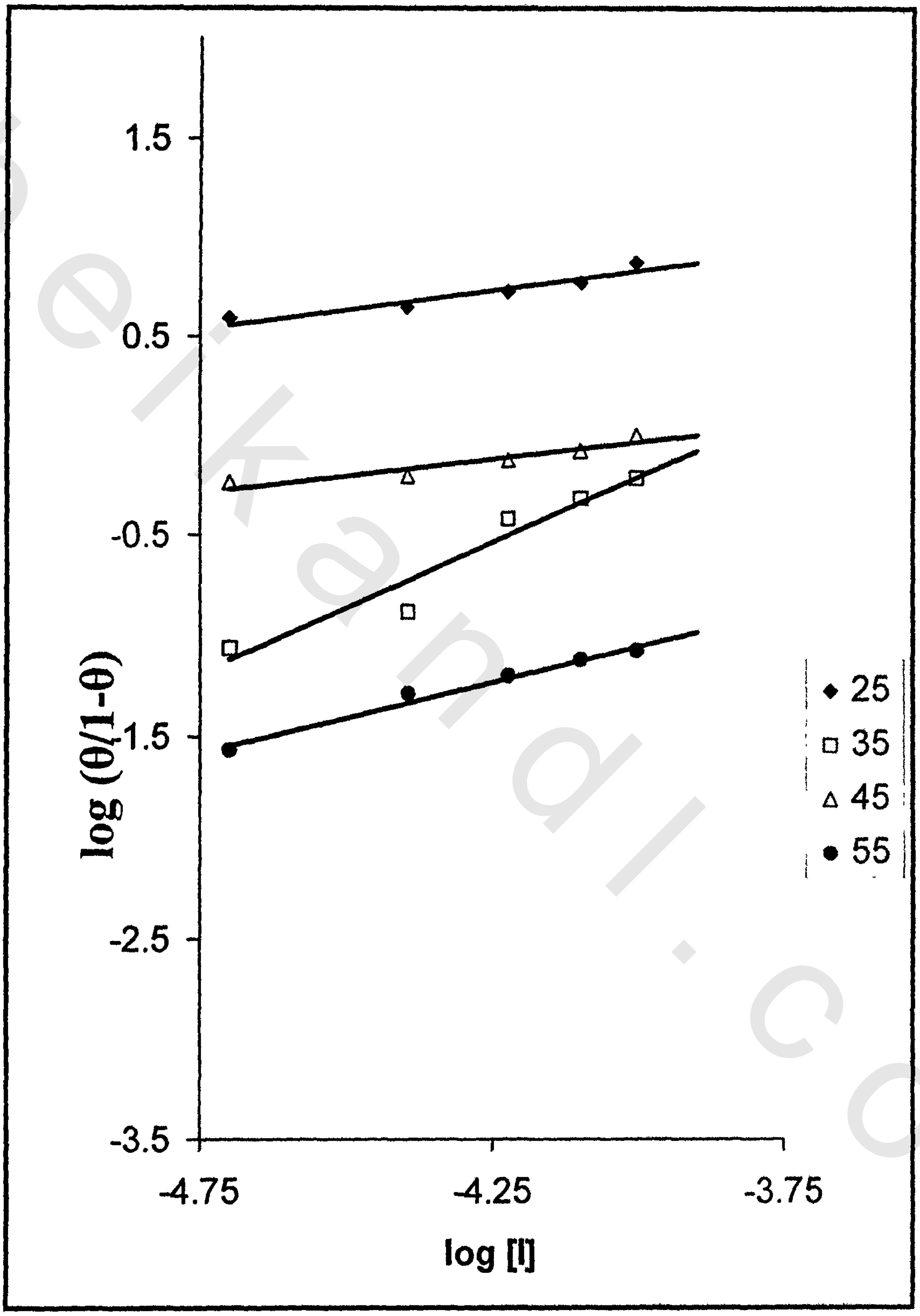
t °C	$[I]\times10^5$ M	-log [I]	-log (θ/1-θ)	log K	X
25	2	4.69	0.41	2.97	4.00
	4	4.39	0.36		
	6	4.22	0.31		
	8	4.09	0.28		
	10	4.00	0.23		
35	2	4.69	1.22	3.63	0.88
	4	4.39	0.79		
	6	4.22	0.65		
	8	4.09	0.52		
	10	4.00	0.42		
45	2	4.69	0.39	3.39	3.24
	4	4.39	0.31		
	6	4.22	0.27		
	8	4.09	0.19		
	10	4.00	0.18		
55	2	4.69	1.69	3.96	0.48
	4	4.39	0.64		
	6	4.22	0.37		
	8	4.09	0.34		
	10	4.00	0.21		

Table(61):Data of El-Awady thermodynamic model application for Quenched L.C.V. steel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

