Corrosion inhibition of pure iron in 0.5 M H$_2$SO$_4$ solutions by ethanolamines

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Abstract

The inhibition of corrosion of pure iron in 0.5 M H$_2$SO$_4$ by ethanolamines such as mono-, di- and triethanolamines has been investigated by dc polarization and ac impedance techniques. The results showed that a strong dependence of inhibitor performance with concentration in addition to the structural effects of amine molecules. From impedance data it is found that the corrosion of iron is controlled by charge transfer process at all concentrations of inhibitors. All the three inhibitors are found to hinder the formation of passive film on iron.
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1. Introduction

The investigation of the inhibition of corrosion of iron is a matter of high theoretical as well as practical interest [1]. Acids are widely used in many industries. Some of the important areas of application are industrial acid cleaning, acid pickling, acid descaling and oil well acidizing [2]. Due to the aggressiveness of acids, inhibitors are used to reduce the rate of dissolution of metals. It is reported that sulphur-containing inhibitors such as sulphoxides [3,4],

sulphides [5] and thioureas [6] are found to be efficient in sulphuric acid environment, whilst nitrogen-containing compounds such as azole derivatives [7–11], imidazolin derivatives [12,13], condensation products of amines with aldehydes [14–16], alkyl and aryl amines [17–19] perform better in hydrochloric acid.

In general, most of the effective and efficient inhibitors in usage are organic compounds having π bonds in their structures. The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface. 4-acetyl pyridine [20], aliphatic amines [21] such as dimethylamine, ethylamine, diethylamine, butylamine, butyldiethylamine and other derivatives of octylamine inhibit the corrosion of steel in acid

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solution by donating the unshared pair of electrons from the N atom and form a surface complex. Alkylene pyridinium compounds inhibit mild steel corrosion in 0.5 M H_2SO_4 due to inter-molecular synergism by the introduction of substituents in the pyridine ring [22]. The inhibitive effect of aniline and alkylamine [23], *p*-substituted anilines [24] and *N*-substituted anilines [25] is attributed to the interaction of π-electron cloud of aromatic ring on iron and steel surface through vacant 'd' orbital of iron leading to the formation of co-ordination bond between Fe–N. The corrosion inhibition property of low molecular weight straight chain amines for steel corrosion have also been studied [26]. Ortho-substituted anilines [27] and polyanilines [28,29] were also studied more recently. In this paper the inhibition effect of ethanolamines on the corrosion of iron in 0.5 M H_2SO_4 is discussed.

2. Experimental

AR grade chemicals were used with triple distilled water. Experiments were made using a conventional three-electrode cell assembly. The working electrode was a pure iron (Johnsons Mattey Ltd., UK) sample of 1 cm^2 area with the rest being covered with araldite epoxy and a platinum foil of 6 cm^2 area was used as counter electrode and saturated calomel electrode as reference electrode. The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers, washed with distilled water and degreased with trichloroethylene. All the experiments were carried out at 28 ± 1 °C. The solutions were deaerated by purging purified nitrogen gas for half-an-hour before the start of the experiment. Solatron Electrochemical analyzer (Model 1280 B) interfaced with an IBM computer was used for electrochemical studies. The polarization and impedance studies were made after 30 min of immersion of specimen in the solution. The polarization was carried out using a Corware software from a cathodic potential of −0.2 V to an anodic potential of +1.2 V with respect to the corrosion potential at a sweep rate of 0.5 mV/s in order to find the effect of inhibitors on the corrosion and passivation. The data in the Tafel region (−0.2 to +0.2 V versus corrosion potential) has been processed for evaluation of corrosion kinetic parameters by plotting *E* versus log *I* curves. The linear TAFEL

segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. For linear polarization measurements, a sweep from −0.02 to +0.02 V versus open circuit potential at a sweep rate of 0.5 mV/s was used. Z plot software was used for data acquisition and analysis of interfacial impedance. Ac signals of 10 mV amplitude and a frequency spectrum from 10 kHz to 0.01 Hz was impressed and the Nyquist representations of the impedance data were analysed with Zview software.

