

Full Paper

Thermodynamic, Electrochemical and Surface Studies of Dendrimers as Effective Corrosion Inhibitors for Mild Steel in 1 M HCl

Chandrabhan Verma and Mumtaz A. Quraishi*

Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India

*Corresponding Author, Tel.: +91-9307025126; Fax: +91- 542- 2368428

E-Mails: maquraishi.apc@itbhu.ac.in; maquraishi@rediffmail.com

Received: 9 October 2015 / Accepted: 23 January 2016 /

Published online: 15 February 2016

Abstract- the Corrosion inhibition of mild steel in 1 M HCl has been investigated using three dendrimers by means of gravimetric, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. Results showed that inhibition efficiency increases with increasing concentration of dendrimers. Among the studied inhibitors, the DENDs-G₂ showed maximum efficiency of 96.95% at 25 concentrations. The potentiodynamic study revealed that investigated dendrimers act as mixed type inhibitors. EIS plots indicated that the addition of dendrimers increases the charge-transfer resistance (R_{ct}), decreases the double-layer capacitance (C_{dl}) of the corrosion process, and hence increases inhibition efficiency. The adsorption of the dendrimers on the mild steel surface in acid solution obeys the Langmuir adsorption isotherm. Moreover, the thermodynamic activation parameters for the corrosion reaction were calculated and discussed in relation to the stability of the protective inhibitor layer.

Keywords- Dendrimers, Mild steel EIS, Corrosion, 1 M HCl, SEM-EDX

1. INTRODUCTION

Dendrimers are highly branched star shape nano sized macromolecules, which are associated with large number of functional groups, and a compact molecular structure [1].

Due to their multivalent and monodisperse character; dendrimers have stimulated wide interest in the field of chemistry and biology. They are especially used as carriers for drug delivery [2-4], gene delivery [5], targeting [6], solubilization [7], and diagnosis [8], chemical catalysis [9] and as multivalent legends for interesting biological applications [10,11].

In our present investigation, corrosion inhibition behavior of three generation ethylene diamine cored PAMAM dendrimers, namely generation-0 (DEND-G₀), generation-1 (DEND-G₁) and generation-2 (DEND-G₂) in 1 M HCl for mild steel has been studied by gravimetric and electrochemical methods. The scanning electron microscopy (SEM) was used for surface examination of mild steel. Elemental composition was examined using energy dispersive X-ray (EDX) technique. Choice of these compounds as corrosion inhibitors is based on the facts: Dendrimers can be easily and conventionally synthesized from commercially available chemicals, they contain –CO-NH₂ group and electronegative heteroatoms (O,N), and they are highly soluble in studied medium. The higher solubility, and reactivity of dendrimer is due to presence of polar end group (-NH₂) [12-15] and polar groups present in dendrimers facilitate the adsorption process.

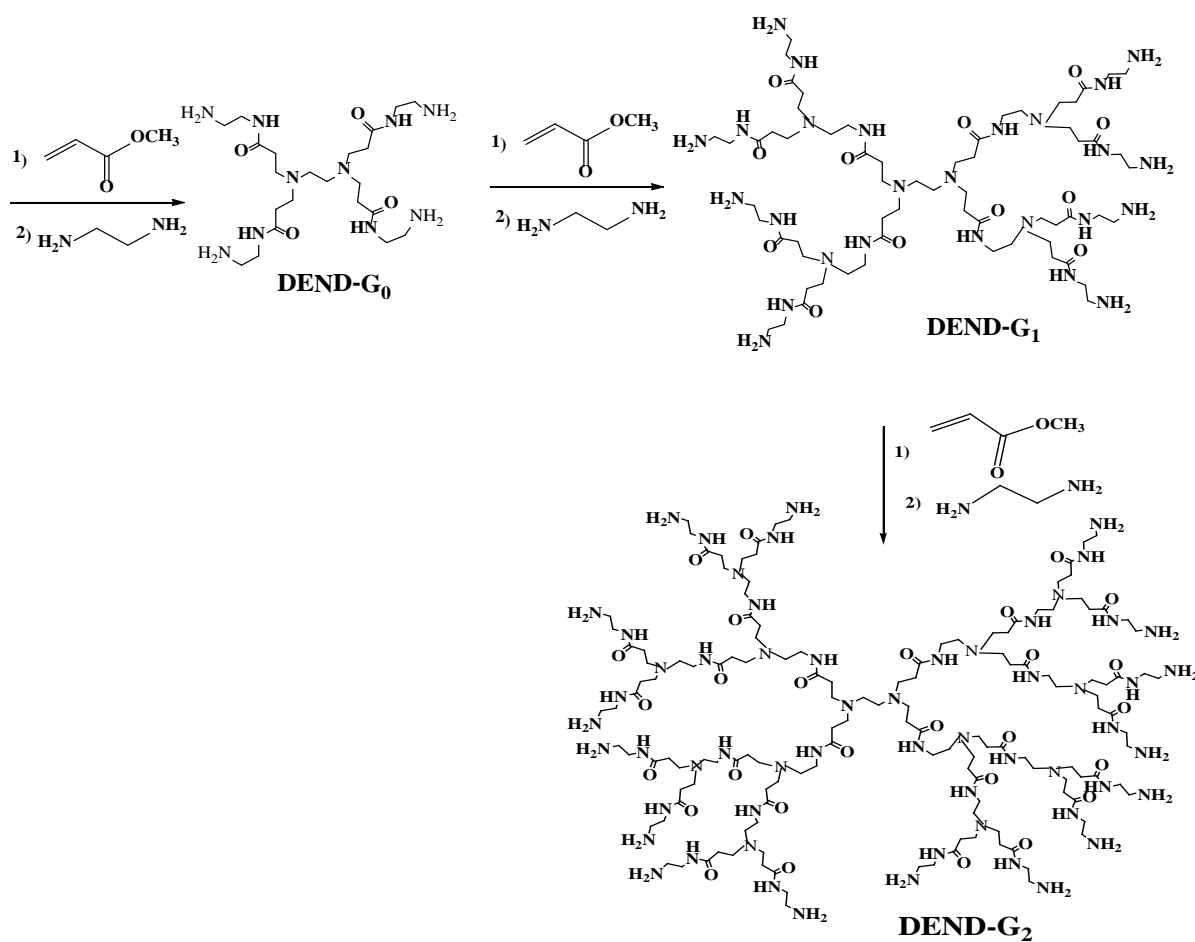


Fig. 1. Synthetic scheme for investigated inhibitors

2. EXPERIMENTAL SECTION

2.1. Synthesis of Corrosion Inhibitors

The dendrimers used in the present study as corrosion inhibitors were synthesized using previously described method as shown in Fig. 1 [16].

2.2. Material

Mild steel specimens with composition (wt %) Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr 0.050%, Ni 0.050%, Al 0.023%, and Cu 0.135%, were ground with 600-1200 grade SiC papers, washed with double distilled water, degreased with acetone in ultrasonic bath and finally allowed to dried in hot air. The gravimetric experiments were performed on mild steel specimens having dimension of $2.5 \times 2.0 \times 0.025$ cm³, whereas mild steel specimens with an expose area of 1 cm² were used as working electrode for all electrochemical measurements. All the gravimetric and electrochemical experiments were performed in 1 M HCl, prepared by AR-grade HCl (35%, MERCK) and double distilled water.

2.3. Gravimetric measurements

The gravimetric experiments were performed as described previously [17]. All experiments were triply performed and mean values were reported. Corrosion rate C_R (mg cm⁻² h⁻¹) was calculated using following relation:

$$C_R = \frac{W}{At} \quad (1)$$

Where W is the average weight loss of three parallel mild steel strips, A the exposed area of mild strip and t is immersion time (3h). From this calculated corrosion rate (C_R), the inhibition efficiency ($\eta\%$) and surface coverage (θ) were calculated using following relationship:

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \quad (2)$$

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \quad (3)$$

Where C_R and $C_{R(i)}$ are the corrosion rate values in absence and presence of dendrimers respectively.