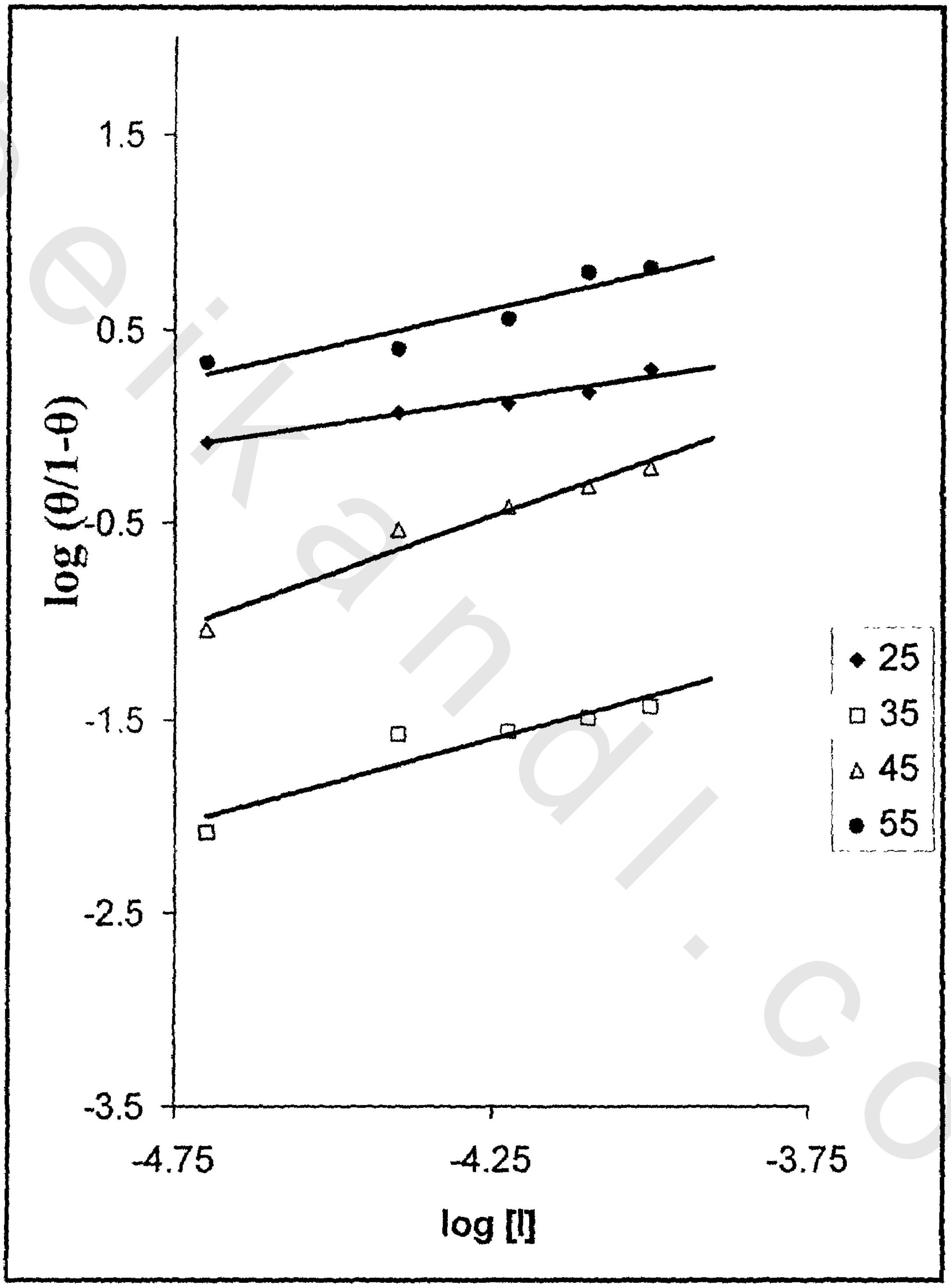
t °C	$[I]\times10^5$ M	-log [I]	-log (θ/1-θ)	log K	X
25	2	4.69	0.41	3.15	2.60
	4	4.39	0.35		
	6	4.22	0.27		
	8	4.09	0.23		
	10	4.00	0.12		
35	2	4.69	1.05	3.83	0.78
	4	4.39	0.87		
	6	4.22	0.41		
	8	4.09	0.32		
	10	4.00	0.22		
45	2	4.69	0.24	3.97	3.03
	4	4.39	0.21		
	6	4.22	0.12		
	8	4.09	0.08		
	10	4.00	0.01		
55	2	4.69	0.55	3.99	1.42
	4	4.39	0.28		
	6	4.22	0.18		
	8	4.09	0.11		
	10	4.00	0.07		

Table(62):Thermodynamic parameters of adsorption-desorption process for L.C.V. steel samples in 0.1M HNO_3 in presence of different concentrations of HEAA Calculated from equilibrium constant of El-Awady equation.