The corrosion inhibition efficiency (IE) was evaluated from the measured i_{corr} values obtained from Tafel polarization method using the relationship

$$IE\% = \left\{ \frac{i_{corr} - i'_{corr}}{i_{corr}} \right\} \times 100$$

where i_{corr} and i'_{corr} are the corrosion current densities without and with the addition of various concentrations of the inhibitor. The inhibition efficiencies were evaluated from the polarization Resistance, R_p, values as

$$IE\% = \left\{ \frac{R'_p - R_p}{R'_p} \right\} \times 100$$

where R_p and R'_p are the polarization resistances without and with the addition of inhibitors. In the case of impedance measurements, the inhibition efficiency was evaluated from the measured charge transfer resistance R_{ct} values as

$$IE\% = \left\{ \frac{R'_{ct} - R_{ct}}{R'_{ct}} \right\} \times 100$$

where R_{ct} and R'_{ct} are the charge transfer resistance values in the absence and presence of inhibitors.

The interfacial capacitance has been estimated from the impedance value of the frequency having maximum imaginary component with Nyquist plot by using the following relationship:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

3. Results and discussion

The potentiodynamic polarization behaviour in the Tafel region for iron in 0.5 M H_2SO_4 with and without the addition of various concentrations of mono-, di-

and triethanolamines is shown in Figs. 1–3. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) and Tafel constants (b_a and b_c) derived from these figures are given in Table 1.

In the case of di- and triethanolamines, the inhibition efficiencies increase with increasing the concentration of the amines, while in the case of monoethanolamine, the efficiency increases up to 5.0×10^{-3} M and beyond this the increase in inhibitor concentration results in decrease in inhibition efficiency.

Addition of all the amines shifts the corrosion potential slightly in the positive direction without an appreciable change in b_a and b_c values. This suggests that the added amines do not change the mechanism of iron dissolution and hydrogen evaluation reactions and the inhibitors decrease both reactions by surface coverage.

The polarization resistance (Table 2) values increase from $34\ \Omega\ cm^2$ of the blank acid to $225\ \Omega\ cm^2$ and $116\ \Omega\ cm^2$, respectively, for the highest concentrations of di- and triethanolamine, while in the case of monoethanolamine, there exists a critical concentration of the inhibitor beyond which

the inhibition efficiency is decreased. The polarization resistance value is increased to $182\ \Omega\ cm^{-2}$ for 5.0×10^{-3} M and started decreasing with higher concentrations of inhibitor.

