Accepted Manuscript

Dendrimers: A new class of corrosion inhibitors for mild steel in 1 M HCl: Experimental and quantum chemical studies

Chandrabhan Verma, Eno E. Ebenso, Yeddu Vishal, M.A.Quraishi

PII: DOI: Reference: S0167-7322(16)32541-7 doi: 10.1016/j.molliq.2016.10.117 MOLLIQ 6521

To appear in: Journal of Molecular Liquids

Received date:1 September 2016Revised date:22 October 2016Accepted date:24 October 2016



Please cite this article as: Chandrabhan Verma, Eno E. Ebenso, Yeddu Vishal, M.A.Quraishi, Dendrimers: A new class of corrosion inhibitors for mild steel in 1 M HCl: Experimental and quantum chemical studies, *Journal of Molecular Liquids* (2016), doi: 10.1016/j.molliq.2016.10.117

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Dendrimers: A new class of corrosion inhibitors for mild steel in 1M HCl: Experimental and Quantum Chemical Studies

Chandrabhan Verma¹, Eno E. Ebenso^{*,2}, Yeddu Vishal³, M.A.Quraishi¹

- 1. Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi-221005
- 2. Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
- 3. Department of Metallurgical Engineering, Indian Institute of Technology, Banaras Hindu University, Varanasi-221005
- *Corresponding Author: E-mail: Eno.Ebenso@nwu.ac.za; Fax: +27183892052; Tel: +27 183892050, +27 183892051; Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

Abstract:

The inhibition properties of two ammonia cored dendrimers have been investigated for mild steel corrosion in 1M hydrochloric acid solution using chemical, electrochemical, surface and quantum chemical calculation methods. It was observed that inhibition efficiency increases with increasing the concentration of both the dendrimers and maximum efficiency was obtained at 50 ppm (50 mgL⁻¹) concentration. Potentiodynamic study suggested that investigated dendrimers behaved as mixed inhibitors and their adsorption on mild steel surface obeyed the Langmuir adsorption isotherm. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) examinations of mild steel surface confirmed the inhibition behavior of investigated inhibitor molecules. Atomic force microscopic (AFM) study revealed that studied compounds increases the surface smoothness of AFM micrographs by adsorbing on the metallic surface. Several quantum chemical calculations parameters were calculated and the results obtained were found to be consistent with the experimental findings.

Keywords: Dendrimer, Polarization, Corrosion inhibition, SEM/EDX/AFM, Quantum Chemical calculation

1. Introduction

Mild steel is a major construction material in various industries including food, petroleum, and power production, chemical and electrochemical industries. The acidic solutions are widely used to remove the rust and scales from the corroded mild steel for further uses such as rolling, galvanizing etc. This process of rust removal is pronounced as acid pickling and the acid pickling requires use of corrosion inhibitors in order to protect metals from aggressive dissolution. Due to their ease synthesis and high effectiveness, organic compounds containing heteroatoms particularly oxygen (O), nitrogen (N) and sulfur (S) have been reported as good corrosion inhibitors for mild steel in acidic media [1-7]. Literature survey reveals that a large number of organic compounds having heteroatoms have been utilized as effective corrosion inhibitors for mild steel in acidic media. The nanometer scaled materials have gained much attention due to the novel properties such as their high surface-to-volume ratio [8]. In wives of this, the corrosion inhibition property of two ammonia cored dendrimers (nano material) namely, Generation-G₀ and Generation-G₁ on mild steel corrosion in 1 M HCl was investigated.

A large number of synthetic methods have been developed to synthesis different types of dendrimers having various chemical, biological and medicinal applications [9-11]. However, literature survey reveals that only few of the dendrimers have been employed previously as corrosion inhibitors. Khaled et al. [12] investigated the inhibition efficiency of polyamidoamine dendrimer (PAMAM) on steel corrosion in 1M HCl solution using electrochemical and computational analyses. These authors were found that investigated PAMAM dendrimer acts as cathodic type inhibitors. Molecular dynamics simulation study revealed that the PAMAM adsorb over the metallic surface through unshared electron pair of nitrogen as well as pi-electrons of aromatic rings and amide groups. Verma et al. [13] studied the inhibition performance of three ethylene diamine cored dendrimers, synthesized by condensation of ethylene diamine and methyl acrylate, on mild steel corrosion in 1M hydrochloric acid solution using weight loss, electrochemical and surface analyses methods. These authors were found that adsorption of these dendrimers on metallic surface obeyed the Langmuir adsorption isotherm. Results also showed that investigated dendrimers act as mixed type inhibitors. These authors were observed that dendrimers acted as effective corrosion inhibitors and exhibited highest inhibition efficiency of 96.95% just only 25 mg/L (ppm) concentration. In view of this, in our present investigation we

have reported the corrosion inhibition performance of two ammonia cored dendrimers using weight loss, electrochemical impedance, potentiodynamic polarization, atomic force microscopic (AFM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and quantum chemical calculations methods. The novelty of the present work is that in our previous investigation we have employed ethylene diamine to condense with methyl acrylate, while in our present investigation we have employed cost effective ammonia to condense with methyl acrylate. Therefore, unlike to previous analyses, dendrimers used in the present study are cost effective and thereby green corrosion inhibitors for mild steel in hydrochloric acid solution. Several quantum chemical calculation parameters such as energies of highest occupied (E_{HOMO}) and lowest unoccupied molecular orbitals (E_{LUMO}), energy band gap (E_{LUMO} - E_{HOMO} ; ΔE), global hardness (ρ) and softness (σ) were calculated for neutral and protonated form of dendrimers in order to corroborate experimental results. The choice of these inhibitors as corrosion inhibitors is based on following considerations:

- 1. The dendrimers can be easily synthesized from commercially available starting materials
- 2. The dendrimers contain –CO-NH₂ group and electronegative heteroatoms (O, N).
- These compounds are highly soluble in the tested acidic media due to presence of polar NH₂ groups
- 4. The dendrimers cover large surface area due to their nano size nature [14-17].