2.4. Electrochemical measurements

The conventional three electrode cell was used for electrochemical experiments. The mild steel specimens with exposed area 1 cm^2 as working electrode, high purity platinum as auxiliary and saturated calomel electrode as reference electrode were used for electrochemical measurements. All the electrochemical experiment was performed with Gamry Potentiostat/Galvanostat (Modal G-300) in absence and presence of different concentrations of dendrimers in 1 M HCl after 30 minutes immersion time. Echem analyst 5.0 software was used to analyze the experimental data derived from electrochemical studies.

The EIS measurements were performed in frequency range of 10^5 to 10^{-2} Hz under potentiodynamic condition having amplitude 10 mV peak to peak using AC signal at open circuit potential. From Nyquist plots charge transfer resistance (R_{ct}) were calculated. Corrosion inhibition efficiency was calculated from charge transfer resistance using following relationship:

$$\eta\% = \left(1 - \frac{R_{ct}}{R_{ct(i)}}\right) \times 100 \quad (4)$$

Where $R_{ct(i)}$ and R_{ct} are the charge transfer resistance in presence and absence of dendrimers, respectively.

The potentiodynamic polarization experiments were performed by automatic changing the electrode potential of -0.25 V vs. SCE (cathodic potential) to $+0.25 \text{ vs SCE}$ (anodic potential) with respect to open circuit potential at a sweep rate of 1.5 mVs^{-1} . The corrosion current densities (I_{corr}) were obtained by extrapolating the linear segment of cathodic and anodic curves. From corrosion current density, inhibition efficiency was calculated using following equation:

$$\eta\% = \left(1 - \frac{I_{corr(i)}}{I_{corr}}\right) \times 100 \quad (5)$$

Where $I_{corr(i)}$ and I_{corr} are corrosion current density without and with presence of dendrimers, respectively.

2.5. Surface characterization

The mild steel specimens were immersed in 100 ml HCl solution in absence and presence of optimum concentration of dendrimers for 3 h immersion time. After elapse of time, mild steel specimens were withdrawn and their surface was examined by scanning electron microscopy (SEM) using SEM modal, Ziess Evo 50 XVP instrument at an accelerating voltage of 5 kV at 100 magnifications. The surface elemental composition was also analyzed for each mild steel sample using energy dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurement

3.1.1. Effect of concentration

Corrosion inhibition efficiency ($\eta\%$), corrosion rate (C_R) and corresponding surface coverage (θ) for mild steel sample in 1 M HCl after 3 h immersion time was evaluated using gravimetric measurements and is summarized in Table 1. The variation of inhibition efficiency with different concentrations of dendrimers is shown in Fig. 2 (a). Results obtained from gravimetric measurements reveals that inhibition efficiency and surface coverage increases with increasing dendrimers concentration. The maximum surface coverage occurs obtained at 25 ppm (MgL^{-1}). It is observed from Table 1, that corrosion rate is much lower in presence of dendrimers than in absence of dendrimers [18,19]. The inhibition efficiency of the investigated dendrimers DEND-G₂ (96.95%) > DEND-G₁ (96.08%) > DEND-G₀ (94.78%).

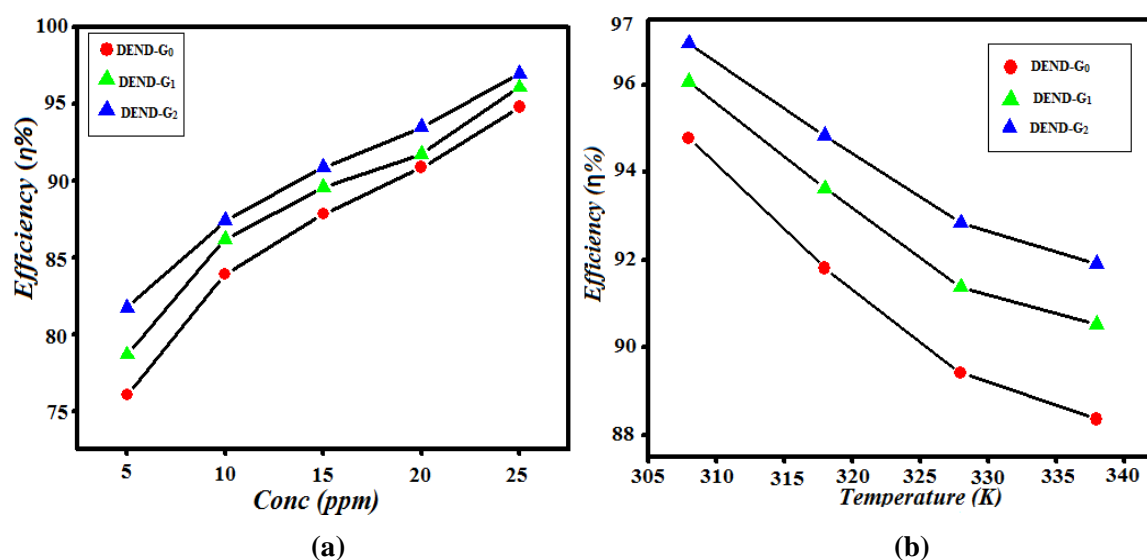


Fig. 2. Variation of inhibition efficiency (a) with concentration and (b) with temperature

3.1.2. Effect of temperature

Corrosion inhibition study at optimum concentration was also carried out at different temperatures ranging from 308 to 338 K. The variation of inhibition efficiency with temperature is shown in Fig. 2 (b). It is observed that corrosion inhibition efficiency decreases and corrosion rate increases with increasing temperature. The decrease in inhibition efficiencies might be due desorption of adsorbed dendrimers film from the mild steel surface at elevated temperature.

Table 1. Weight loss parameters for mild steel corrosion in 1 M HCl in absence and presence of different concentration of dendrimers

Inhibitor	Inhibitors Conc. ppm /M	Corrosion rate (mg cm ⁻² h ⁻¹)	Surface coverage (θ)	η%
Blank	0.0/0.0	28.45	-----	-----
DEND-G ₀				
	5/2.5×10 ⁻⁵	6.80	0.7608	76.08
	10/4.6×10 ⁻⁵	4.60	0.8391	83.91
	15/6.9×10 ⁻⁵	4.57	0.8782	87.82
	20/9.2×10 ⁻⁵	2.59	0.9086	90.86
	25/11.6×10 ⁻⁵	1.48	0.9478	94.78
DEND-G ₁				
	5/2.5×10 ⁻⁵	6.06	0.7869	78.69
	10/4.6×10 ⁻⁵	3.83	0.8621	86.21
	15/6.9×10 ⁻⁵	2.96	0.8956	89.56
	20/9.2×10 ⁻⁵	2.34	0.9173	91.73
	25/11.6×10 ⁻⁵	1.11	0.9608	96.08
DEND-G ₂				
	5/2.5×10 ⁻⁵	5.19	0.8173	81.73
	10/4.6×10 ⁻⁵	3.58	0.8739	87.39
	15/6.9×10 ⁻⁵	2.59	0.9086	90.86
	20/9.2×10 ⁻⁵	1.83	0.9347	93.47
	25/11.2×10 ⁻⁵	0.86	0.9695	96.95

3.1.3. Thermodynamic and Activation Parameters

The weight loss experiment were performed in the temperature range of 308-338 K in 1 M HCl in absence and presence of optimum concentration of dendrimers in order to derive thermodynamic and activation parameters.