The Nyquist representation of the impedance values of the iron in 0.5 M H_2SO_4 with and without the addition of various concentrations of amines are shown in Figs. 4–6. The existence of a single semicircle depicts the presence of single charge transfer process during dissolution, which is unaffected by the presence of added amines. The slightly depressed nature of the semicircle, which has the center below the x-axis, indicates the generation of micro-roughness at the surface during the corrosion process [30–32]. The impedance data were analysed with Zview software for the equivalent circuit [33].
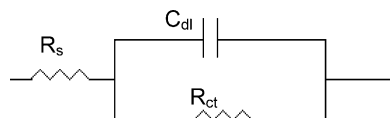
In the above circuit, R_s is the solution resistance, C_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance. The diameter of the semicircle, the charge transfer resistance, R_{ct} and
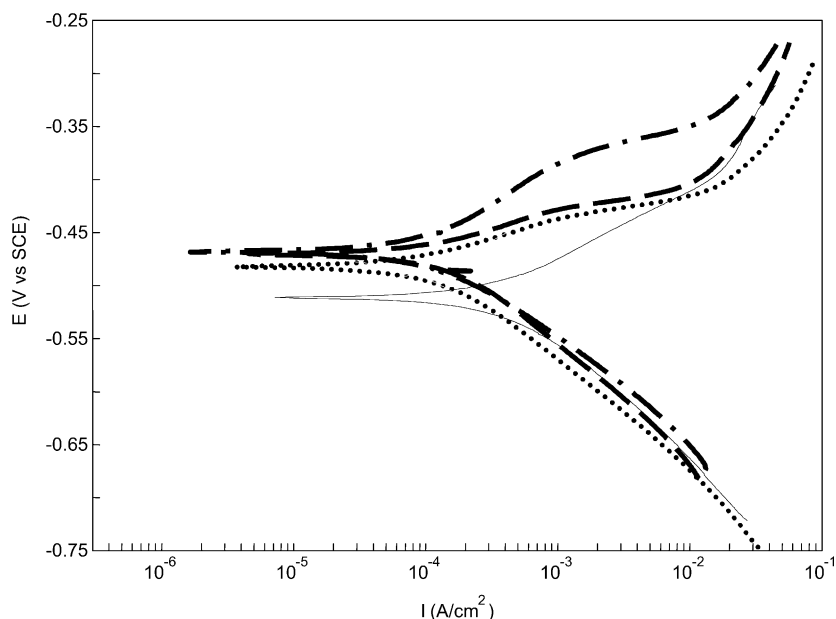

Fig. 1. Potentiodynamic polarization behaviour of iron in 0.5 M H_2SO_4 with the addition of monoethanolamine; (—) blank; (⋯) 1.0×10^{-3} M; (– · –) 5.0×10^{-3} M; (– –) 10×10^{-3} M.
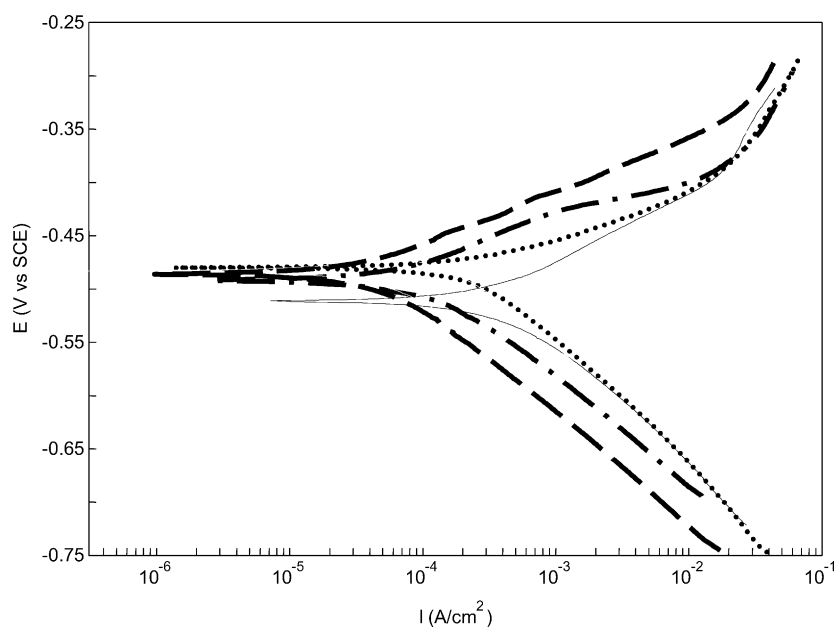
Fig. 2. Potentiodynamic polarization behaviour of iron in 0.5 M H$_2$SO$_4$ with the addition of diethanolamine; (—) blank; ($\cdots$) 1.0×10^{-3} M; (– · –) 5.0×10^{-3} M; (– –) 10×10^{-3} M.
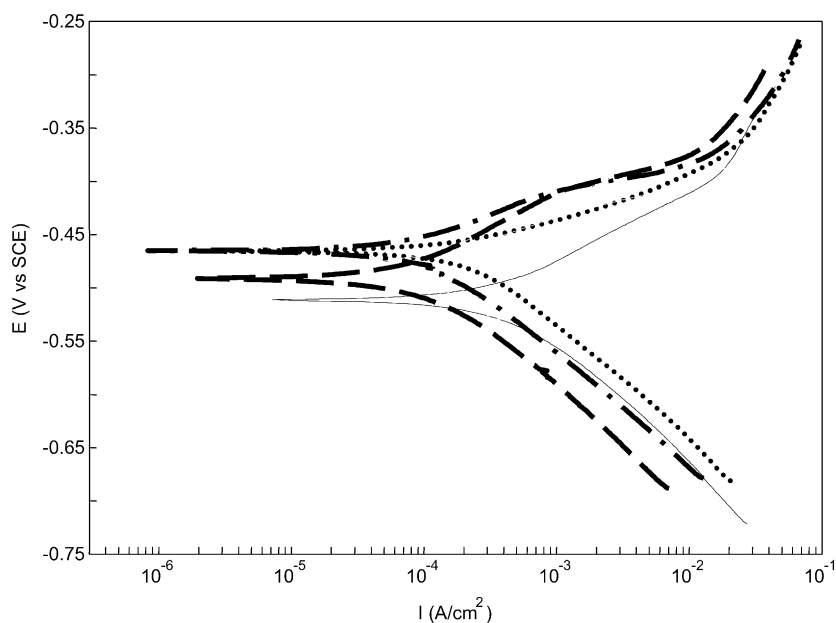