2. Experimental section

2.1 Synthesis of Corrosion Inhibitors:

The dendrimers used in present investigation were synthesized by condensation of ammonia and methyl acrylate in methanol as described earlier in literature [18] as shown in Fig. 1. Ammonia and 100 equivalent of methyl acrylate were mixed in methanol. The ammonia solution was added drop wise in methanolic solution of methyl acrylate. After mixing, reaction mixture was stirred for 48 h at 37°C. After completion of the reaction, the residual solvent was removed by rotary evaporator and product was collected. Similar step was adopted for synthesis of other generation dendrimer synthesis. The characterization data of investigated dendrimers are: (1) 3,3',3''-nitrilotripropanamide (DENG-G₀): IR spectrum (KBr cm⁻¹): 3456, 3348, 2854,

1680, 1530, 1484, 1236, 1012; 856; ¹H NMR (300 MHz, DMSO) δ (ppm): 2.56, 2.83, 3.24, 8.52, (2) N1, N1, N7, N7-tetrakis(3- amino-3-oxopropyl)-4-(3-(bis(3-amino- 3-oxopropyl) amino)-3-oxopropyl)heptanediamide (DENG-G₁): IR spectrum (KBr cm⁻¹): 3532, 3446, 3342, 2972, 2848, 1653, 1575, 1456, 1226, 1145; 968; ¹H NMR (300 MHz, DMSO) δ (ppm): 2.64, 2.86, 3.42, 3.58, 8.69.



Fig. 1: Synthesis of investigated inhibitors

2.2 Materials:

Mild steel with chemical 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%, was used for weight loss, surface (SEM/EDX, FM) and electrochemical (potentiodynamic polarization and EIS) measurements. The mild steel specimens were abraded and cleaned by SiC emery of different grade ranging from 600-1200 mesh size, washed with double distilled water, degreased with acetone in ultrasonic bath and finally allowed to dry under hot air blower. The gravimetric experiments were performed on mild steel specimens having dimension of 2.5 cm \times 2.0 cm \times 0.025 cm and mild steel samples 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 1M HCl solution, prepared from AR-grade HCl (35%, MERCK) and double distilled water.

2.3 Gravimetric measurements:

The weight loss experiments were performed on mild steel specimens immersed in 1 M HCl solution in the absence and presence of different concentrations of both studied dendrimers. The volume of the tested solution was 100 ml 1M HCl and immersion time was 3hrs. The weight loss experiments were triply performed to obtain better reproducibility of the data and mean value was reported. Corrosion rate $C_{\rm R}$ (mg cm⁻² h⁻¹) was calculated using following relation:

$$C_{\rm R} = \frac{W}{At} \tag{1}$$

Where, W is the average weight loss of three parallel mild steel strips, A the exposed area of mild strip and t is the immersion time (3hrs). From this calculated corrosion rate (C_R), the inhibition efficiency η % was calculated using the following relationship:

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

The surface coverage (θ) was determined using the following equation:

$$\theta = \frac{C_{\rm R} - C_{\rm R(i)}}{C_{\rm R}} \tag{3}$$

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

2.4. Electrochemical measurements:

The conventional three electrode assembly, consisting of the mild steel with exposed area 1 cm^2 as working electrode, highly pure platinum foil with exposed area 1 cm^2 as counter electrode and saturated calomel electrode (SCE) as reference electrode, was used for all electrochemical experiments. All the electrochemical experiments were performed with Gamry Potentiostat / Galvanostat (Modal G-300) in the absence and presence of optimum concentration of dendrimers in 1M HCl solution after 30 minutes immersion time. Echem analyst 5.0 software was used to collect and analyses all the electrochemical data.

The electrochemical impedance 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 the diameter of Nyquist plots, the charge transfer

resistances (R_{ct}) were calculated and the percentage inhibition efficiency was calculated using the following equation:

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

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

The studied potentiodynamic polarization were performed from -0.25V vs SCE (cathodic potential) to +0.25 vs SCE (anodic potential) with respect to open circuit potential at a sweep rate of 1.5 mVs⁻¹. The corrosion values of current density (i_{corr}) were obtained by extrapolating the linear segment of Tafel cathodic and anodic curves from which the percentage inhibition efficiency was calculated using the following equation:

$$\eta\% = \frac{i_{\rm corr}^0 - i_{\rm corr}^i}{i_{\rm corr}^0} \times 100$$

Where, i_{corr}^0 and i_{corr} are the corrosion current density in the absence and presence of dendrimer, respectively.

(5)

2.5. Surface characterization:

The mild steel samples were immersed in 100 ml HCl solution in absence and presence of optimum concentration of dendrimers for 3hrs immersion time. After elapsed time, mild steel specimens were withdrawn and their surfaces were examined by scanning electron microscopy (SEM) using SEM modal, Ziess Evo 50 XVP instrument at an accelerating voltage of 5 kV at 100 magnifications. For surface morphology measurement by atomic force microscopy (AFM) method the NT-MDT multimode AFM, Russia, controlled by Solver scanning probe microscope controller having single beam cantilever having resonance frequency in the range of 240–255 kHz in Semi-contact mode with corresponding spring constant of 11.5 Nm⁻¹ with NOVA programme was used.