It is previously noted that corrosion rate depends upon temperature which can be expressed in term of Arrhenius and transition state equation [20].

$$\log(C_R) = \frac{-E_a}{2.303RT} + \log \lambda \quad (6)$$

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (7)$$

Where E_a is apparent activation energy (Jmol⁻¹) the λ Arrhenius pre-exponential factor, ΔH^* the enthalpy of activation, ΔS^* the entropy of activation, h is Plank constant, N the Avogadro number, T is absolute temperature and R is gas constant (8.314 JK⁻¹mol⁻¹).

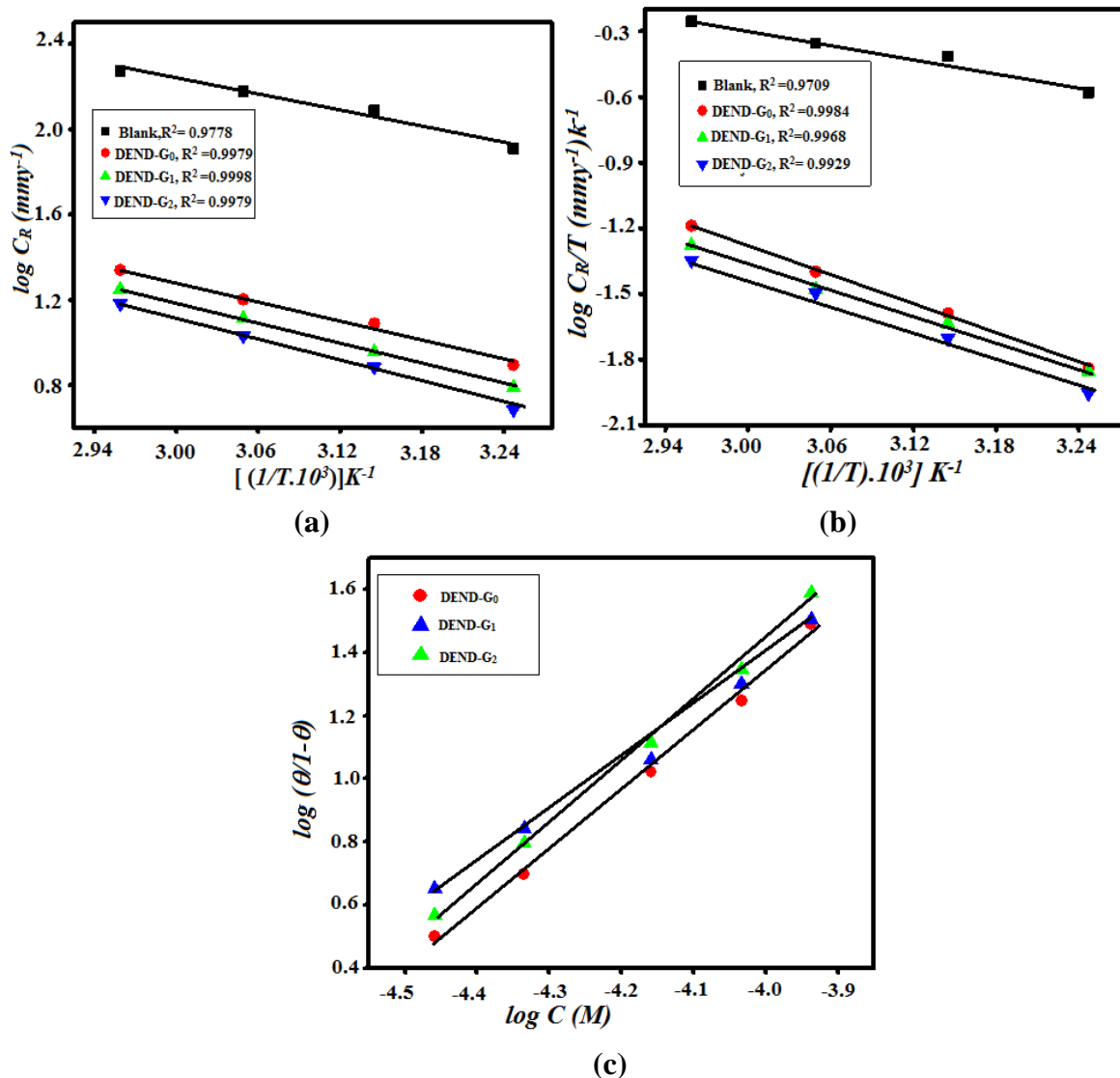


Fig.3. (a) Arrhenius plots; (b) transition state plots and (c) Langmuir isotherm plots for mild steel

Arrhenius plot ($\log C_R$ vs $1/T$) and transition plot ($\log C_R/T$ vs $1/T$) in absence and presence of dendrimers are shown in Fig. 3 (a-b). From the Arrhenius slope ($-E_a/R$), activation energy determined for each line using following equation:

$$E_a = (\text{slop}) \times 2.303 R \quad (8)$$

The E_a calculated using above equation is given in Table 2. Study of Table 2, revealed that E_a in presence of dendrimers is greater than in absence of dendrimers. The considerable increase in activation energy signifies the physical adsorption in initial stage [21].

The transition state plot ($\log C_R/T$ vs $1/T$) gives a straight line with slope value equal to $(-\Delta H^*/2.303R)$ and an intercept of $[\log(R/Nh) + (\Delta S^*/2.303R)]$. The change in ΔH^* and change in ΔS^* were calculated using transition state equation and summarized in Table 2. It is clear

from table that ΔH^* shifted toward more positive value which shows endothermic nature of mild steel dissolution in 1 M HCl in presence of dendrimers [22-24]. It is also obvious that in presence of dendrimers both ΔH and ΔE values increases, which authenticate the known thermodynamic relation $\Delta H = \Delta E - RT$ [25]. It is apparent that ΔS^* increased in presence of the studied dendrimers as compared to free acid solution. Such variation is associated with the phenomenon of ordering and disordering of inhibitors molecules on the mild steel surface. The increased entropy of activation in the presence of dendrimers indicated that disorderness is increased on going from reactant to activated complex on metal/solution interface [26,27].

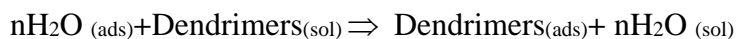
3.1.4. Adsorption Isotherm

Mechanism of corrosion inhibition can be elucidated on the basis of molecular adsorption of dendrimers on metal surface [28]. Adsorption of inhibitors on metal surface depends on an assortment of factors such as chemical structure, temperature and electrochemical potential at metal/electrolyte interface. According to Quasi Lattice model, surface of metals in aqueous solution of inhibitor is covered by water molecules.

Table 2. Values of E_a , ΔH , ΔS and ΔG_{ads}° of DEND s for Mild Steel in 1 M HCl

Inhibitor	E_a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	ΔG_{ads}° (kJ mol ⁻¹)
Blank	28.48	26.04	-148.9	-----
DENG-G ₀	28.91	37.56	-111.02	-36.16
DENG-G ₁	30.71	40.44	-102.9	-36.83
DENG-G ₂	32.68	42.77	-93.81	-37.42

Therefore, adsorption of dendrimers molecules takes place via subsequent replacement of water molecules with dendrimers as given below [29].



