

Dendrimers as novel class of polymeric corrosion inhibitors: A review

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Abstract

Dendrimers are a new class of highly branched, nano-sized, monodisperse macromolecules that have several fascinating physical and chemical characteristics. They are highly soluble in the polar solvents, contain several surface functionality and high surface area which makes them suitable reagents for industrial and biological applications. Recently, several dendrimers have been investigated as effective corrosion and scale inhibitors for metallic and silica corrosion using experimental and theoretical methods. Generally, dendrimers become effective by forming insoluble metal-dendrimer or silica-dendrimer composite on the surface. Their inhibition performance of dendrimers have been measured using several experimental such as weight loss, electrochemical (EIS and PDP) and surface (EDX, SEM and AFM) as well as computation techniques such as molecular dynamics simulation and DFT based quantum chemical calculations. The interactions between metal surface and dendrimers can be explain through some common parameters such as E_{HOMO} , E_{LUMO} , ΔE , electronegativity (χ), hardness (η), softness (σ), dipole moment (μ) and fraction of electron transfer (ΔN). Present book chapter deals with detail description on the corrosion inhibition and anti-scaling behaviours of dendrimers for metals and silica in several electrolytic media.

Keywords: dendrimers, corrosion inhibitors, mixed type, Langmuir adsorption isotherm, DFT study.

1. Introduction

1.1. Corrosion and its adverse effect

Most of the metals are highly unstable and readily react with the components of the surrounding environment by chemical or electrochemical mechanism and convert some more stable forms (rusts and scales). This is an irreversible, spontaneous and damaging phenomenon and commonly termed as corrosion. Corrosion causes huge losses of metallic materials and their properties which ultimately results into big economic and safety losses throughout the world. Therefore, corrosion has become worldwide problem for developed as well as developing nations to be considered by educational as well as industrial sectors [1, 2]. A study conducted by National Association of Corrosion Engineers (NACE; 2002) revealed that in the year 1998, United State annually losses about US \$276 billion which equates about 3.1% of total U.S. gross domestic product (GDP) [3, 4]. The cost of corrosion in U.S. exceeded more than US \$2.2 trillion in the year 2011. In India, according to 1st Global Corrosion Summit held in New Delhi, corrosion causes loss of about Rs. 2 lakhs crores (US \$45 billion) in the year 2011 [3, 4]. According to the most recently published data from the NACE study reveals that annually (worldwide) corrosion causes loss of around US \$2.5 trillion which equates about 3.4% of the world GDP [3, 4]. The annual loss due to corrosion in India and South Africa are about Rs. 6 lacks crores (US \$100-billion) and R130-billion (i.e. about US \$ 9.6 billion), respectively [3, 4].

1.2. Factors affecting corrosion

Corrosion is a spontaneous process in which metals (except gold, silver and platinum) and alloys undergo rapid oxidation in the presence of constituents of the surrounding environment. Because corrosion is a spontaneous phenomenon its rate mainly depends upon the change in the standard Gibbs' free energy (ΔG_{corr}^0). The greater change in standard Gibbs' free energy (ΔG_{corr}^0 ; in negative) results into higher chemical spontaneity or corrosion rate and *vice versa* [5–7]. Generally, rate of metallic corrosion influenced by several factors such as solution temperature, nature of metals and electrolytes and presence of impurities [7–11]. Besides these environmental factors, corrosion rate is also influenced by nature of rusts and scales accumulated on the metallic surface which may or may not be protective. The inhibitive and corrosive nature of the accumulated rusts and scales collected on the metallic surface can be determined by Pilling–Bedworth ratio which is generally expressed by Md/mnD [12, 13]. In the Pilling–Bedworth ratio M and D are respectively, represent the molecular weight and density of the rusts and/or scales gathered on the surface. Whereas, m and d , respectively represent the atomic weight and density of the metal under consideration and n represents the metallic number in the rusts and scales (corrosion products); for example in Fe_2O_3 , Al_2O_3 and Fe_3O_4 , n are 2, 2 and 3 respectively [12, 13]. In general, for case $Md/mnD < 1$, it is expected that volume of metal surface is larger than that of the corrosion products (rusts/scales) and therefore surface film is non-

protective as it contains exposed metallic area. Conversely, for case $Md/mnD > 1$, it is expected that volume of metal surface is smaller than corrosion products and in this situation surface film will be more compact, compressed and protective in nature.