Fig. 3. Potentiodynamic polarization behaviour of iron in 0.5 M H$_2$SO$_4$ with the addition of triethanolamine; (—) blank; ($\cdots$) 1.0×10^{-3} M; (– · –) 5.0×10^{-3} M; (– –) 10×10^{-3} M.

Table 1
Corrosion parameters obtained from potentiodynamic polarization studies on pure iron in 0.5 M H_2SO_4 with and without ethanolamine inhibitors

Concentration ($\times 10^{-3}$ M)	E_{corr} (mV vs. SCE)	I_{corr} (μA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	IE (%)
Blank	−501	410	76	109	–
Monoethanolamine					
1.0	−486	240	70	100	42
2.5	−471	70	61	93	83
5.0	−461	62	56	91	85
7.5	−495	70	66	92	83
10.0	−479	131	70	96	68
Diethanolamine					
1.0	−487	576	70	109	–
2.5	−457	129	67	98	69
5.0	−489	80	67	98	80
7.5	−482	47	70	99	88
10.0	−485	38	74	95	99
Triethanolamine					
1.0	−472	468	71	108	–
2.5	−474	121	52	108	70
5.0	−465	115	74	100	72
7.5	−481	116	61	102	77
10.0	−483	62.5	70	107	85

the interfacial double layer capacitance, C_{dl} derived from these curves are given in Table 3. R_{ct} values increase from the value of 33 to 205 Ω cm^2 and 158 Ω cm^2 for the highest studied concentrations of di- and triethanolamines while it is increased to 160 Ω cm^2 up to 5.0×10^{-3} M of monoethanolamine, and further addition of inhibitor resulted in decrease of R_{ct}. This is in agreement with the results of Tafel and linear polarization methods. Addition of amines decreases the double layer capacitance C_{dl} values from 2244 μF cm^{-2} corresponding to the blank acid value. This type of decrease in C_{dl} values in the presence of inhibitors such as propargyl alcohol [34], thiazole [35], diptropynoxy methylamine alcohol [36], alkylamines [23] and indole [37] for iron in sulphuric

acid medium has been reported. Decrease in the C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer suggests that the inhibitors adsorb at the metal–solution interface [38]. Data showed that monoethanolamine formed a compact adsorbed layer on the iron electrode surface at lower concentrations and at higher concentrations these adsorbed layer lack stability which may be due to the desorption of monoethanolamine molecules from the surface. However, diethanolamine and triethanolamines shows a decrease in C_{dl} values by one order at higher concentrations inferring that these molecules have the capability of forming uniform compact adsorbed layer over iron electrode surface. The