2.7. Theoretical study:

The quantum chemical calculations based on density function theory (DFT) were used in order to perform quantum chemical calculations. Several quantum chemical indices of the molecules have been derived and discussed in order to understand the interaction between metallic surface and inhibitor molecules.

3. Results and discussions

3.1 Weight loss(Gravimetric) experiments:

3.1.1 Effect of concentration and temperature:

The corrosion inhibition efficiency of the dendrimers on mild steel corrosion in 1M HCl solution was investigated after 3 hrs immersion time in the absence and presence of different concentrations of the dendrimers. The variation of inhibition efficiency with inhibitors concentrations is depicted in Fig. 2 (a), and weight loss parameters such as corrosion rate (C_R), surface coverage (θ) and percentage inhibition efficiencies(η %) were calculated and given Table 1. It can be seen form the results that the inhibitions. The maximum values of inhibition efficiency of 94.34% and 96.95% were obtained for DEND-G₀ and DENG-G₁ (Fig. 2), respectively at 50 mg/L concentration. The order of inhibition efficiency follows the order: DEND-G₁> DEND-G₀.



Fig. 2: (a) Variation of inhibition efficiency with concentration

(b) Variation of inhibition efficiency with Temperature

Moreover, from results depicted in Fig. 2(a) and Table 1 it can be seen that further increase in dendrimer concentrations did not cause any appreciable change in the corrosion inhibition performance of the studied inhibitors indicating that 50 ppm is the optimum concentration in the present investigation. The higher inhibition efficiency of the DENG-G₁ as compared to the DENG-G₀ can be attributed to its high molecular size and presence of addition heteroatoms (O and N) which enhances the bonding between the iron on metal surface and inhibitor molecules. The weight loss experiments were also performed in order to the effect of temperature on inhibition efficiency, in temperature range of 308 to 338 K. Moreover, the variation of inhibition performance on increasing solution temperature is attributed due to desorption of adsorbed inhibitors molecules which in turn resulted due to increased kinetic energy of the inhibitor molecules which decreases the interaction between inhibitor and metallic surface [19]. Further, rapid etching, molecular rearrangement and/ or molecular decomposition may also decrease the inhibition efficiency at high solution temperature.

Inhibitor	Conc.	$C_{\mathbf{R}}$	η%	$\boldsymbol{\theta}$
	(mg/L)	$(mgcm^{-2}h^{-1})$		
Blank		7.66		
DEND-G ₀	10	2.80	63.47	0.634
	20	2.16	71.73	0.717
	30	1.33	82.60	0.826
	40	0.80	89.56	0.895
	50	0.43	94.34	0.943
	60	0.40	94.77	0.947
	10	2.60	66.08	0.660
	20	2.06	73.06	0.730
DEND-G ₁	30	1.26	83.47	0.834
	40	0.60	89.56	0.895
	50	0.23	96.95	0.969
	60	0.20	97.38	0.973

Table 1: Weight loss parameters and corresponding inhibition efficiency of mild steel in 1M

 HCl solution.

3.1.2. Adsorption isotherm and free energy of adsorption:

The adsorption isotherm gives mechanistic information about the interaction between inhibitor molecules and metal surface. In this study, several adsorption isotherms including Langmuir, Temkin, Flory–Huggins and Frumkin adsorption isotherms were tested. Langmuir isotherm gave the best fit with the values of regression coefficient very close to unity (Fig. 3 a). The adsorption of the dendrimers in acidic solution can be considered as a quasi-substitution process between the dendrimers in the aqueous phase [DENDs_(sol)] and adsorbed water molecules on metal surface [H₂O_(ads)] as represented by the following equation [20]:

 $DENDs_{(sol)} + x H_2O_{(ads)} \qquad \longleftrightarrow \qquad DENDs_{(ads)} + x H_2O_{(sol)}$

where, x is the number of water molecules replaced by one dendrimer molecule. Thus the adsorption of dendrimers accompanied by removal of adsorbed water molecules from the mild steel surface. The adsorption of dendrimers on the mild steel surface in 1 M HCl solution involves two types of interactions, one is due to electrostatic interaction between charged inhibitor molecules and metal surface (physical adsorption) and other one is due to sharing of charges between inhibitor molecules and vacant d- orbitals of the surface iron atoms (chemical adsorption).



Fig. 3: (a) Langmuir adsorption isotherm (b) Arrhenius plot (c) Transition state plots for mild steel corrosion in 1M HCl solution

The Langmuir isotherms can be represented by the following equation:

(6)

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

where, $C_{(inh)}$ is inhibitor concentration and K_{ads} is equilibrium constant for adsorption-desorption processes. Generally, the value of K_{ads} increases with increasing the concentration of inhibitors and decreases with temperature.

This temperature dependency of K_{ads} can be best represented by following equation:

$$\Delta G_{\rm ads}^{\rm o} = -RT \ln(55.5K_{\rm ads}) \tag{7}$$

where, the ΔG_{ads}° is the free energy of adsorption, R (J mol⁻¹ K⁻¹) is the gas constant, the value 55.5 represents the molar concentration of water in acid solution and the T is temperature (K). The values of ΔG_{ads}° and K_{ads} were calculated at studied temperatures and are given in Table 2. Inspection of the results depicted in the Table reveals that the values of K_{ads} decreases with increasing the temperature (K) which is attributed to decreased extent of adsorption at elevated temperatures. In this study the value of ΔG_{ads}° ranges from -34.28 to -37.18 kJ mol⁻¹ suggesting that dendrimers adsorbed on mild steel surface by both physiosorption and chemisorption methods and predominantly by chemisorption method as values of ΔG_{ads}° are more close to -40 kJ mol⁻¹ [21].