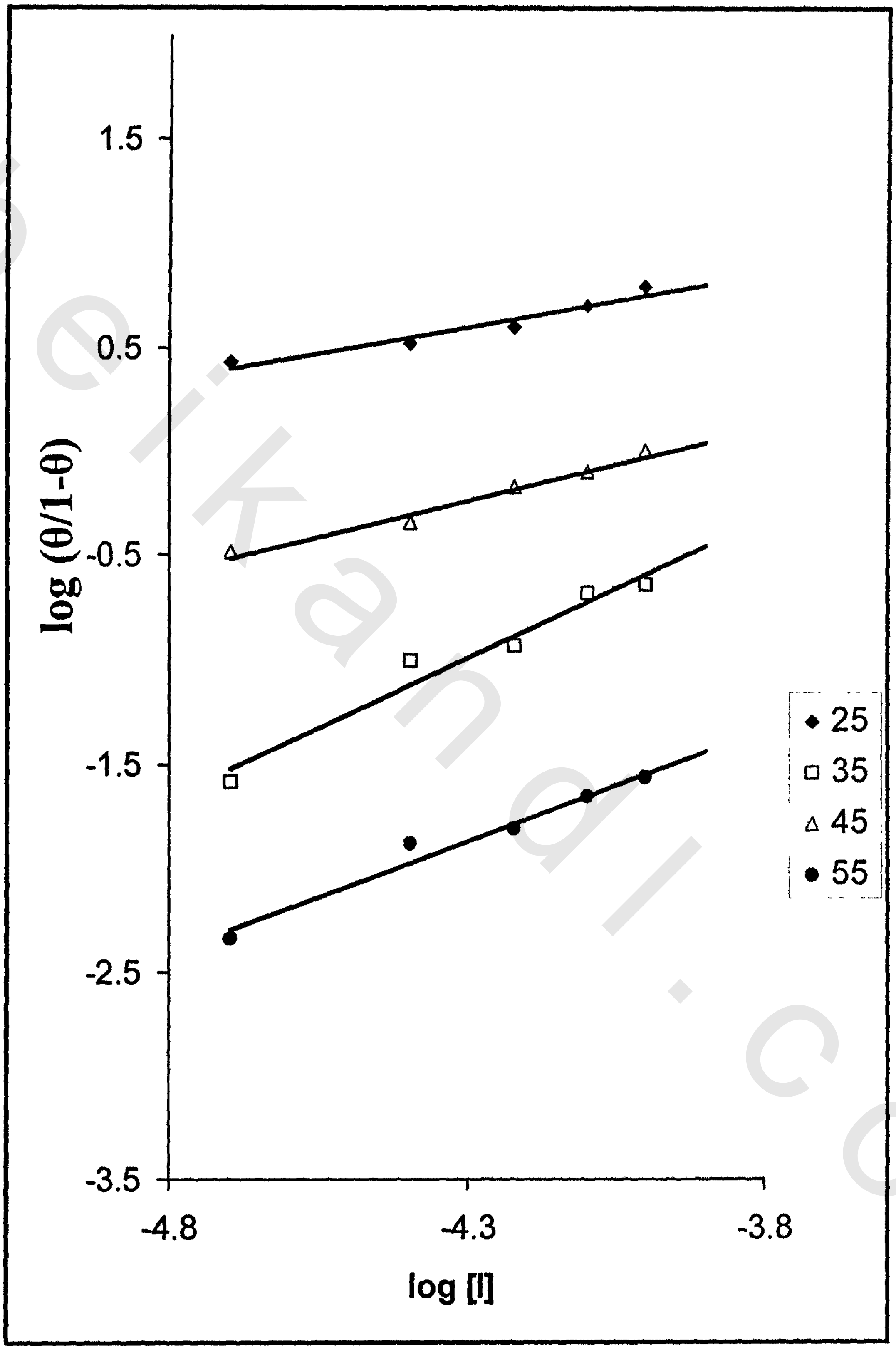
Sample	t °C	log K	- ΔG° KJ/mol	ΔH° KJ/mol	ΔS° J/mol.K
A	25	3.23	18.43	46.60	218.25
	35	3.41	20.11	46.60	216.63
	45	3.88	23.67	46.60	221.01
	55	3.89	24.48	46.60	216.74
N	25	3.41	19.47	19.95	132.28
	35	3.66	21.60	19.95	134.93
	45	3.93	23.96	19.95	138.10
	55	3.66	23.02	19.95	131.03
S	25	2.97	17.016	50.99	228.17
	35	3.63	21.46	50.99	235.25
	45	3.39	20.67	50.99	225.36
	55	3.96	24.91	50.99	231.44
Q	25	3.15	18.02	50.03	228.36
	35	3.83	22.62	50.03	235.89
	45	3.97	24.18	50.03	233.38
	55	3.99	25.06	50.03	228.94