Table 2
Linear polarization studies of pure iron in 0.5 M H_2SO_4 with and without ethanolamine inhibitors

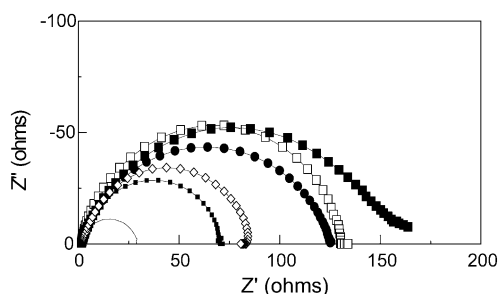| Concentration ($\times 10^{-3}$ M)	Monoethanolamine		Diethanolamine		Triethanolamine	
	R_p (Ω cm^2)	IE (%)	R_p (Ω cm^2)	IE (%)	R_p (Ω cm^2)	IE (%)
Blank	34	–	34	–	34	–
1.0	81	58	46	26	48	59
2.5	159	79	52	35	99	66
5.0	182	81	110	69	102	67
7.5	136	75	179	81	121	72
10.0	86	61	225	85	116	80

Fig. 4. Impedance plots for iron in 0.5 M H_2SO_4 with the addition of monoethanolamine; (—) blank; (■) 1.0×10^{-3} M; (□) 2.5×10^{-3} M; (■) 5.0×10^{-3} M; (●) 7.5×10^{-3} M; (◇) 10.0×10^{-3} M.

surface coverage θ was estimated from the measured double layer capacitance C_{dl} values using the relationship [27]

$$\theta = \frac{C_{dl} - C'_{dl}}{C_{dl}}$$

where C_{dl} and C'_{dl} are the double layer capacitance values in the absence and presence of inhibitors indicating a good coverage of the iron surface by the amine molecules. The information on the interaction between the inhibitor and iron surface can be provided by the adsorption isotherm. Fig. 7 gives the plot of θ versus log c. A linear relationship is observed for diethanolamines and triethanolamines for all concentrations and for monoethanolamines at low concentrations. The adsorbed inhibitors are found to follow Temkin adsorption isotherm (Fig. 7).

From the surface coverage data of the ethanolamines, it is inferred that the adsorption of ethanolamines on the iron surface inhibits corrosion. Generally, four types of adsorption may take place
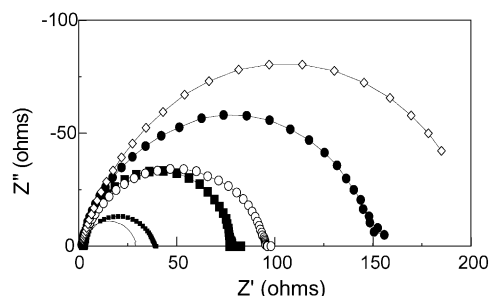

Fig. 5. Impedance plots for iron in 0.5 M H_2SO_4 with the addition of Diethanolamine; (—) blank; (■) 1.0×10^{-3} M; (■) 2.5×10^{-3} M; (○) 5.0×10^{-3} M; (●) 7.5×10^{-3} M; (◇) 10.0×10^{-3} M.

Fig. 6. Impedance plots for iron in 0.5 M H_2SO_4 with the addition of triethanolamine; (—) blank; (■) 1.0×10^{-3} M; (□) 2.5×10^{-3} M; (■) 5.0×10^{-3} M; (○) 7.5×10^{-3} M; (●) 10.0×10^{-3} M.
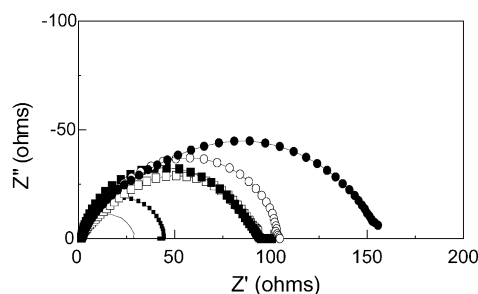
involving organic molecules at the metal–solution interface [39]:

(i) electrostatic attraction between charged molecules and the charged metal,
(ii) interaction of unshared electron pairs in the molecules with the metal,
(iii) interaction of π electrons with the metal and
(iv) a combination of the above.