Where n is total number of water molecules replaced by one molecule of dendrimers from metal surface, commonly known as size ratio. It gives fundamental information about interaction between metal surface and dendrimers. Various isotherms were tested but Langmuir adsorption isotherm [Fig. 3 (c)] was best fitted which can be expressed by the equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{(ads)}} + C_{inh} \quad (9)$$

Where K_{ads} is the equilibrium constant of the adsorption–desorption process, θ is the degree of surface coverage and C_{inh} is molar concentration of dendrimers. Adsorption constant related to standard energy of adsorption (ΔG°_{ads}) by the equation [30]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \quad (10)$$

Where R is gas constant, T is absolute temperature and 55.5 represent the concentration of water in acid solution (mol/dm^3). The value of standard free energy change (ΔG°_{ads}) at optimum concentration of dendrimers is given in Table 2. From table, it is obvious that the value of ΔG°_{ads} are negative in presence of dendrimers which disclose that adsorption of dendrimers on metal surface is a spontaneous process and dendrimers form a strong film mild steel surface [31]. Moreover, literature studied reveals that the value of ΔG°_{ads} , -20 kJ/mol or less associated with electrostatic interaction between metal surface and charge inhibitor molecule i.e. physisorption and value of ΔG°_{ads} , -40 kJ/mol or more negative related to the charge transfer from inhibitor molecule to the mild steel surface to form coordinate type of interaction i.e. chemisorption [32-34]. In our present case the value of ΔG°_{ads} is around -36 kJ /mol which suggest the mixed mode of adsorption of dendrimers.

3.2. Electrochemical Measurements

3.2.1. Potentiodynamic polarization measurement

The polarization behavior of mild steel in absence and presence at different concentrations dendrimers is shown in Fig. 4 (a-c). Various potentiodynamic polarization parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic (β_c) and anodic (β_a) Tafel slops were derived from extrapolation of linear segments of cathodic and anodic curves and represented in Table 3. It is also depicted from Fig. 4, that both cathodic (hydrogen evolution) and anodic reactions (mild steel dissolution) are affected in presence of dendrimers. It is also obvious from the potentiodynamic studies that in presence of dendrimers corrosion current density (I_{corr}) remarkably decreased which may be due to formation of protective film of dendrimers on mild steel surface [35,36]. Potentiodynamic study also reveals that corrosion potential (E_{corr}) value shows a significant change in presence of dendrimers thereby suggesting that they can classified as cathodic or anodic type inhibitors [37-42]. Result obtained from potentiodynamic study reveals that values of β_c show much more shifted as compare to values of β_a suggesting that dendrimers are cathodic inhibitors. This significant change in β_c may be due to the chloride ions/or inhibitor molecules adsorbed onto steel surface [43]. The order inhibition efficiency obtained from potentiodynamic measurement is DEND-G₂> DEND-G₁>DEND-G₀.

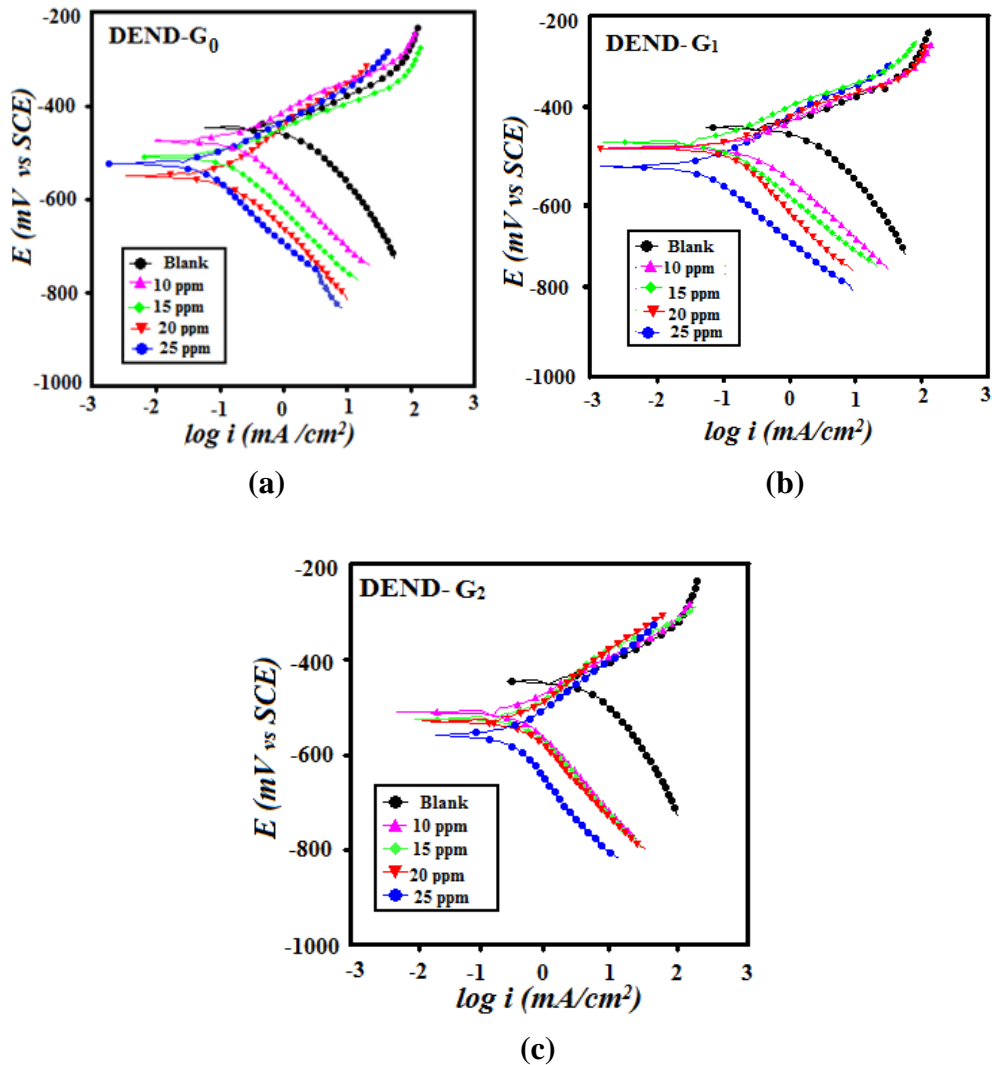


Fig. 4. (a-c) Tafel polarization curves for mild steel in 1 M HCl in the absence and presence of different concentration of dendrimers

3.2.2. Electrochemical impedance spectroscopic measurements

The impedance behavior of mild steel in 1 M HCl in absence and presence of different concentration of dendrimers has been shown in Fig. 5 (a-c) and equivalent circuit used to fit the data is given in Fig. 5 (d). Table 4 represents various impedance parameters such as R_s , R_{ct} , n , Y^0 , C_{dl} , θ and $\eta\%$. The depressed capacitive loop in Nyquist plot at high frequency region may be attributed due to charge transfer reaction between metal and dendrimers, formation of electrical double layer and surface inhomogeneity [44,45]. The impedance CPE was calculated using following formula:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \quad (11)$$

Where Q is CPE coefficient, n is CPE exponent, ω is the angular frequency ($\omega=2\pi ff$, where f is AC frequency). For CPE to behave like an ideal capacitance (C_{dl}), value of n should be one [46].

Table 3. Tafel polarization parameters for mild steel in 1 M HCl solution containing different concentrations of DEND at 308 K

Inhibitor	Conc (ppm)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV/SCE)	β_a (mV/dec)	β_c (mV/dec)	θ	$\eta\%$
Blank	0.0	1150	-445	70.5	114.6	---	----
DEND-G ₀							
	10	160	-472	76.1	114.6	0.8608	86.08
	15	140	-530	116.2	153.0	0.8782	87.82
	20	139	-524	109.8	149.9	0.8791	87.91
	25	90.9	-559	106.0	163.3	0.9295	92.95
DEND-G ₁							
	10	142	-549	78.0	131.0	0.8765	87.65
	15	127	-508	66.0	124.9	0.8895	88.95
	20	91.5	-510	77.7	119.9	0.9204	92.04
	25	67.7	-522	77.2	164.5	0.9411	94.11
DEND-G ₂							
	10	138	-489	84.2	117.7	0.8800	88.00
	15	109	-492	83.0	159.4	0.9052	90.52
	20	89.5	-479	74.5	111.7	0.9221	92.21
	25	46.3	-533	81.0	118.6	0.9597	95.97

From Table 4, it is clear that values of C_{dl} decreases with dendrimers concentration. This decrease may be partially due to replacement of water molecules by dendrimers and partially due to increase in the thickness of double layer [47,48]. This modal suggests the strong adsorption of dendrimers on mild steel surface.