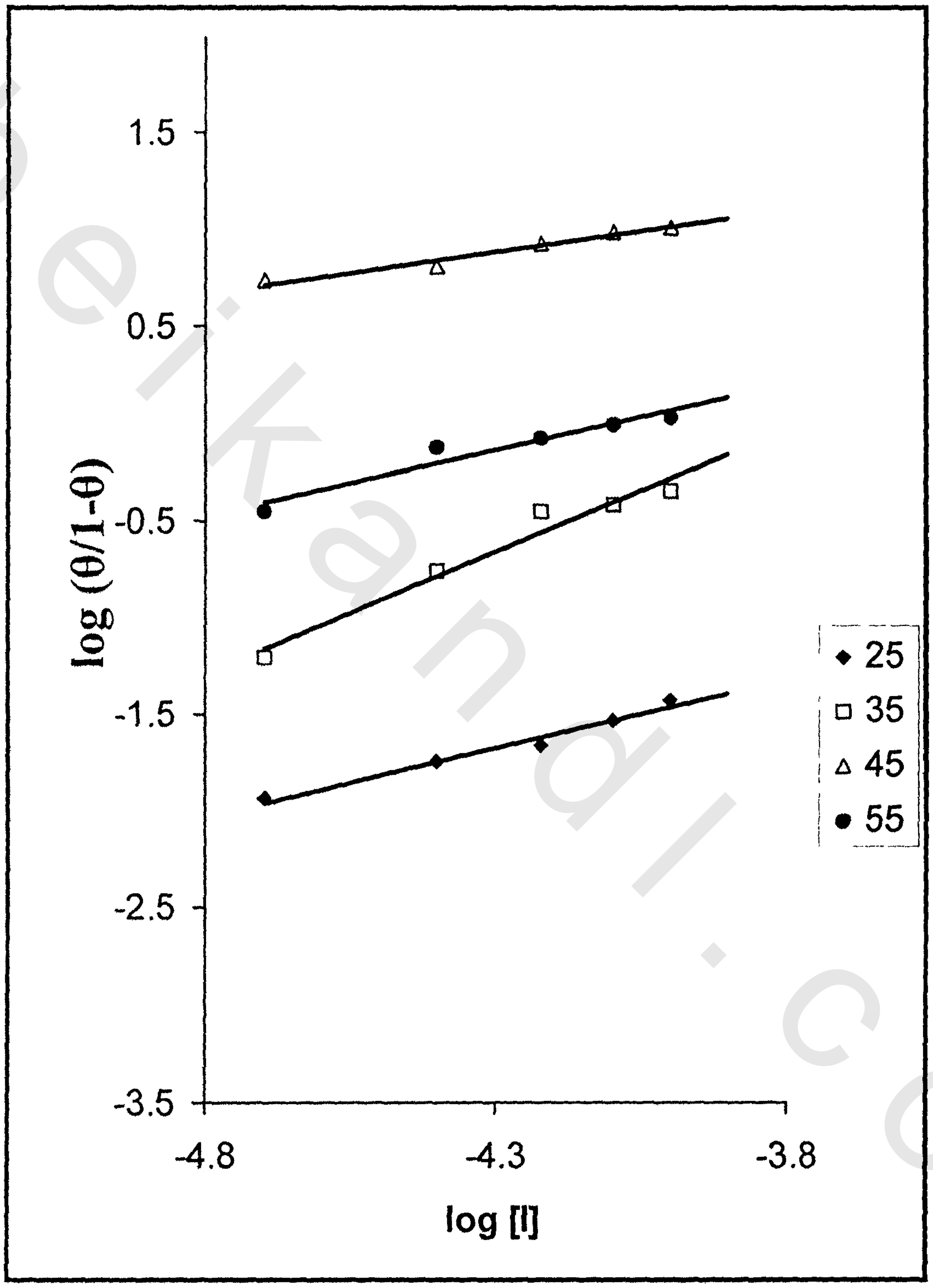
Fig(180):The relation between log (θ/1-θ) and log [I]in 0.1M HNO_3 for As cast M.C.V. steel sample at various temperatures.



Fig(181):The relation between log (θ/1-θ) and log [I] in 0.1M HNO_3 for Normalized M.C.V. steel sample at various temperatures.



Fig(182):The relation between log (θ/1-θ) and log [I] in 0.1M HNO_3 for Spheroidized M.C.V. steel sample at various temperatures.



Fig(183):The relation between log (θ/1-θ) and log [I] in 0.1M HNO_3 for Quenched M.C.V. steel sample at various temperatures.

Table(63):Data of El-Awady thermodynamic model application for As cast M.C.Vsteel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

t °C	[I]x10^5 M	-log [I]	-log (θ/1-θ)	log K	X
25	2	4.69	0.94	3.55	2.61
	4	4.39	0.75		
	6	4.22	0.67		
	8	4.09	0.54		
	10	4.00	0.43		
35	2	4.69	1.20	3.83	0.78
	4	4.39	0.76		
	6	4.22	0.45		
	8	4.09	0.41		
	10	4.00	0.35		
45	2	4.69	0.26	3.87	3.03
	4	4.39	0.19		
	6	4.22	0.07		
	8	4.09	0.02		
	10	4.00	-0.01		
55	2	4.69	0.45	3.93	1.42
	4	4.39	0.11		
	6	4.22	0.07		
	8	4.09	0.01		
	10	4.00	-0.02		

Table(64):Data of El-Awady thermodynamic model application for Normalized M.C.V. steel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

t °C	$[I] \times 10^5$ M	-log [I]	-log (θ/1-θ)	log K	X
25	2	4.69	0.57	3.52	2.02
	4	4.39	0.41		
	6	4.22	0.37		
	8	4.09	0.31		
	10	4.00	0.19		
35	2	4.69	1.08	3.57	1.12
	4	4.39	0.57		
	6	4.22	0.55		
	8	4.09	0.49		
	10	4.00	0.42		
45	2	4.69	1.03	3.85	0.87
	4	4.39	0.52		
	6	4.22	0.41		
	8	4.09	0.30		
	10	4.00	0.20		
55	2	4.69	0.65	3.74	1.32
	4	4.39	0.59		
	6	4.22	0.44		
	8	4.09	0.19		
	10	4.00	0.17		

Table(65):Data of El-Awady thermodynamic model application for Spheroidized M.C.V. steel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

t °C	$[I]\times10^5$ M	-log [I]	-log (θ/1-θ)	log K	X
25	2	4.69	0.57	3.94	1.95
	4	4.39	0.48		
	6	4.22	0.40		
	8	4.09	0.29		
	10	4.00	0.20		
35	2	4.69	1.08	3.97	0.74
	4	4.39	0.50		
	6	4.22	0.42		
	8	4.09	0.17		
	10	4.00	0.13		
45	2	4.69	0.48	3.96	1.42
	4	4.39	0.34		
	6	4.22	0.17		
	8	4.09	0.10		
	10	4.00	-0.01		
55	2	4.69	0.83	3.51	0.93
	4	4.39	0.37		
	6	4.22	0.30		
	8	4.09	0.14		
	10	4.00	-0.06		