Temperature	DEN	D-G ₀	DEND-G ₁		
	ΔG_{ads}^{0} (k J mol ⁻¹)	$\frac{K_{\rm ads}}{(10^3 {\rm M}^{-1})}$	$-\Delta G_{ads}^{\circ}$ (k J mol ⁻¹)	$\frac{K_{\rm ads}}{(10^4 {\rm M}^{-1})}$	
308	-35.52	19.00	-37.18	36.31	
318	-34.62	7.79	-35.71	11.57	
328	-34.32	5.86	-35.36	8.74	
338	-34.28	5.34	-35.24	7.13	

Table2: Value of free energy of adsorption $(-\Delta G_{ads})$ and adsorption constant (K_{ads}) at various temperature

3.1.3. Kinetic and thermodynamic consideration:

The weight loss experiments were also performed at different temperature ranging from 308 to 338 K, in order to derive the kinetic and thermodynamic parameters. It is generally reported that the value of corrosion rate (C_R) increases with increasing temperature and the temperature dependency of corrosion rate (C_R) can be best represented by Arrhenius and transition state equations [22]:

$$\log(C_{\rm R}) = \frac{-E_{\rm a}}{2.303RT} + \log \lambda$$

$$C_{\rm R} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$
(8)
(9)

where E_a is the apparent effective activation energy, R is the general gas constant, T is the absolute temperature, λ is the Arrhenius pre-exponential factor, h is the Plank's constant, N is the Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. In Fig. 3 (b), linear plots between log C_R vs 1/T are obtained with values of regression coefficient (R^2) close to unity. From the slopes $(-\Delta E_a/2.303R)$ the values of E_a in the absence and presence of optimum concentrations of inhibitor molecules were calculated and are given given in Table 3.

The transition state plots give a straight line between log C_R/T vs 1/T [Fig. 3 (c)] with the values of regression coefficient close to unity. From the slope $(-\Delta H^*/2.303R_{,})$ and intercept ($[\log(R/Nh)+(\Delta S^*/2.303R)])$ of which the values of ΔH^* and ΔS^* were calculated and given in Table 3. Inspection of the Tabulated data reveals that the values of E_a in the presence of dendrimers are higher as compared to that in their absence. The increased values of E_a in the presence of inhibitors is resulted either due to physical adsorption that occurs in first stage [23, 24] or due to decrease in the adsorption of inhibitor molecules on the mild steel surface with increase in solution temperature [25]. The increased values of ΔH^* in presence of both inhibitor molecules as compared to that in their absence, suggest that the dissolution of mild steel in presence of dendrimers is difficult as compare to in their absence [26]. Inspection of the Table 3,

further suggests that values of the ΔS^* increases in presence of dendrimers which clearly indicates that disorderness going to increase from reactant to product site due to increases in entropy of the solution during adsorption process [27].

Table 3: Values of $E_{a,}$ - ΔH^* , ΔS^* in absence and presence of optimum concentration of dendrimers

Inhibitor	E_a	ΔH^*	ΔS^*
	(kJmol ⁻¹)	(kJmol ⁻¹)	$(\text{Jmol}^{-1} \text{ K}^{-1})$
Blank	28.48	26.04	-148.9
DEND-G0	55.47	52.79	-58.77
DEND-G1	65.42	62.74	-31.15

3.2 Electrochemical measurements:

3.2.1. Electrochemical impedance measurements:

Fig. 4(a) represents the Nyquist plot in absence and presence of optimum concentration of the dendrimers in 1M HCl solution. The Bode phase angle and equivalent circuit used for evaluation of electrochemical data are shown in Fig. 4(b) and (c), respectively. It can be observed that the impedance nature of mild steel changes significantly in the presence of the dendrimers without affecting the common features of the Nyquist plots. This finding suggests that dendrimers inhibits mild steel corrosion through adsorption process without affecting the mode of mild steel dissolution [28].

The Nyquist plots show a depressed capacitive loop in the high frequency (HF) range. The formation of HF capacitive loop can be attributed to the charge transfer reaction and time constant of the electric double layer and to the surface inhomogeneity of structural or interfacial origin, such as those found in adsorption processes [29]. Several parameters including solution resistance (R_s), charge transfer resistance (R_{ct}), pseudo capacitance (C_{dl}) and η % calculated from Nyquist plots are given in Table 4.The double layer capacitance (C_{dl}) values in the absence and presence of inhibitors are calculated using the following equation [30]:

$$C_{dl} = \frac{Y\omega^{n-1}}{\sin(n(\pi/2))}$$
(10)

where Y^0 is the CPE coefficient, *n* is the CPE exponent (phase shift), ω is the angular frequency. The ω_{max} represents the frequency at which the imaginary component reaches at maximum. It is the frequency at which the real part (Z_{real}) is midway between the low and high frequency x-axis intercepts. The phase shift provides a general idea about surface morphology of the metal/ electrolyte interfaces. In general, high value of phase shift associated with high surface smoothness. The increased values of phase shift in presence of inhibitor molecules indicate that surface smoothness increased owing to the formation of protective film by inhibitor molecules at metal/ electrolyte interfaces [31].

From Table 4 it is seen that the C_{dl} values decrease in the presence of dendrimers which is attributed to a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer. This finding suggests that dendrimers inhibit the mild steel corrosion by adsorption at the metal/electrolyte interfaces [32].From Table 4 it is also clear that the values of R_{ct} increases in the presence of dendrimers. Generally, higher value of R_{ct} associated with high charge transfer resistance and therefore high inhibition efficiency [33].