The direct relationship between C_{dl} and thickness of double layer can be expressed by Helmholtz equation [49]:

$$C_{dl} = \frac{\varepsilon\varepsilon_0}{d} S \quad (12)$$

Where ε_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ Fm}^{-1}$) and ε is the local dielectric constant of medium (1 M HCl), S is the surface area of the electrode (mild steel) and d is thickness of protective film. It is also depicted from table 4, R_{ct} values increases with increase

in dendrimers concentration which suggests strong metal surface coverage by dendrimers [50,51].

Table 4. Electrochemical impedance parameters and the corresponding inhibition efficiencies for mild steel in 1 M HCl in the absence and presence of different concentrations of DENDs at 308 K

<i>Inhibitor</i>	Conc ppm	R_s (Ω)	R_{ct} (Ω cm²)	n	Y₀ (μF cm⁻²)	C_{dl} (μF cm⁻²)	θ	η%
Blank	0.0	1.12	9.58	0.827	249.8	106.21	-----	----
DEND- G ₀	10	0.763	71.03	0.813	197.52	84.87	0.8656	86.56
	15	1.057	108.0	0.841	172.25	81.44	0.8855	91.12
	20	1.182	173.5	0.893	142.12	77.90	0.9289	94.47
	25	1.321	270.5	0.872	137.67	50.12	0.9545	96.45
DEND- G ₁	10	0.742	76.76	0.851	159.56	82.83	0.8389	87.51
	15	0.895	117.7	0.869	136.12	71.71	0.8952	91.86
	20	0.951	172.0	0.812	131.48	46.79	0.9284	94.43
	25	0.921	316.50	0.816	109.78	43.36	0.9611	96.97
DEND- G ₂	10	0.748	85.05	0.871	146.54	82.80	0.8547	88.73
	15	0.621	122.4	0.855	151.19	74.57	0.8994	92.17
	20	1.006	179.25	0.851	111.45	48.63	0.9313	94.65
	25	1.759	364.12	0.809	97.99	34.34	0.9662	97.13

Fig. 6-(a-c) shows the Bode plots for mild steel in absence and presence of different concentration of dendrimers at their open circuit potential. From Bode plots, it is observed that value of $\log |Z|$ and phase angle (α^0) decreases at high frequency region. This decrease is due to solution resistance between reference (saturated calomel) and working electrodes (mild steel) [52]. A linear relationship between $\log |Z|$ and $\log f$ with slope value near to -1 and phase angle nearly -70 have been observed around intermediates frequencies. For ideal system, the value of slope and phase angle should be -1 and -90 respectively [53]. This deviation from ideal capacitive behavior at intermittent frequencies may be related to dawdling dissolution rate of mild steel in presence of dendrimers with time. The Bode phase angle plot shows a single maximum (at one time constant) at intermittent frequencies. The

broadening at maximum in bode plot is due to formation of protective film of dendrimers on mild steel surface.

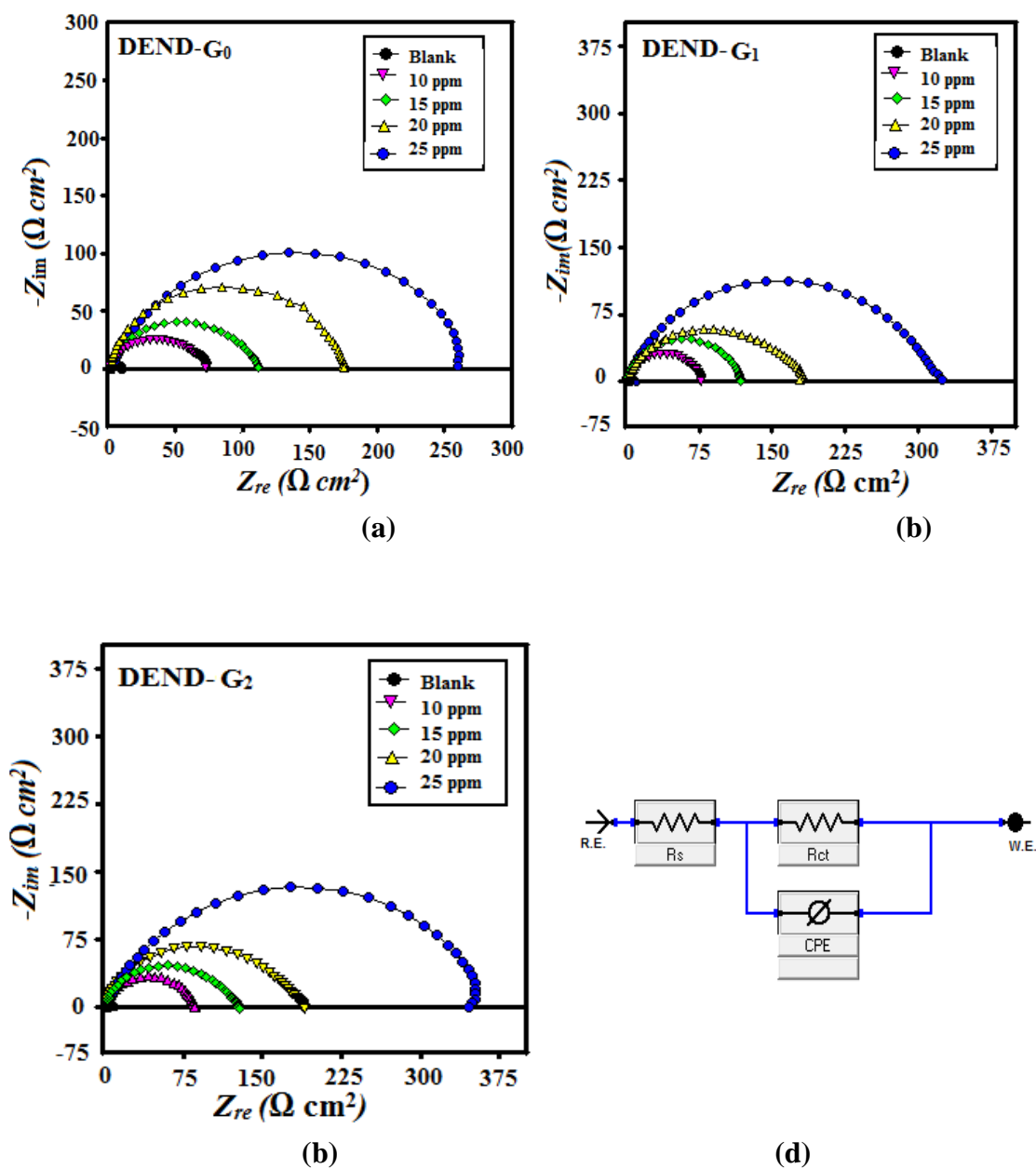


Fig. 5. (a-d), (a-c) Nyquist plot in absence and presence of different concentration of dendrimers: (d) Equivalent circuit used to fit the electrochemical impedance data