Inhibition efficiency depends on several factors, such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and the formation of metallic complexes [40].

The action of amine inhibitor molecules is due to the adsorption of the inhibitor molecules on an exposed metal surface. Amines may be adsorbed over the metal surface in the form of neutral molecules involving replacement of water molecules from the metal surface as

$$\text{Amine}_{(s)} + n\text{H}_2\text{O}_{ads} \rightarrow \text{Amine}_{ads} + n\text{H}_2\text{O}_{(s)}$$
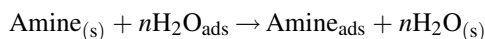
and sharing of electron between the "N" atom of the inhibitor molecule and metal surface [41] or by the electrostatic interaction between the positively charged "N" atom and negatively charged metal surface [42,43]. The inhibitive properties of amines are mainly dependent on the electron densities around the nitrogen atoms; the higher the electron densities at the nitrogen atom, the more effect is inhibitor. Due to adsorption, inhibitor molecules block the reaction sites and reduce the rate of corrosion reaction [44,45].

Table 3
Impedance studies of pure iron in 0.5 M H_2SO_4 with and without ethanolamine inhibitors

Concentration ($\times 10^{-3}$ M)	Charge transfer resistance R_{ct} (Ω cm^2)	Double layer capacitance C_{dl} (μF cm^{-2})	Surface coverage (θ)	IE (%)
Blank	33	2244	–	–
Monoethanolamine				
1.0	70	915	0.59	52
2.5	130	757	0.66	75
5.0	160	724	0.67	79
7.5	124	875	0.61	73
10.0	84	918	0.59	61
Diethanolamine				
1.0	38	2389	–	13
2.5	76	700	0.49	57
5.0	95	690	0.63	65
7.5	152	497	0.77	78
10.0	205	471	0.79	84
Triethanolamine				
1.0	42	967	0.56	21
2.5	93	540	0.75	64
5.0	94	546	0.75	65
7.5	103	327	0.85	68
10.0	158	210	0.90	78

In the case of ethanolamines, the interaction may take place through the interaction of unshared pair of electrons of the nitrogen atom with the metal surface. The possibility of interaction through cationic mode is less since the iron surface is positively charged in sulphuric acid medium at corrosion potential [23]. All the studied amines show the inhibition efficiency of 70–90% in the concentration range of 2.5×10^{-3} to 7.5×10^{-3} M. However, at 10×10^{-3} M concentration, the monoethanolamine shows lower efficiency in comparison with other inhibitors due to less surface coverage. The order of inhibitor efficiency is

Diethanolamine > Triethanolamine

> Monoethanolamine

Fig. 8 compares the passivation behaviour of iron in the absence and presence of inhibitor. It is seen that in the absence of inhibitor, a well-defined passive region is observed which is due to the formation of γFe_2O_3 on the iron surface [46,47]. The passivation of iron corresponding to the primary passivation is due to the formation of $FeSO_4$, which started at a potential around +0.3 V and this is not a stable one. Due to the instability of film, some current oscillations are observed in the primary passivation region, i.e., +0.3 to +0.6 V. Further increase of potential in the anodic direction causes a sudden decrease of current by about 10 times due to the formation of thin, non-porous, passivating higher oxide of iron, which is stable up to +1.2 V. Further increase of potential leads
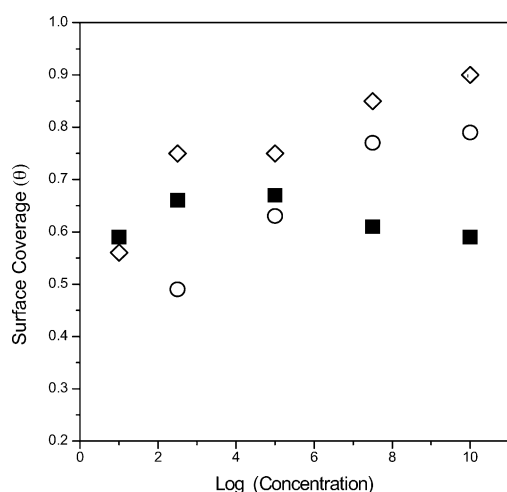