Table(66):Data of El-Awady thermodynamic model application for Quenched M.C.V. steel sample in 0.1M HNO_3 in presence of different concentrations of HEAA at various temperatures

t °C	[I]x10^5 M	-log [I]	-log (θ/1-θ)	log K	X
25	2	4.69	0.94	3.32	1.43
	4	4.39	0.75		
	6	4.22	0.67		
	8	4.09	0.54		
	10	4.00	0.43		
35	2	4.69	1.20	3.77	0.79
	4	4.39	0.76		
	6	4.22	0.45		
	8	4.09	0.41		
	10	4.00	0.35		
45	2	4.69	0.26	4.02	2.40
	4	4.39	0.19		
	6	4.22	0.07		
	8	4.09	0.02		
	10	4.00	0.01		
55	2	4.69	0.45	4.10	1.47
	4	4.39	0.11		
	6	4.22	-0.07		
	8	4.09	-0.01		
	10	4.00	0.02		

Table(67):Thermodynamic parameters of adsorption-desorption process for M.C.V. steel samples in 0.1M HNO_3 in presence of different concentrations of HEAA Calculated from equilibrium constant of El-Awady equation.

Sample	t °C	log K	- ΔG° KJ/mol	ΔH° KJ/mol	ΔS° J/mol.K
A	25	3.55	20.24	22.95	144.92
	35	3.83	22.59	22.95	147.86
	45	3.87	23.60	22.95	146.39
	55	3.93	24.72	22.95	145.33
N	25	3.52	20.08	17.44	125.93
	35	3.57	21.09	17.44	125.09
	45	3.85	23.44	17.44	128.55
	55	3.74	23.47	17.44	124.71
S	25	3.94	22.46	-23.20	-2.49
	35	3.97	23.39	-23.20	0.61
	45	3.96	24.11	-23.20	2.85
	55	3.51	22.07	-23.20	-3.44
Q	25	3.32	18.97	48.33	225.86
	35	3.77	22.26	48.33	229.22
	45	4.02	24.49	48.33	229.01
	55	4.10	25.73	48.33	225.79

Recommendations

(A) Recommendation of applying the above three heat treatment regimes (normalizing, quenching and spheroidizing) on two types of carbon vanadium steel for the following causes:

1. **The heat treatment regimes are changing of microstructure for metal samples and resist the corrosion processes.**
2. **The resistance of corrosion is large in case of *spheroidizing* (L.C.V. and M.C.V.steel) samples**
3. **The martensitic surfaces of (L.C.V. or M.C.V.steel samples) are the best suitable surfaces when using HEAA as inhibitor.**
4. **The activation energy values of the normalizing samples for (L.C.V. and M.C.V.steel samples) in presence and absence of the inhibitor are higher than those of the other samples.**
5. **The adsorption processes of inhibitor on surfaces of heat treated samples are strongly than unheated treatment samples.**

(B) Recommendation of using N,N di hydroxyethyl acryl amid (HEAA) as a corrosion inhibitor for the following causes:

1. **The structure of HEAA has all the advantage of the efficiency inhibitor such as unsaturated bond, C=O group, nitrogen atom and tow alcoholic groups. These characteristic group of the inhibitor as well as the large molecule of this organic compound increase the property of adsorption and the surface coverage.**
2. **The activation energy values for solutions with HEAA inhibitor are higher than those for without inhibitor.**
3. **The adsorption processes of HEAA molecule on surfaces of L.C.V. and M.C.V.steel samples are mixed (physical and chemical) adsorption.**

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ARABIC SUMMARY

جامعة الأزهر
كلية العلوم
قسم الكيمياء

دراسات ديناميكية حرارية لبعض العمليات الكهروكيميائية في المحاليل المختلفة

رسالة مقدمة
من
حسن حفني حسن حفني
بكالوريوس علوم ـ كيمياء خاصة (٢٠٠٢)

إلى
قسم الكيمياء ـ كلية العلوم
جامعة الأزهر

لاستكمال متطلبات الحصول على درجة الماجستير
في الكيمياء

تحت إشراف

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كلية العلوم ـ جامعة الأزهر
القاهرة

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٢٠٠٦

بسم الله الرحمن الرحيم

سبحانك لا علم لنا إلا ما علمتنا إنك أنت العليم الحكيم

صدق الله العظيم

جامعة الأزهر ـ كلية العلوم (بنين)

الدراسات العليا والبحوث

اسم مقدم الرسالة : ....

في موضوع : ....

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لجنة الإشراف

١ـ أ . د .... الوظيفة : .... التوقيع ....

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المختص ( )   شئون التعليم ( )   مدير إدارة الكلية ( )

عميد الكلية

( )

الملخص العربى

الملخص العربي

تتناول هذه الرسالة دراسات ديناميكية حرارية لبعض العمليات الكهروكيميائية في المحاليل المختلفة ومن هذه العمليات الكهروكيميائية عمليات تآكل صلب الفناديوم المنخفض والمتوسط الكربون في محاليل مائية من حمض النيتريك ذات التركيزات المختلفة في درجات الحرارة المختلفة، و يدخل صلب الفناديوم الكربوني في صناعة حديد التسليح المستخدم في إنشاء مواسير الصرف الصحي الخرسانية والتي يمر بها محاليل حمضية، مما يجعل الصلب داخل المواسير عرضة للتآكل .