1.3. Corrosion monitoring techniques

The corrosion is a dangerous phenomenon and therefore previously several methods of its protection have been developed by properly applying then the cost of corrosion can be reduced from 15% (US \$ 375 billion) to 35% (US \$ 875 billion). The available methods of corrosion protection is shown in the Figure 1. Among the commonly used corrosion control methods such as coating, plating, potential change, design improvement and environmental modification, use of synthetic corrosion inhibitors is the most common and effective methods due to their ease synthesis and application as well as cost effective nature [14, 15]. The anodic inhibitors are also known as passivation inhibitors as they generally inhibit corrosion by forming the passive film on the metal surface that causes a large shift in the corrosion potential (E_{corr}) towards anodic direction [16]. There are several anodic inhibitors such as nitrate, chromate and nitrite, known those can passivate metallic surface even in the absence of oxygen and called as oxidizing anodic (anions) inhibitors. On the other hands there are several other inhibitors such as molybdate, tungstate and phosphate those can passivate metallic surface only in the presence of oxygen. These passivating inhibitors are known as non-oxidizing anions. The cathodic inhibitors either retards the cathodic reaction or precipitates on the cathodic area which retort the rate of diffusion of reducible species like H^+ and thereby increase the surface impedance [16, 17]. The cathodic inhibitors generally act by three different mechanisms namely, cathodic precipitates, cathodic poisons and oxygen scavengers. The sodium sulphide and hydrazine react with the surrounding oxygen and behave as most common oxygen scavengers. Arsenic and antimony are two most common cathodic poisons as they retard the combination of hydrogen ions during their cathodic reduction. The calcium, magnesium and zinc easily form oxides which generally precipitate on the cathodic area and act as cathodic precipitates [18–20]. It is recalled that out of various corrosion control methods, the use of organic inhibitors is the most common and popular method.

These inhibitors contain several heteroatoms those exist in the form of polar functional groups like $-\text{NO}_2$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{NMe}_2$, $-\text{COOC}_2\text{H}_5$, $-\text{CN}$ and $-\text{O}-$ etc. [21–23]. The polar functional groups along with the non-bonding electrons of heteroatoms and pi-electrons of the multiple bonds behave as adsorption centres during interactions between inhibitor and metal surface. The interactions of inhibitors with metal result into their adsorption on the surface which is behaves as barrier for corrosion process [21–27].