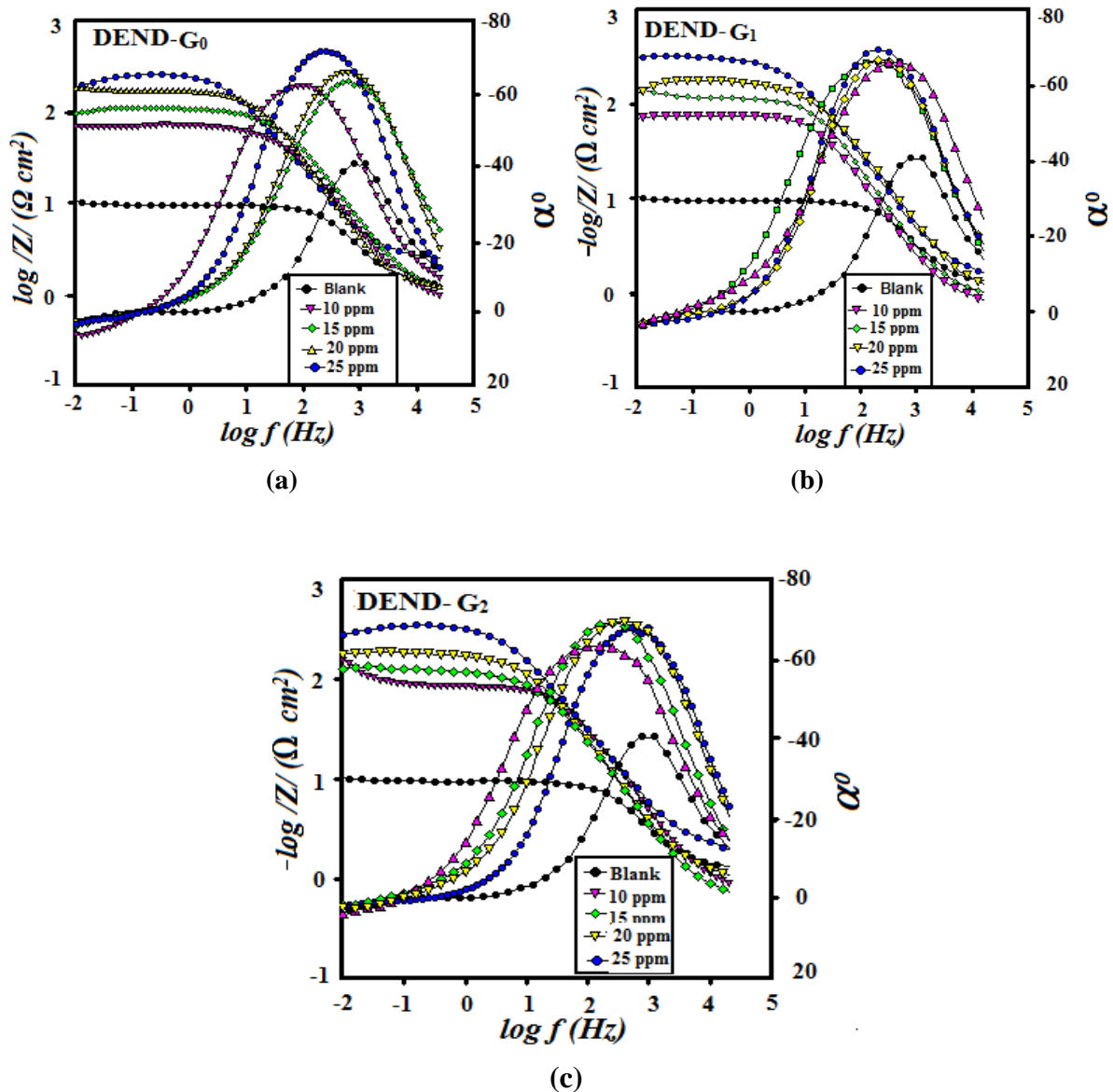


Fig. 6. (a-c) Bode plots in absence and presence of different concentrations of dendrimers

3.3. Surface Investigation

3.3.1. SEM Analysis

The surface morphology of mild steel specimens in 1 M HCl after 3h immersion time using scanning electron microscopy in absence and presence of optimum concentration of dendrimers is shown in Fig. 7 (a-d). It is seen that specimens in absence of dendrimers is badly corroded with pits and cracks resulting due to significant corrosion. It is clearly visible that mild steel surface morphology remarkably improved in presence of dendrimers which may be due to formation of protective film of dendrimers on mild steel.

3.3.2. EDX Analysis

The EDX spectra were performed in absence and presence of optimum concentration of dendrimers in 1 M HCl in order to determine the elements present on mild steel surface. The various elements present on mild steel surface obtained from EDX spectroscopy is given in Table 5. The EDX spectra of mild steel are shown Fig. 8 (a-d).

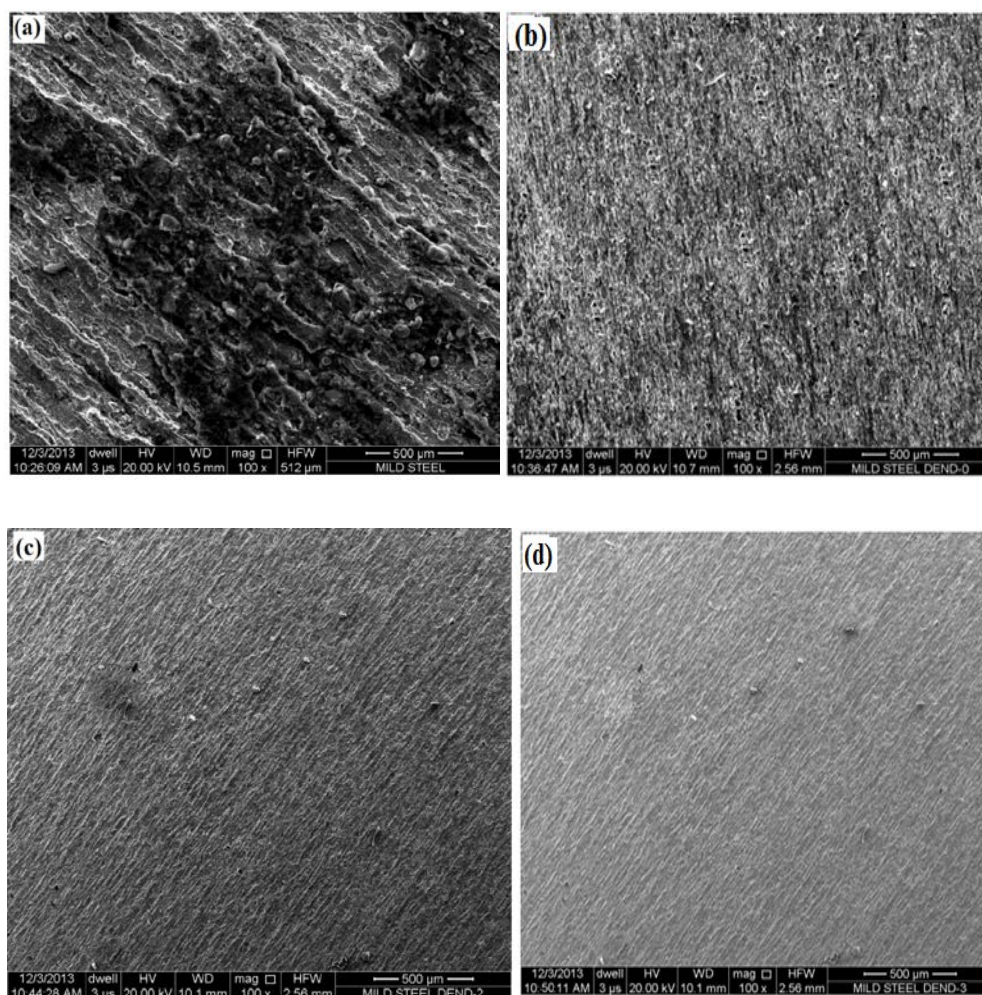


Fig. 7. SEM images of mild steel (a) in absence of dendrimers and in presence of DEND-G₀ (b), DEND-G₁ and (c) DEND-G₂

In EDX spectrum of uninhibited mild steel specimen shows absence of peak for O, which confirms the dissolution of oxide film present on mild steel surface and free corrosion of bare metal. However, EDX spectra in presence of dendrimers show additional peaks for O and N (due to presence of N & O in dendrimers). The EDX spectroscopic results further support the formation of protective film of dendrimers on mild steel surface.