وتهدف هذه الرسالة إلى دراسة مقاومة التآكل لصلب الفناديوم بطريقتين:

أولا: تغيير الشكل البنائي لنوعي صلب الفناديوم بإجراء المعالجة الحرارية لهما بثلاثة أساليب مختلفة وهي المراجعة (Normalizing)، والتصلد (Quenching)، والتخمر التكويري(Spheroidizing)، وبذلك نحصل على ثماني عينات تكون محلا للدراسة اثنتين منها غير معالجتين حراريا واحدة لصلب الفناديوم منخفض الكربون والأخرى لمتوسط الكربون وست معالجة حراريا ثلاثة لمنخفض الكربون وثلاثة لمتوسط الكربون.

ثانيا: تثبيط التآكل بالمركب العضوي (ثنائي هيدروكسي إيثيل أكريل أميد) عند تركيزات مختلفة لجميع العينات المستخدمة في الدراسة .

وتشتمل الرسالة على الآتي:

الباب الأول : المقدمة

وتتناول المقدمة خلفية تاريخية عن ظاهرة التآكل وفكرة عامة عن عمليات التآكل ، وعرض أنواع التآكل وخاصة أنواع التآكل المعدني، وأيضا عرض الطرق المختلفة لقياس معدلات التآكل ، ثم استعراض أساسيات علم الميتالورجي، واستعراض بعض أنواع المثبطات الهامة لعمليات التآكل، وأيضا أهم الأبحاث والدراسات المنشورة حديثا في المجلات والدوريات العلمية عن تآكل صلب الفناديوم بنوعيه في الأوساط والظروف المختلفة.

الباب الثاني: الجزء المعملي

ويتناول الوصف الدقيق لجميع المواد والمحاليل المستخدمة في الرسالة وكيفية تحضيرها، ووصف التركيب الكيميائي لنوعي صلب الفناديوم وأساليب المعالجة الحرارية لهما وشرح خطوات تجهيز العينة قبل القياس، ووصف التقنية المستخدمة في قياس

معدلات التآكل وهي تقنية الاستقطاب الكاثودي- الأنودي ووصف الجهاز المستخدم لهذه التقنية.

والعينات التي تمي دراستها هي:

١. صلب الفناديوم منخفض الكربون غير المعالج حراريا (LA).
٢. صلب الفناديوم متوسط الكربون غير المعالج حراريا (MA).
٣. صلب الفناديوم منخفض الكربون المعالج حراريا بواسطة المراجعة (LN).
٤. صلب الفناديوم منخفض الكربون المعالج حراريا بواسطة التصلد (LQ).
٥. صلب الفناديوم منخفض الكربون المعالج حراريا بواسطة التخمر التكويري(LS).
٦. صلب الفناديوم متوسط الكربون المعالج حراريا بواسطة المراجعة (MN).
٧. صلب الفناديوم متوسط الكربون المعالج حراريا بواسطة التصلد (MQ).
٨. صلب الفناديوم متوسط الكربون المعالج حراريا بواسطة التخمر التكويري(MS).

حيث تم إجراء القياسات اللازمة على هذه العينات في أوساط مختلفة التركيزات من حمض النيتريك ، وهي (٠,١ ، ٠,٣ ، ٠,٥ مولاري) عند درجات حرارة مختلفة (٢٥ ، ٣٥ ، ٤٥ ، ٥٥°م)

كما تم إجراء القياسات أيضا على نفس العينات في تركيز ٠,١ مولاري من حمض النيتريك وتركيزات مختلفة من المركب العضوي ثنائي هيدروكسي إيثيل أكريل أميد (٢×١٠$^{-٥}$، ٤×١٠$^{-٥}$، ٦×١٠$^{-٥}$، ٨×١٠$^{-٥}$ ، ١٠$^{-٤}$ مولاري) عند نفس درجات الحرارة السابقة .

الباب الثالث: النتائج و مناقشتها

ويشمل النتائج التي تم الحصول غليها وتقييمها ومناقشتها والتعليق عليها ، وقد تم تسجيل هذه النتائج إما في جداول أو أشكال بيانية أو على هيئة صور فوتوغرافية كالتي أخذت لعينات صلب الفناديوم الكربوني المنخفض والمتوسط قبل وبعد المعالجة الحرارية .

ويمكن استعراض النتائج ومناقشتها وتقييمها كالتالي:

أولا: السلوك التآكلي لعينات صلب الفناديوم في محاليل مختلفة التركيز من حمض النيتريك

لقد بينت النتائج أن معدلات التآكل لجميع عينات صلب الفناديوم المنخفض والمتوسط الكربون المعالج وغير المعالج حراريا تزداد بزيادة تركيز حمض النيتريك كما في الترتيب التالي (٠,٥>٠,٣>٠,١ مولاري) وذلك بسبب ازدياد أيونات الهيدروجين الموجبة (متفاعلات الكاثود) ، وقد بينت النتائج أيضا أن معدلات التآكل للعينات الغير المعالجة حراريا أعلى من معدلات التآكل للعينات المعالجة حراريا كما في الترتيب التالي

(A>Q>N>S) ويرجع هذا إلى أن المعالجة الحرارية غيرت من الشكل البنائي للعينات وجعلتها أكثر مقاومة للتآكل.

وقد أوضحت النتائج أيضا أن معدلات التآكل لعينات منخفض الكربون أعلى من معدلات التآكل لعينات متوسط الكربون.