The Bode plots of impedance magnitude and phase angles were recorded for working electrode in 1 M HCl solution in the absence and presence of optimum concentration of dendrimers at its open circuit potential. The phase angle having magnitude -90^{0} with slope value unity is associated with ideal capacitive behavior. The deviation from the ideal capacitive behavior of mild steel in present study is due to rough electrode surface which is caused by aggressive attack of corrosion [33]. However, from the Bode plots, it is clear that phase angle remarkably increased in presence dendrimers suggesting that dendrimers retard the corrosion process by adsorption on the metal surface.



Fig. 4 (a-c)(a) Nyquist plot in absence and presence of optimum concentration
(b) Bode plot in absence and presence of optimum concentration
(c) Equivalent circuit used for analysis of EIS data

Table 4: Electrochemical impedance parameters and corresponding inhibition efficiency of dendrimers in 1M HCl solution

Inhibitor	Conc (ppm)	$\frac{R_{\rm s}}{(\boldsymbol{\varOmega}~{\rm cm}^2)}$	$\frac{R_{\rm ct}}{(\boldsymbol{\Omega}~{\rm cm}^2)}$	п	Y^0	$C_{\rm dl}$ ($\mu F {\rm cm}^{-2}$)	η%
Blank	.0	1.12	9.58	0.827	249.8	106.2	
DEND-G ₀	50	1.182	173.7	0.893	101.4	42.03	94.48
DEND-G ₁	50	1.117	259.2	0.838	124.4	31.24	96.30

3.2.2. Potentiodynamic polarization measurements:

The Tafel polarization studies were also performed on the mild steel surface in absence and presence of the optimum concentration of inhibitors in 1M HCl solution. The potentiodynamic polarization nature of mild steel in the absence and presence of optimum concentration of dendrimers is shown in Fig. 5. From this Figure it is clear that both cathodic and anodic reactions were affected in presence of dendrimers suggesting that dendrimers retard the corrosion process by altering the mechanism of mild steel dissolution. The various potentiodynamic polarization parameters were derived from Tafel slopes are given in Table 5. From this Table, it is depicted that corrosion current densities (i_{corr}) decreases in the presence of dendrimers. This finding suggests that dendrimers inhibit the mild steel corrosion in 1M HCl solution. The corrosion potential (E_{corr}) does not change significantly in presence of dendrimers suggesting that investigated dendrimers were mixed type inhibitors [34].



Fig. 5: Potentiodynamic polarization curves for mild steel corrosion in 1M HCl solution in absence and presence of optimum concentration of dendrimers

Inhibitor	Conc (mg/L)	i _{corr} (μA/cm ²)	E _{corr} (mV/SCE)	β_{a} (mV/dec)	β_{c} (mV/dec)		η%
Blank	0.0	1150	-445	70.5	104.7		
DEND-G ₀	50	71.35	-507	88.40	115.2	0.9379	93.79
DEND-G ₁	50	28.4	-489	76.7	147.2	0.97.53	97.53

Table 5: Potentiodynamic polarization parameters and corresponding inhibition efficiency

3.3 Surface studies

3.3.1 Scanning electron microscopic study:

The mild steel specimens were immersed in test solution for 3 hrs immersion time in the absence and presence of optimum concentration of the investigated dendrimers. After the elapsed time, the specimens were taken out and their surface morphology was determined. Fig. 6 (a) represents the SEM micrograph of the mild steel specimen corroded in the acidic solution in absence of the inhibitors which is characterized by highly corroded and damaged surface with pits and cracks. However, in the presence of optimum concentrations of the studied dendrimers [Fig. 6 (b-c] the surface morphologies of the specimens have been remarkably improved owing to the formation of the protective film on the metallic surface. This finding further suggests that dendrimers inhibit mild steel corrosion in acid solution by adsorption process.





Fig. 6: SEM micrographs in absence (a) and presence of DEND- G_0 (b) and DEND- G_1 (c) after 3h immersion time

3.3.2 EDX analysis:

The EDX spectra of the mild steel after 3h immersion time in the absence and presence of optimum concentration of the dendrimers are shown in Fig. 7(a-c). Fig. 7(a), represents the EDX spectrum of mild steel corroded in free acid without any inhibitor which clearly shows the signals for the presence of iron (Fe), carbon (C) and oxygen (O). Presence of oxygen in the EDX spectrum of uninhibited mild steel specimen is attributed due to formation of ferrous and ferric oxide due to atmospheric oxidation during SEM-EDX analyses. Moreover, signal for nitrogen is absent in the EDX spectrum of uninhibited mild steel specimen. However, EDX spectra in presence of dendrimers [Fig. 7(b-c)] shows the characteristics peaks for nitrogen and oxygen which is might be due to formation of protective film by dendrimers on mild steel surface. Further, careful examination of the EDX spectra of inhibited mild steel specimens revealed that intensity for signal corresponding to oxygen have been significantly increased due to adsorption of the dendrimers over metallic surface.



Fig. 7: EDX spectra of mild steel surface of (a) 1M HCl solution (b) inhibited mild steel (1 M HCl + 50 mg/L DEND-G₀), (1 M HCl + 50 mg/L DEND-G₁)

3.3.3 Atomic force microscopy:

The three dimensional picture of mild steel surfaces in the absence and presence of optimum concentration of the dendrimers after 3h immersion time is shown in Fig. 8. Fig. 8(a), represent the surface of mild steel in free acid solution, showing characteristics pits and cracks with badly damaged surface. The calculated average surface roughness was 392 nm in absence of dendrimers. However, in presence of dendrimers surface morphologies remarkably improved due to formation of protective film on mild steel surface. The average surface roughnesses were 119 nm and 84 nm in presence of DEND- G_0 and DEND- G_1 , respectively.