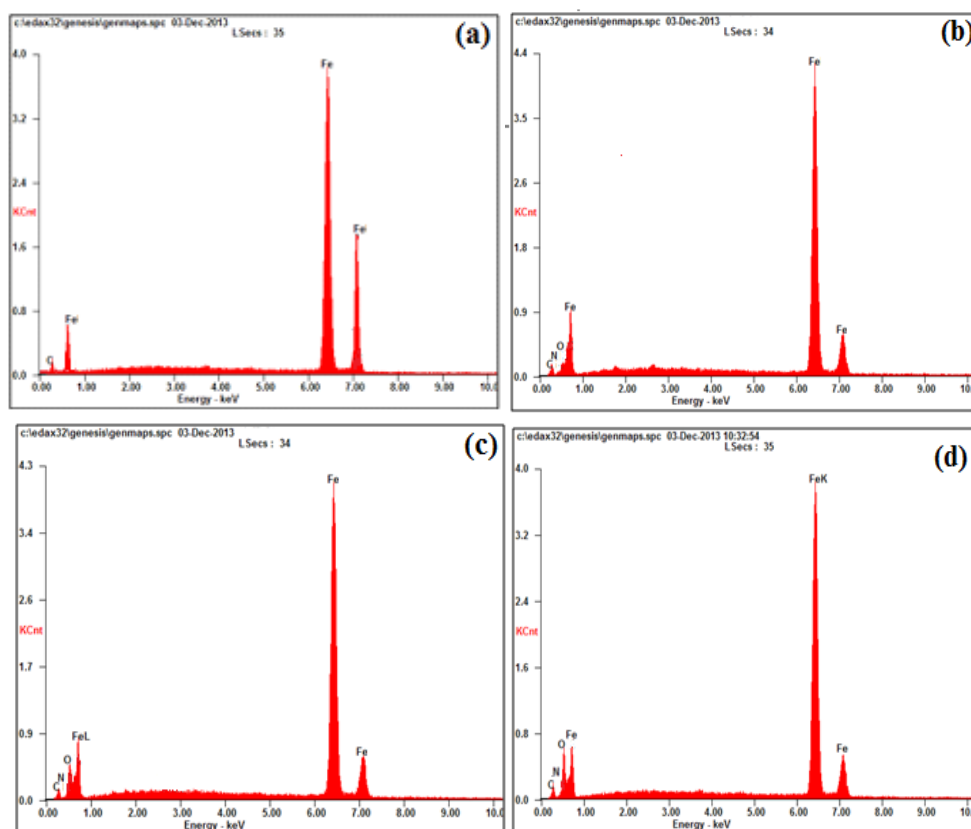


Fig. 8. EDX images of mild steel (a) in absence of dendrimers and in presence of DEND-G₀ (b), DEND-G₁ and (c) DEND-G₂

Table 5. Percentage atomic contents of elements obtained from EDX spectra

Inhibitor	Fe	C	N	O
Blank	63.09	36.10	---	---
DEND-G ₀	66.53	25.13	2.71	5.62
DEND-G ₁	65.02	24.20	3.88	6.86
DEND-G ₂	63.25	23.72	4.77	8.26

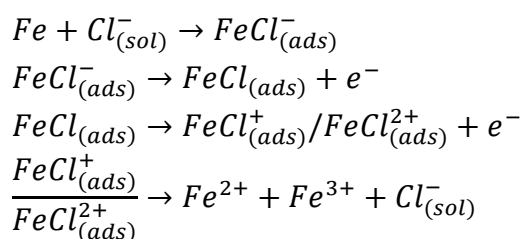
3.4. Mechanism of Corrosion Inhibition

Adsorption of inhibitor is the first step in the corrosion inhibition of metals in acidic media. The adsorption depends upon chemical composition of inhibitor and charge present on metal surface. The development of charge on metal surface is due to electric field development at metal/ electrolyte interface. In acidic media, it is well reported that mild steel possesses the positive charge [54]. The adsorption of inhibitors on metal surface cannot be considered as purely chemical or as physical.

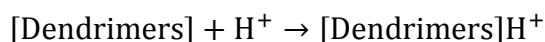
The thermodynamic study reveals that adsorption of dendrimers on mild steel surface is of mixed type. The dendrimers may adsorb on mild steel surface by following way:

1. Electrostatic interaction between positively charged dendrimers and negatively charged mild steel surface (physisorption).
2. Unshared electron pair of heteroatoms (O, N) and vacant d-orbitals of surface iron atoms of mild steel (chemisorption).
3. Interaction of d-electrons of surface iron atoms to the vacant antibonding orbitals of dendrimers (retro-donation)

The anodic dissolution of mild steel in 1 M HCl follows the following steps [55]:

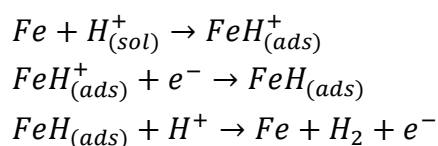


In strong acidic medium Dendrimers molecules get protonated as shown below:



The adsorption of Cl^- ions creates an excessive negative charge on mild steel surface which favor the adsorption of positively charged dendrimers [56]. Initially, positively charged dendrimers start competing with the H^+ ions for electrons on metal surface in acidic medium, thus prevent the oxidation reaction of $FeCl^-$ as shown above [57-58] However, after release of H_2 gas dendrimers molecules returns their neutral forms and lone pairs of heteroatoms facilitate the chemical adsorption.

The cathodic hydrogen evolution can be expressed as follows:



The accumulation of excessive electron density on mild steel surface render it more and this extra negative charged, the electrons from d- orbitals of iron might be transferred to the antibonding orbitals of dendrimers molecules (retro-donation) and hence strengthen the adsorption. From experimental observation it is concluded that the corrosion inhibition efficiency for both the dendrimers is in order: DEND-G₂>DEND-G₁> DEND-G₀. This order of inhibition efficiency of can be best explained on the basis of molecular size and number of heteroatoms present in dendrimers. It is well reported in literature that larger size and higher molecular weight favor the adsorption.

4. CONCLUSION

From weight loss and electrochemical studies it is concluded that:

- 1) All the three studied dendrimers are good corrosion inhibitors for mild steel in 1.0 HCl and their inhibition efficiency values follow the order: DEND-G₂ > DEND-G₁ > DEND-G₀.
- 2) Inhibition efficiency of all dendrimers increases with concentration and maximum efficacy was obtained at 25 ppm concentration.
- 3) Potentiodynamic studied shows that dendrimers are mixed-type inhibitors.
- 4) The adsorption of dendrimers on mild steel surface follows the Langmuir adsorption isotherm.