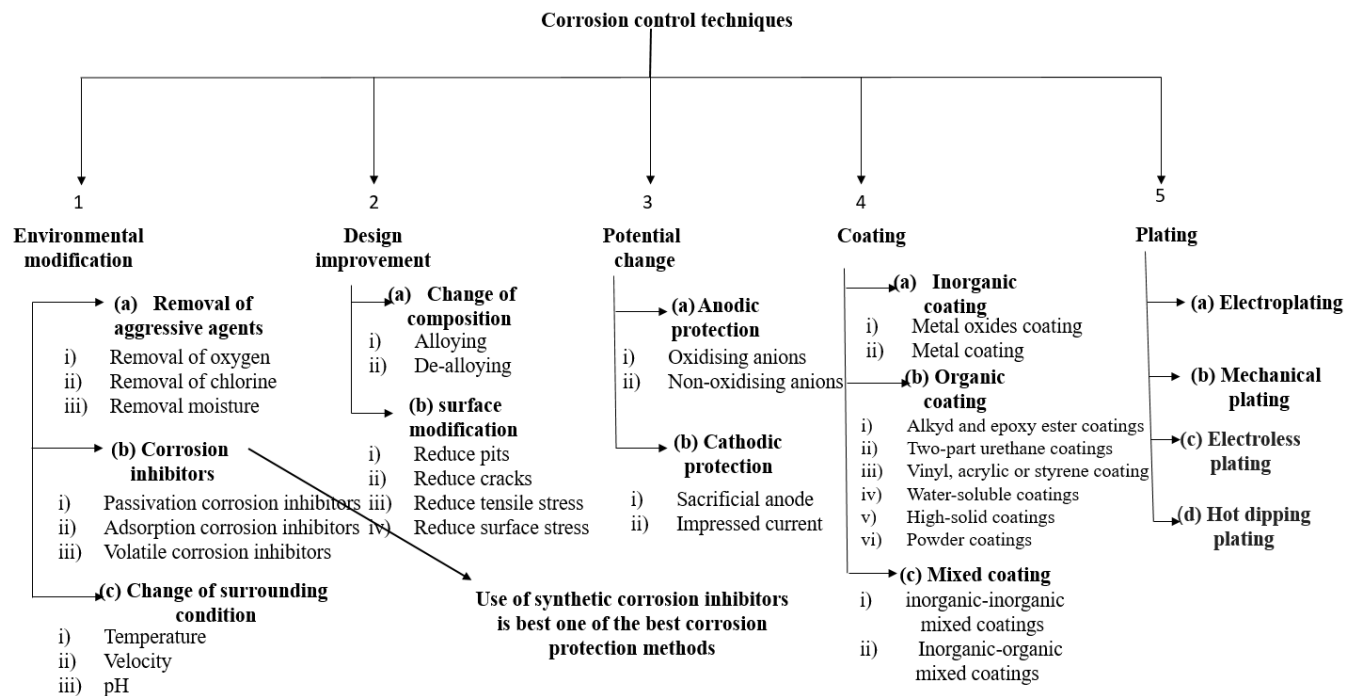


Figure 1. Methods of corrosion protection.

1.4. Salient features and classification of dendrimers

Dendrimers are highly branched polymeric materials which consist of three different architecture components namely, core, branches and terminal functional groups [28]. Core constitutes the central part of the dendrimeric architecture which may be either an atom or a molecule with at least two identical functionality (chemical functional groups). The branches are the repeat units of dendrimers which start from core *i.e.* focal point. The geometric repetition of the dendrimeric branches results into the formation of radially centric layers called as “generations” [28, 29]. The terminal functional groups are positioned at the periphery of the dendrimeric architecture and is the most critical factor which determines the property of the dendrimers. The nano-sized dendrimeric polymers differ from the linear (ordinary) polymers in the sense that dendrimers are highly precise controlled architecture with high surface functionality. Moreover, in contrast to linear, dendrimeric polymers are synthesized by controlled chemical reaction that leads to the construction of globular, monodisperse and macromolecular polymeric architecture [28, 29]. The dendrimers architectures can be further classified into dendrigraft polymers, hyper-branched polymers, dendrons and dendrimers [28, 29]. There are two different approaches namely, divergent and convergent are being utilized for the synthesis of variety of dendrimeric polymers. In divergent approach, synthesis of the dendrimers starts from the core and rapidly grown away to the periphery. In contrast, convergent synthesis starts from the periphery and proceeds toward interior before their joining two pre-synthesized dendrons to the dendrimer core [28, 29]. Several types of dendrimers are being synthesized

using various core and surface functional molecules. Figure 2 briefly describes the different types of dendrimers studied in the literature.