Fig. 8: Atomic force micrographs of mild steel surface of (a) mild steel in 1 M HCl, (b) inhibited mild steel (1 M HCl + 50 mg/L DEND-G0), (c) inhibited mild steel (1 M HCl + 50 mg/L DEND-G₁).

3.4 Quantum Chemical calculation:

Figs. 9 and 10 represent the geometrically optimized structures and frontier electron distribution of the neutral inhibitor molecules. Several quantum chemical parameters such as such as energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), $E_{HOMO}-E_{LUMO}$ energy gap (ΔE), dipole moments (μ), global hardness (ρ) and softness (σ) are summarized in the Table 6. Generally, E_{HOMO} represents the electron donating ability of the inhibitor molecule to the d-orbital of the surface metal atoms. An inhibitor having larger value of the E_{HOMO} associated with higher electron donating ability and lower electron accepting ability of the inhibitor molecules. Moreover, the highest occupied molecular frontier electron distribution represents the region susceptible for electron donation. From the $E_{\rm HOMO}$ electron distribution it can be seen that frontier electron density is mainly localized over the center nitrogen atom, suggesting that this nitrogen atom mainly participating in the electron donation. Conversably, E_{LUMO} represents the electron accepting tendency of the inhibitor molecule into its empty anti-bonding molecular orbitals. Generally, the inhibitors having larger values of E_{LUMO} associated with lesser electron donating ability and greater electron accepting ability of the molecules [35]. From the frontiers molecular electron distribution it can be observed that LUMO is also mainly localized over the center nitrogen atom and few adjacent carbon atoms, indicating that this part mainly accepting electrons from d-orbital of the surface iron atoms during retro-donation.



Fig. 9: Optimized structure of (a) DEND- G_0 (b) DEND- G_1



Fig. 10: Frontier molecular orbitals of (a) DEND-G₀ (b) DEND-G₁

From the theoretical data depicted in Table 6, it can be observed that DEND-G₁ associated with larger value of E_{HOMO} and smaller value of E_{LUMO} as compared to DEND-G₀ suggesting that DEND-G₁ possesses higher corrosion inhibition ability than DEND-G₀. The energy band gap; ΔE (E_{LUMO} - E_{HOMO}) is another important reactivity parameter that can be used to predict the relative order of adsorption. In general, a lower value of ΔE is associated with higher chemical reactivity and therefore high inhibition efficiency. In our present investigation values of ΔE obeyed the order: DENG-G₀ > DENG-G₁ indicating that DENG-G1 has greater tendency of adsorption [36]. The global hardness (ρ) and softness (σ) were also calculated from the values of E_{HOMO} and E_{LUMO} using equations 11 and 12 [37]. A lower value of hardness and higher value of softness is consisted with high chemical reactivity and therefore high inhibition efficiency. In our

present case, the values of softness follow the order: $DENG-G_0 < DENG-G_1$, which in accordance to the order of inhibition efficiency obtained experimentally [38].

global hardness (
$$\rho$$
) = $\frac{\Delta E}{2}$ (11)
global hardness (ρ) = $\frac{1}{\text{global softness (σ)}}$ (12)

Lastly, the corrosion inhibition efficiency of both the studied dendrimers was correlated with their dipole moment obtained by quantum chemical calculations. Generally, an organic compound having higher value of dipole moment is more susceptible for polarization when come to the metallic surface [37,38]. I our present study, results depicted in Table show that DENG-G₁ is associated with high dipole moment indicating that it is more polarization and cover the larger metallic surface area, and therefore acted as better inhibitor as compared to DENG-G₀.

Organic compounds containing heteroatoms in form of polar group and/ or in cyclic ring exist in protonated form due to presence of unshared electron pairs. Therefore, in our present investigation, quantum chemical calculation was also performed on protonated form of the inhibitor molecules. The fully optimized and frontier electron distribution pictures of the studied dendrimers are shown in Figs. 11 and 12 and derived parameters are given in Table 6. Form the frontier molecular electron distribution pictures it can be seen that unlike to neutral DENG-G₀ HOMO is localized almost entire part of the molecule and therefore the inhibitor would act as better inhibitor in protonated form. Moreover, careful examination of the Fig. 12 shows that for DENG-G₀ LUMO is mainly concentrated on the terminal amide groups, unlike to neutral form of the inhibitor were LUMO was localized over central nitrogen atom only. In DENG-G1, HOMO is localized around the central nitrogen atom similar to the neutral from of the inhibitor. However, unlike to neutral form, LUMO is concentrated mainly on the ethyl group embedded between central nitrogen and terminal amide groups. The quantum chemical calculation parameters calculated for protonated form of dendrimers are given in Table 6. Inspection of the results shown in Table 6 showed that E_{HOMO} , E_{LUMO} , ΔE , hardness (ρ), softness (σ) and dipole moment (μ) calculated for protonated form of dendrimers obeyed the same order that obtained for neutral form of dendrimers.



Fig. 11: Optimized structure of protonated form of DEND- $G_0(a)$, and DEND- $G_1(b)$.



Fig. 12: Frontier molecular orbitals of protonated form of DEND- G_0 (a) and DEND- G_1 (b).