REFERENCES

- [1] S. A. Ali, M. T. Saeed, and S. V. Rahman, *Corros. Sci.* 45 (2003) 253.
- [2] M. Lagrenee, B. Mernari, M. Bouanis, M. Traisnel, and F. Bentiss, *Corros. Sci.* 44 (2002) 573.
- [3] K. C. Emregul, and O. Atakol, *Mater. Chem. Phys.* 82 (2003) 188.
- [4] C. Kaan, A. Emregul, A. Akay, and O. Atakol, *Mater. Chem. Phys.* 93 (2005) 325.
- [5] M. Elayyachi, A. El Idrissi, and B. Hammouti, *Corros. Sci.* 48 (2006) 2470.
- [6] S. A. Ali, H. A. Al-Muallem, S. U. Rahman, and M. T. Saeed, *Corros. Sci.* 50 (2008) 3070.
- [7] M. A. Quraishi, I. Ahamad, A. K. Singh, S. K. Shukla, B. Lal, and V. Singh, *Mater. Chem. Phys.* 112 (2008) 1035.
- [8] D. A. Tomalia, A. M. Naylor, and W. A. Goddard, *Angew. Chem., Int. Ed. Engl.* 29 (1990) 138.
- [9] E. R. Gillies, and J. M. J. Frechet, *Drug. Discovery. Today.* 10 (2005) 35.
- [10] T. Kim, J. Baek, C. Z. Bai, and J. Park, *Bull. Korean Chem. Soc.* 27 (2006) 11.
- [11] D. Boris, and M. Rubinstein, *Macromolecules* 29 (1996) 7251.
- [12] M. Chai, Y. Niu, W. J. Young, and P. L. Rinaldi, *J. Am. Chem. Soc.* 123 (2001) 4670.
- [13] A. M. Caminade, R. Laurent, and J. P. Majoral, *Adv. Drug. Delivery Reviews* 57 (2005) 2130.
- [14] V. Damme, F. Th, and L. Brobeck, *J. Controll Release* 102 (2005) 23.
- [15] J. Peterson, A. Ebber, V. Allikmaa, M. Lopp, *Proc. Estonian Acad. Sci. Chem.* 50 (2001) 156.
- [16] Q. B. Zhang, and Y. X. Hua, *Electrochim. Acta* 54 (2009) 1881.
- [17] C. B. Verma, M. J. Reddy, and M. A. Quraishi, *Anal. Bioanal. Electrochem.* 6 (2014) 321.

- [18] L. Fragoza-Mar, O. Olivares-Xometl, M. A. Domínguez-Aguilar, E. A. Flores, P. Arellanes-Lozada, and F. Jimenez-Cruz, *Corros. Sci.* 61 (2012) 171.
- [19] C. B. Verma, M. J. Reddy, and M. A. Quraishi, *Anal. Bioanal. Electrochem.* 6 (2014) 515.
- [20] D. K. Yadav, M. A. Quraishi, and B. Maiti, *Corros. Sci.* 55 (2012) 254.
- [21] C. Verma, M. A. Quraishi, and E. E. Ebenso, *Int. J. Electrochem. Sci.* 8 (2013) 7401.
- [22] A. Popova, E. Sokolova, S. Raicheva, and M. Chritov, *Corros. Sci.* 45 (2003) 33.
- [23] G. Quartarone, G. Moretti, A. Tassan, and A. Zingales, *Mater. Corros.* 45 (1994) 641.
- [24] M. J. Reddy, C. B. Verma, E. E. Ebenso, K. K. Singh, and M. A. Quraishi, *Int. J. Electrochem. Sci.* 9 (2014) 4884.
- [25] M. A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav, and A. K. Singh, *Mater. Chem. Phys.* 122 (2010) 114.
- [26] B. Ateya, E. Anadauli, and F. El-Nizamy, *Corros. Sci.* 24 (1984) 509.
- [27] S. T. Hirozawa, *Proc. 8th Eur. Symp. Corros. Inhib. Ann. University, Ferrara, Italy,* (1995) 25.
- [28] O. O. James, K. O. Ajanaku, K. O. Ogunniran, O. O. Ajani, T. O. Siyanbola, and M. O. John, *Trends Appl. Sci. Res.* 6 (2011) 910.
- [29] B. S. Sanatkumar, J. Nayak, and A. N. Shetty, *Int. J. Hydrogen Energy.* 37 (2012) 9431.
- [30] M. Abdallah, *Corros. Sci.* 44 (2002) 717.
- [31] C. Verma, M. A. Quraishi, and E. E. Ebenso, *Int. J. Electrochem. Sci.* 8 (2013) 12894.
- [32] Z. S. Smialowska, and J. Mankowski, *Corros. Sci.* 18 (1978) 953.
- [33] A. Yurt, S. Ulutas, and H. Dat, *Appl. Surf. Sci.* 253 (2006) 919.
- [34] C. Verma, M. A. Quraishi, A. Singh, and J. Taiwan. *Ins. Chem. Eng.* 49 (2015) 229.
- [35] M. A. Quraishi, M. A. Wajid Khan, M. Ajmal, S. Muralidharan, and I. S. Venkatakrisna, *J. Appl. Electrochem.* 26 (1996) 1253.
- [36] O. L. Riggs, Jr. In *Corrosion Inhibitors*, 2nd ed.: Nathan, CC Ed.: NACE: Houston, TX, (1973) pp. 43.
- [37] W. H. Li, Q. He, C. L. Pei, and B. R. H. Hou, *J. Appl. Electrochem.* 38 (2008) 289.
- [38] E. S. Ferreira, C. Giancomelli, F. C. Giacomelli, and A. Spinelli, *Mater. Chem. Phys.* 8 (2004) 129.
- [39] J. Gopal, S. K. Shukla, P. Dwivedi, S. Sundaram, and R. Prakash, *Ind. Eng. Chem. Res.* 5040 (2011) 11954.
- [40] F. Bentiss, M. Traisnel, H. Vezin, and M. Lagrenee, *Ind. Eng. Chem. Res.* 39 (2000) 3732.
- [41] M. A. Quraishi, and D. Jamal, *Mater. Chem. Phys.* 78 (2003) 608.
- [42] Y. J. Tan, S. Bailey, and B. Kinsellal, *Corros. Sci.* 38 (1996) 1545.
- [43] R. S. Goncalves, D. S. Azambuja, and A. M. Serpa Lucho, *Corros. Sci.* 44 (2002) 467.

- [44] C. Verma, E. E. Ebenso, I. Bahadur, I. B. Obot, and M. A. Quraishi, *J. Mol. Liq.* 212 (2015) 209.
- [45] S. L. A. Kumar, M. Gopiraman, M. S. Kumar, and A. Sreekanth, *Ind. Eng. Chem. Res.* 50 (2011) 7824.
- [46] C. Verma, A. Singh, G. Pallikonda, M. Chakravarty, M. A. Quraishi, I. Bahadur, and E. E. Ebenso, *J. Mol. Liq.* 209 (2015) 306.
- [47] B. Mernari, H. Elattari, M. Traisnel, and F. Bentiss, *Corros. Sci.* 40 (1998) 391.
- [48] C. Verma, M. A. Quraishi, L. O. Olasunkanmi, and E. E. Ebenso, *RSC. Adv.* DOI: 10.1039/C5RA16982H
- [49] D. K. Yadav, M. A. Quraishi, and B. Maiti, *Corros. Sci.* 55 (2012) 254.
- [50] C. Verma, M. A. Quraishi, P. Singh, I. Bahadur, and E. E. Ebenso, *J. Mol. Liq.* 209 (2015) 767.
- [51] C. Verma, M. A. Quraishi, A. Singh, and J. Taiwan. *Ins. Chem. Eng.* (2015) <http://dx.doi:10.1016/j.jtice.2015.06.020>.
- [52] S. Deng, X. Li, H. Fu, *Corros. Sci.* 53 (2011) 760.
- [53] C. Verma, P. Singh, and M. A. Quraishi, *J. Ass. Arab. Uni. Basic. Appl. Sci.* (2015) <http://dx.doi.org/10.1016/j.jaubas.2015.04.003>.
- [54] M. Abdallah, *Corros. Sci.* 44 (2002) 717.
- [55] R. Solmaz, G. Kardas, B. Yazıcı, and M. Erbil, *Colloids Surf.* 312 (2008) 7.
- [56] H. Keles, M. Keles, I. Dehri, and O. Serindag, *Mater. Chem. Phys.* 112 (2008) 173.
- [57] O. O. Xometl, N. V. Likhanova, M. A. D. Anguilar, E. Arce, H. Dorantes, and P. A. Lozada, *Mater. Chem. Phys.* 110 (2008) 344.
- [58] A. K. Singh, and M. A. Quraishi. *Corros. Sci.* 51 (2009) 2752.