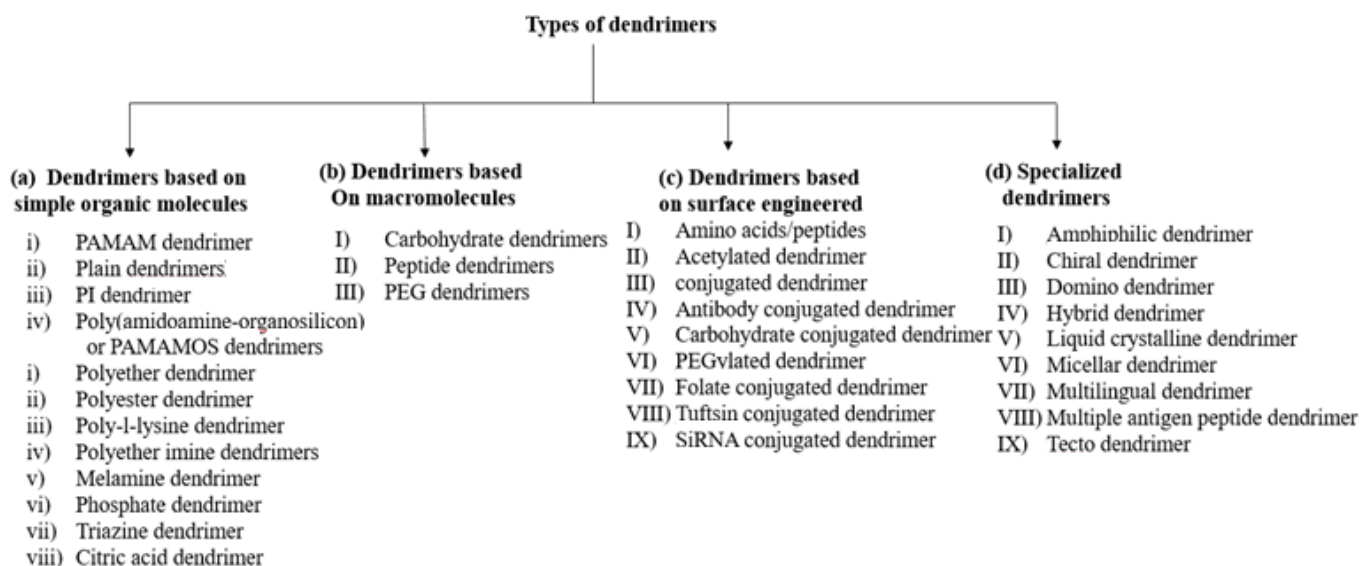


Figure 2. Types of dendrimers.

2. Dendrimers as corrosion inhibitors

Most of the known corrosion inhibitors are small organic molecules and therefore either they occupy lower metallic area or require high concentration as compared to the polymeric corrosion inhibitors [30–32]. Several kinds of the polymers have been used as corrosion inhibitors for metals and alloys in the different kinds of electrolytic media. Literature survey reveals that recently few dendrimeric polymers have also been investigated as effective corrosion inhibitors particularly for mild steel in acidic and CO₂ solutions. Due to presence of long molecular chain, their ease and effective synthesis, nano-sized (high surface area), high solubility in the polar electrolytic media like H₂O and HCl and presence of polar functional groups at the periphery, dendrimers can adsorb and act as good corrosion inhibitors for metallic corrosion in the different electrolytic media. Moreover, due to their polymeric nature they cover the larger surface area and form relatively more effective corrosion barrier on the metal surfaces which isolates them from surrounding environments and thereby inhibit metals corrosion. Khaled and co-workers [33] study the inhibition property of ethylenediamine cored, hydrophilic and highly branched PAMAM dendrimer on steel corrosion in 1 M hydrochloric acid medium using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and molecular dynamics simulation methods. These authors studied the inhibition effect of PAMAM at 5, 15, 20, 30, 50 and 100 ppm (mg L⁻¹) concentrations and observed that it shows the maximum inhibition efficiency of 88.78% at 100 ppm concentration. PDP study revealed that investigated PAMAM dendrimer behaves as cathodic type inhibitor and EIS study showed that addition of the PAMAM in the corrosive environment increases the polarization resistance and thereby retards the metallic corrosion. The molecular dynamics

simulation study suggests that the PAMAN dendrimer inhibits steel corrosion by adsorbing on the surface in which nitrogen atoms as well as π -electrons act as adsorption centres.