				L					
Inhibitor	E _{HOMO}	$E_{\rm LUMO}$	ΔE	μ	ρ	σ			
	(Hartree)	(Hartree)	(Hartree)	(D)	(Hartree)	(Hartree)			
	Neutral from of dendrimers								
DEND-G ₀	-0.246	0.314	0.560	4.75	0.280	3.57			
DEND-G ₁	-0.014	0.246	0.260	15.33	0.130	7.67			
			6						
Protonated form of dendrimers									
DEND-G ₀ .H ⁺	-0.25317	0.00082	0.253	2.157	0.127	7.874			
- 0-									
DEND- G_1 . H^+	-0.23291	0.00762	0.240	9.702	0.120	8.333			

Table 6: Quantum chemical calculation parameters obtained from geometrically optimized molecules.

4. Mechanism of inhibition

The mild steel dissolution in acid solution can occur by two steps i.e. anodic mild steel dissolution and cathodic hydrogen evolution. The anodic dissolution of the mild steel in acid hydrochloric acid solution follows the steps given below [39,40]:

$$Fe + Cl \leftrightarrow FeCl_{(ads)}$$
(13)

$$FeCl_{(ads)} \longrightarrow FeCl_{(ads)} + e^{-}$$
 (14)

$$FeCl_{(ads)} \longrightarrow FeCl_{(ads)}^{+} + e^{-}$$
(15)

$$\operatorname{FeCl}_{(ads)} \longrightarrow \operatorname{Fe}^{2+}/\operatorname{Fe}^{3+} + \operatorname{Cl}$$
 (16)

It is well known that organic inhibitors containing heteroatoms exist in their cationic forms due to protonation of the heteroatoms and mild steel surface become negatively charged due to adsorbed chloride ions. These two appositively charged species attracted each other by electrostatic force of attraction. The cathodic hydrogen evolution cam be represented by following steps [39,40]:

$$Fe + H^+ \longrightarrow FeH^+_{(ads)}$$
 (17)

$$FeH_{(ads)}^{+} + e^{-} \iff FeH_{(ads)}$$
(18)

$FeH_{(ads)} + H^+ + e^- \quad \longleftarrow \quad Fe + H_2 \tag{19}$

The positively charged inhibitor adsorbed to the cathodic site of metal and thereby reduces the rate of hydrogen evolution. An organic inhibitor can adsorb on mild steel by:

- 1. Electrostatic interaction between charged inhibitors and charged mild steel surface (physisorption).
- 2. unshared electron pairs of heteroatoms and vacant d-orbital of Fe surface atoms (chemisorption), or
- interaction of d-electron of iron surface atom to the vacant orbital of inhibitor molecule (retro donation) and
- 4. Combination of above processes [39-41].

During first step of adsorption, the protonated form of dendrimers in 1M HCl start competing with H^+ ions for electrons on metal surface. However, after evolution of H_2 gas, the positively charged dendrimers returns to their neutral form and heteroatoms (O, N) with free lone pairs of electrons promote chemical adsorption [42]. The accumulation of extra negative charge on mild steel surface render it's to donate electrons to anti bonding molecular orbitals. It is well stabilized that inhibitors can also accept the electrons into their anti-bonding molecular orbitals from the surface iron atoms and thus strengthens the adsorption by synergism [43]. In our present case the order of efficiency is: DEND-G₁ > DEND-G₀.

5. Conclusions

From above study this can be concluded that:

- 1. Dendrimers are good corrosion inhibitors for mild steel in 1M HCl solution.
- 2. The inhibition efficiency increases with the increase of the concentration of the inhibitors and maximum was found at 50 ppm concentration.
- 3. The potentiodynamic polarization study reveals that dendrimers are mixed type inhibitors
- 4. The adsorption of the dendrimers follows the Langmuir adsorption isotherm.
- 5. The negative value of Gibb's free energy suggests the spontaneous nature of adsorption.
- 6. SEM analysis suggests that dendrimers form protective film on the mild steel surface.
- 7. Theoretical calculation is in good agreement with the experimental data.

References

- [1] S.A. Ali, M.T. Saeed, S.V. Rahman, *Corros. Sci.*, 45 (2003) 253-266.
- [2] M. Lagrenee, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, *Corros. Sci.*, 44 (2002) 573-588.
- [3] C. Verma, M.A. Quraishi, A. Singh, J. Mol. Liq., 212 (2015) 804–812
- [4] K. C. Emregul, A. A. Akay, O. Atakol, *Mater. Chem. Phys.*, 93 (2005) 325-329.
- [5] M. Elayyachi, A. El Idrissi, B. Hammouti, *Corros. Sci.*, 48 (2006) 2470-2479.
- [6] C. Verma, L. O. Olasunkanmi, E. E. Ebenso, M. A. Quraishi, I. B. Obot, *J. Phys. Chem. C*, 120 (2016) 11598–11611.
- [7] M.A. Quraishi, I. Ahamad, A.K. Singh, S.K. Shukla, B. Lal, V. Singh, *Mater. Chem. Phys.* 112 (2008) 1035-1039.
- [8] H.J. Shin, I.W. Hwang, Y.N. Hwang, J. Phys. Chem. B., 107 (2003) 4699-4704.
- [9] D. A. Tomalia, A. M. Naylor, W. A. Goddard, Angew. Chem., Int.Ed., 29 (1990) 138-175.
- [10] E. R.Gillies, J. M. J. Frechet, Drug. Disco. Very Today., 10 (2005) 35-43.
- [11] U. Boas, P. M. H. Heegaard, *Chem. Soc. Rev.*, 33 (2004) 43-63.
- [12] K.F. Khaled, A. A. Atta, N. S. Abdel-Shafi, J. Mater. Environ. Sci., 5 (2014) 831-840.
- [13] C. Verma, M. A. Quraishi, Anal. Bioanal. Electrochem., 8 (2016) 104-123.
- [14] D. Boris, M. Rubinstein, *Macromolecules*, 29 (1996) 7251-7260.
- [15] Chai, M. Y. Niu, W.J. Youngs and P.L. Rinaldi, J. Am. Chem. Soc., 123 (2001) 4670-4678.
- [16] A. M. Caminade, R. Laurent and J.P. Majoral, *Advan. Drug Delivery Reviews*, 57 (2005) 2130-2146.
- [17] V. Damme, F. Th, L. Brobeck, J. Control. Relea., 102 (2005) 23-38.
- [18] Tae-il Kim, Jung-un Baek, Cheng Zhe Bai, and Jong-sang Park, Bull. Korean Chem. Soc., 27 (2006) 1894-1896.
- [19] N. K. Gupta, C. Verma, M.A. Quraishi, A. K. Mukherjee, J. Mol. Liq., 215 (2016) 47–57
- [20] N.A. Negm, N.G. Kandile, E.A. Badr, M.A. Mohammed, *Corros. Sci.*, 65 (2012) 94-103.
- [21] C. Verma, P. Singha, I. Bahadur, E.E. Ebenso, M.A. Quraishi, J. Mol. Liq., 209 (2015) 767–778.