ثانيا: تأثير درجات الحرارة على السلوك التآكلي لعينات صلب الفناديوم

لقد تم دراسة السلوك التآكلي لعينات صلب الفناديوم في درجات الحرارة (٢٥ ، ٣٥ ، ٤٥ ، ٥٥ ^{0}م)

وقد أوضحت النتائج أنه عند زيادة درجات الحرارة فإن معدلات التآكل تزداد لجميع العينات التي تمت دراستها كما في الترتيب التالي (٥٥ > ٤٥ > ٣٥ > ٢٥ ^{0}م) .

ثالثا: كفاءة مادة ثنائي هيدروكسي إيثيل أكريل أميد كعامل مثبط على السلوك التآكلي لعينات صلب الفناديوم

لقد تم دراسة معدلات التآكل لعينات صلب الفناديوم في محلول ٠,١ مولاري من حمض النيتريك وتركيزات مختلفة من مادة ثنائي هيدروكسي إيثيل أكريل أميد (٢×١٠^{-٥}، ٤×١٠^{-٥}، ٦×١٠^{-٥}، ٨×١٠^{-٥}، $١٠^{-٤}$ مولاري) عند نفس درجات الحرارة السابقة .

وقد أوضحت النتائج أنه بزيادة تركيز مادة ثنائي هيدروكسي إيثيل أكريل أميد تقل معدلات التآكل وذلك لجميع العينات المدروسة طبقا للترتيب التالي (٢×١٠^{-٥} > ٤×١٠^{-٥} > ٦×١٠^{-٥} > ٨×١٠^{-٥} > $١٠^{-٤}$ مولاري) ، مما يدل على الفعل المثبط لهذه المادة على عمليات التآكل لصلب الفناديوم منخفض ومتوسط الكربون المعالج والغير معالج حراريا .

أيضا بينت النتائج أن كفاءة مادة ثنائي هيدروكسي إيثيل أكريل أميد كعامل مثبط تزداد بزيادة تركيز هذه المادة مما يدل على زيادة ادمصاص هذه المادة على أسطح العينات المدروسة ، حيث أن زوج الإلكترونات الحر الموجود على ذرتي النيتروجين والأكسجين بجانب الرابطة الثنائية يعملا على زيادة قدرة ادمصاص هذه المادة على الأسطح وتكوين طبقة عازلة تقاوم التآكل .

رابعا: طاقة التنشيط (E^*)

لقد تم حساب طاقة التنشيط لجميع المحاليل التي استخدمت في الدراسة سواء في وجود العامل المثبط أوفي عدم وجوده ، وقد أثبتت النتائج ما يلي:

١. بالنسبة لعينات صلب الفناديوم منخفض الكربون ، فإن طاقة التنشيط سجلت أعلى قيم لها في حالة عينة المراجعة (LN) عن العينات الأخرى سواء في وجود العامل المثبط أو في عدم وجوده ، كما أن قيم طاقة التنشيط في وجود العامل المثبط لنفس العينة كانت أعلى من قيمها في عدم وجوده.

٢. بالنسبة لعينات صلب الفناديوم متوسط الكربون ، فإن طاقة التنشيط سجلت أعلى قيمة لها في حالة عينة التصلد (MQ) عن العينات الأخرى وذلك في عدم وجود العامل المثبط ، أما في وجود العامل المثبط كانت قيم طاقة التنشيط في حالة عينة المراجعة (MN) أعلى عن قيمها في العينات الأخرى.

ومن ذلك نستدل على أن المعالجة الحرارية تعمل على زيادة طاقة التنشيط ، وبالتالي فإنها تقلل من معدلات التآكل .

خامسا: معاملات الديناميكا الحرارية لعملية الادمصاص

تتوقف عمليات الادمصاص على عدة عوامل ، من أهمها: تركيب المثبط ، ونوع المعدن ، وطبيعة سطحه ، وطبيعة وسط التآكل ، ودرجة الحرارة.
وتوجد عدة علاقات رياضية مختلفة مقترحة لمناقشة النتائج من خلال معاملات الديناميكا الحرارية لعمليات الادمصاص ، ومن أهم هذه العلاقات:

١. معادلة لانجماير

لقد تم حساب معاملات الديناميكا الحرارية القياسية ($\Delta G^\circ, \Delta H^\circ$, and ΔS°) لعمليات الادمصاص بواسطة معادلة لانجماير لجميع العينات المدروسة.

ولقد أثبتت النتائج التي تم الحصول عليها أن قيم ΔG° لجميع عينات صلب الفناديوم المنخفض والمتوسط الكربون المعالج والغير معالج حراريا جميعها قيم سالبة ، مما يدل على أن عمليات الادمصاص تمت بصورة تلقائية ، ويؤكد ذلك أن قيم ΔS° لجميع العينات المدروسة قيم موجبة ، كما أثبتت النتائج أيضا
أن قيم ΔH° لجميع العينات قيم موجبة مما يدل على أن عمليات الادمصاص عمليات ماصة للحرارة ،

٢. معادلة فرومكين

لقد تم الحصول على معاملات الديناميكا الحرارية القياسية ($\Delta G^\circ, \Delta H^\circ$, and ΔS°) لعمليات الادمصاص بواسطة معادلة فرومكين لجميع العينات المدروسة.