Fig. 7. Temkin adsorption isotherm plots for ethanolamines; (■) monoethanolamine; (○) diethanolamine; (◇) triethanolamine.
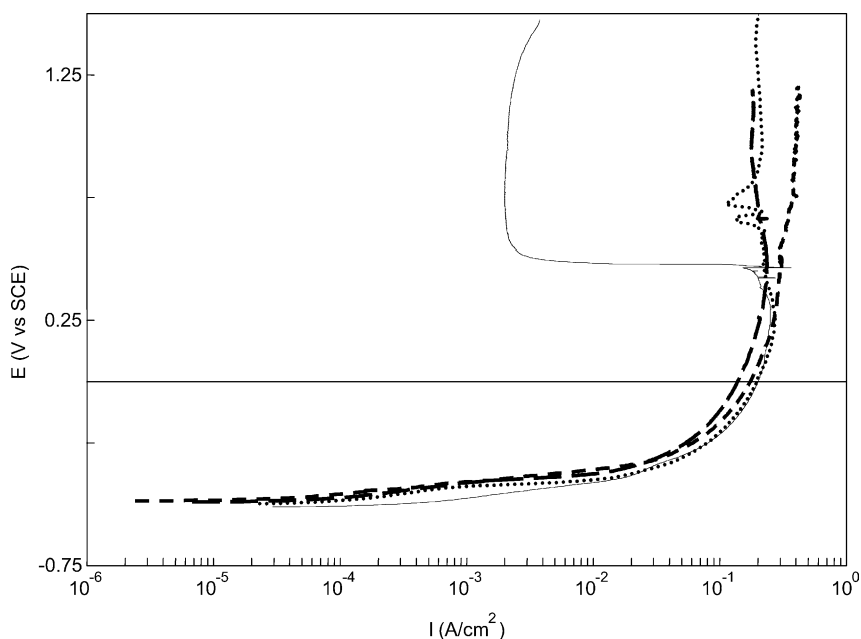
Fig. 8. Anodic polarization curve of iron in 0.5 M H_2SO_4 with the addition of 10.0×10^{-3} M ethanolamines; (—) blank; ($\cdots$) mono-ethanolamine; (- - -) diethanolamine; (– –) triethanolamine.

to the dissolution of oxide film. In the presence of inhibitors, it is observed that the formation of passive film is not observed. This may be due to the fact that the adsorbed amines hinders the formation of passive film on iron surface by preventing the $FeSO_4$ intermediate adsorption over iron surface, which is responsible for the formation of passive film. This observation is in contrary to the study of iron dissolution in H_2SO_4 containing cyclohexylamine [48], where the inhibitor has been found to improve the passivity.

4. Conclusions

Ethanolamines are found to be good inhibitors for iron corrosion in 0.5 M H_2SO_4. The inhibition is accomplished by adsorption of amine molecules on to the iron electrode surface without changing the mechanism of partial corrosion reactions. Among the three ethanolamines studied, diethanolamine offers higher inhibition efficiency. However, the amines hinder the formation of passive film on iron surface. EIS measurements indicate the single charge transfer process controlling the corrosion of iron.

Adsorption of ethanolamines follows Temkin adsorption isotherm.

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