- [22] E.E. Ebenso, N.O. Eddy, A. O .O Odiongenyi, *Portugaliae Electrochimica. Acta.*, 27 (2009) 13-22.
- [23] E.A. Noor, A.H. Al-Moubaraki, Mater. Chem. Phys., 110 (2008) 145-154.
- [24] L. Larabi, Y. Harek, O. Benali, S. Ghalem, Prog. Org. Coat., 54 (2005) 256-262.
- [25] C. Verma, A. Singh, G. Pallikonda, M. Chakravarty, M.A. Quraishi, I. Bahadur, E.E. Ebenso, J. Mol. Liq., 209 (2015) 306–319
- [26] C. Verma, L. O. Olasunkanmi, E. E. Ebenso, I. B. Obot, M. A. Quraishi, RSC Adv., 6 (2016) 53933–53948.
- [27] I. Ahamad, M.A. Quraishi, Corros. Sci., 51 (2009) 2006-2013.
- [28] I. Ahamad, R. Prasad, M. A. Quraishi, Corros. Sci., 52 (2010) 1472-1481.
- [29] C. Verma, E.E. Ebenso, I. Bahadur, I.B. Obot, M.A. Quraishi, J. Mol. Liq., 212 (2015)
 209–218
- [30] A. K. Singh, M. A. Quraishi, Corros. Sci., 52 (2010) 152-160.
- [31] C. B. Verma, M.A. Quraishi, E.E. Ebenso, Int. J. Electrochem. Sci., 8 (2013) 10864-10877.
- [32] M.A. Quraishi, J. Rawat, Mater. Chem. Phys., 70 (2001) 95-99.
- [33] E. Naderi, A. H. Jafari, M. Ehteshamzadeha, M. G. Hosseini, *Mater. Chem. Phys.*, 115 (2009) 852-858.
- [34] R. Solmaz, G. Kardas, B. Yazıcı, A M. Erbil, *Colloids Surf.*, 312 (2008) 7-17.
- [35] H. Keles, M. Keles, I. Dehri, O. Serindag, Mater. Chem. Phys., 112 (2008) 173-179.
- [36] O. O. Xometl, N. V. Likhanova, M. A. D. Anguilar, E. Arce, H. Dorantes, P. A. Lozada, *Mater. Chem. Phys.*, 110 (2008) 344-351.
- [37] V. S. Sastri, J. R. Perumareddi, *Corrosion.*, 53 (1997) 617-622.
- [38] I. Lukovits, E. Klaman, F. Zucchi, Corrosion., 57 (2001) 3-8.
- [39] R. Solmaz, G. Kardas, B. Yazıcı, M. Erbil, *Colloids Surf.*, A 312 (2008) 7–17.
- [40] A. K.Singh, Ind. Eng. Chem. Res. 51 (2012) 3215–3223.
- [41] D.P. Schweinsberg, G.A. George, A.K. Nanayakkara, D.A. Steiner, Corros. Sci. 28 (1988) 33-42.
- [42] H. Shorky, M. Yuasa, I. Sekine, R.M. Issa, H.Y. El-Baradie, G.K. Gomma, *Corros.Sci.*, 40 (1998) 2173-2186.

- [43] C. Verma, M. A. Quraishi, L. O. Olasunkanmi, E. E. Ebenso, *RSC Adv.*, 5 (2015) 85417– 85430.
- [45] D. K. Yadav, M. A. Quraishi, Ind. Eng. Chem. Res., 51 (2012) 8194-8210.
- [46] C. Verma, L. O. Olasunkanmi, I. B. Obot, Eno E. Ebenso, M. A. Quraishi, RSC Adv., 6 (2016) 15639–15654.

A CER MAN

Highlights

- Dendrimers were studied as corrosion inhibitors.
- Their corrosion inhibiting effect against steel in 1M HCl solution was studied.
- EIS, potentiodynamic polarization methods, Quantum chemical studies were used for analysis.
- These inhibitors were adsorbed onto surfaces obeying Langmuir adsorption model
- o Theoretical and experimental results were in agreement

A CERTING