لقد أثبتت النتائج أن عمليات الادمصاص لجميع العينات تتم بصورة تلقائية وذلك بسبب قيم ΔG^0 السالبة، وبالنسبة لقيم $\Delta S^\circ,\Delta H^\circ$ فكانت قيم سالبة في حالة عينات صلب الفناديوم منخفض الكربون و أيضا عينات (MN) ، (MS) من صلب الفناديوم متوسط

الكربون مما يدل على أن عمليات الادمصاص عمليات طاردة للحرارة وأن قيم$\Delta S°$ غير مواكبة لقيم $\Delta G°$ أي أن هذه الأسطح غير مناسبة لعمليات الادمصاص ، و بالنسبة لعينات صلب الفناديوم متوسط الكربون(MA) ، (MQ) فكانت قيم $\Delta S°,\Delta H°$ قيم موجبة مما يدل على أن عمليات الادمصاص على سطح البيرليت-الفيريت وسطح المارتينزيت ماصة للحرارة وقيم$\Delta S°$ متطابقة مع قيم$\Delta G°$ أي أن هذه الأسطح مناسبة لعمليات الادمصاص.

كما أن قيم العامل (a) تكون في معظم الحالات أقل من الصفر أو أقل من الواحد الصحيح مما يدل على ضعف عمليات الادمصاص

٣. معادلة العوضي

لقد تم الحصول على معاملات الديناميكا الحرارية القياسية ($\Delta G°$, $\Delta H°$, and $\Delta S°$) لعمليات الادمصاص بواسطة معادلة العوضي لجميع العينات المدروسة.

لقد أثبتت النتائج أن قيم $\Delta G°$ لجميع الأنظمة المدروسة سالبة مما يدل على تلقائية عمليات الادمصاص ويؤكد ذلك قيم $\Delta S°$ الموجبة لمعظم العينات ، كما أن قيم $\Delta H°$موجبة أيضا لجميع العينات ما عدا (MS) حيث تكون قيمة سالبة ، مما يدل على أن عمليات الادمصاص ماصة للحرارة لجميع العينات ما عدا (MS) حيث تكون طاردة للحرارة.

ومما يجدر الإشارة به أن قيم العامل (x) في معظم الحالات أكبر من أو تساوي الواحد الصحيح مما يدل على قوة عمليات الادمصاص.

ومن قيم ($\Delta G°$, $\Delta H°$, and $\Delta S°$) التي تم الحصول عليها من المعادلات الثلاث السابقة نستدل على أن عمليات الادمصاص تمت بالادمصاص المختلط (الادمصاص الفيزيائي الكيميائي).

وعند المقارنة بين نتائج العلاقات الثلاث السابقة نجد عدم صلاحية نموذج فرومكين بسبب الحصول على منحنى ولم يتم الحصول على خط مستقيم ولذلك تمت حسابات نظرية لاستنتاج قيم معاملات الديناميكا الحرارية بعمل خط مستقيم باستخدام برنامج كمبيوتر للحصول على أقرب خط مستقيم ، كما أن العامل (a) تكون قيمه في معظم الحالات سالبة أو أقل من الواحد الصحيح ،

وعند المقارنة بين نموذجي العوضي ولانجماير نجد أن نموذج لانجماير هو أصلح النماذج لوصف عملية الادمصاص لأن علاقته تعطي أفضل قيم لمعاملات الديناميكا

الحرارية وثابت الاتزان ، كما أنها تعطي خطا مستقيما صحيحا ، أما قيم العامل (x) في معادلة العوضي تكون أقل من الواحد الصحيح في بعض الحالات.

سادسا: التوصيات

أ- نوصي بتطبيق المعالجات الحرارية الثلاث السابقة](المراجعة (Normalizing)، والتصلد (Quenching)، والتخمر التكويري(Spheroidizing) [لنوعي صلب الفناديوم الكربوني وذلك للأسباب الآتية:

١- المعالجة الحرارية تغير من الشكل البنائي لنوعي صلب الفناديوم وتجعله أكثر مقاومة للتآكل .
٢- مقاومة التآكل تسجل أعلى قيم لها في حالة عينة السمنتيت المتكور (S) المنخفض والمتوسط الكربون.
٣- سطح المارتينزيت (Q) المنخفض والمتوسط الكربون هو أفضل سطح يستخدم مادة (ثنائي هيدروكسي إيثيل أكريل أميد) كمثبط لعمليات التآكل
٤- أعلى قيمة لطاقة التنشيط كانت عند البيرليت الناعم (N) المنخفض والمتوسط الكربون سواء في المحاليل في وجود العامل المثبط أو في عدم وجوده.
٥- عمليات الادمصاص تكون قوية على أسطح العينات المعالجة حراريا بخلاف العينات غير المعالجة حراريا.

ب- نوصي باستخدام مادة (ثنائي هيدروكسي إيثيل أكريل أميد) كمثبط لعمليات التآكل للأسباب الآتية:

١- احتواء هذه المادة العضوية على رابطة غير مشبعة ، ومجموعة الكربونيل (C=O) ، وذرة النيتروجين ، واثنين من المجموعات الكحولية (OH) والتي تزيد من الكفاءة المثبطة لهذه المادة
٢- قيم طاقة التنشيط للمحاليل في وجود العامل المثبط أعلى من قيمها في عدم وجوده.
٣- ادمصاص جزيئات هذه المادة على أسطح نوعي صلب الفناديوم الكربوني يتم بالادمصاص المختلط (الكيميائي الفيزيائي).