The inhibition property of ethylenediamine core based three generation namely, DENG-G₀, DENG-G₁ and DENG-G₂ dendrimers on mild steel corrosion in the solution of 1M HCl using weight loss, PDP, EIS, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques has been studied by Verma and Quraishi [34]. All the studied dendrimers act by adsorbing on the surface through their non-bonding electrons of oxygen and nitrogen as well as π -electrons of $>C=O$ bonds. Their adsorption on the test material obeyed the Langmuir adsorption isotherm. The studied dendrimers act as mixed type inhibitors as depicted by their polarization study. The inhibition efficiency of the tested dendrimers at their optimum concentration of 25 ppm/ 11.2×10^{-5} M follows the sequence: DENG-G₀ (94.78%) < DENG-G₁ (96.08%) < DENG-G₂ (96.95%). The EIS results suggest that the dendrimers adsorb on the interfaces of metal and electrolyte and act as barrier for corrosive metallic dissolution. The adsorption mechanism of corrosion inhibition derived from weight loss, EIS and PDP methods was supported by SEM and EDX analyses. SEM images in presence of optimum concentration of the dendrimers show significant smoothness in the surface morphology as compared to the SEM image of uninhibited metal specimen. This finding revealed that dendrimers adsorb on the metal surface and protect from corrosion. The EDX spectra of inhibited metallic specimens showed signals for the presence of nitrogen and oxygen which was absent in the EDX spectrum of uninhibited mild steel specimen conforming that dendrimers adsorbed on the metal specimens. Moreover, the intensity of the signals correspond to nitrogen and oxygen enhance from going DENG-G₀ to DEND-G₂ which suggests that effectiveness of the adsorption increases in the same order.

Zhang *et al.* [35] reported the inhibition properties of ethylenediamine based polyamidoamine (PAMAM) dendrimer in the combination with sodium silicate for carbon steel in soft water using weight loss, EIS, PDP, EDX and atomic force microscopic (AFM) methods. The study reveals that investigated dendrimer is an eco-friendly inhibitor and its lower doses are required for effective corrosion inhibition. Both the tested components *i.e.* PAMAM and sodium silicate inhibit carbon steel corrosion by the mechanism of adsorption. The adsorption of sodium silicate and PAMAM obeyed the Langmuir adsorption isotherm. PDP study revealed that addition of the dendrimer and sodium silicate in the corrosive medium affected both anodic as well as cathodic reactions and did not caused any significant change in the value of E_{corr} suggesting that PAMAM and sodium silicate undertaken in the investigation are mixed type inhibitors. The different combinations of PAMAM and sodium silicate at the concentration of 15 mg L^{-1} were tested for effect of synergism. Results of the analysis showed that significant enhancement in the inhibition performance of PAMAM dendrimer was observed in the different combination of sodium silicate. The PAMAM exhibited inhibition efficiencies of only 52.2%, 55.1% and 57.5% at 15, 20 and 30 mg L^{-1} concentrations, respectively. However, the PAMAM and sodium silicate (9:6 ratio) combination shows a substantial synergism.

The PAMAM and sodium silicate (in 9:6 ratio) composite showed optimum inhibition efficiencies of 91.7%, 92.4% and 97.3% at the same studied concentrations *i.e.* at 15, 20 and 30 mg L⁻¹, respectively. The EIS study reveals that PAMAM and sodium silicate act as interface corrosion inhibitors and their adsorption on the metal/ electrolyte interfaces have been supported by EDX and AFM analysis. EDX study suggests that in the presence of PAMAM and sodium silicate composite intensity for the EDX signals correspond to the carbon, nitrogen and oxygen increases on increasing composite concentration. AFM analysis showed that after 72 hrs immersion time metallic surface badly rough and damaged due to free acid attack in the absence of inhibitor. However, in the presence of composite the surface became smoother due to adsorption of composite at metal surface.

El-Mahdy *et al.* [36] synthesized new water soluble dendritic polyether abbreviated as HPAE-PEG600 using pentaerythritol tetracrylate and diethanolamine as precursor molecule *via* Michael addition reaction. The synthesized dendrimer was characterized using FT-IR, ¹H and ¹³C NMR techniques. The inhibition characteristics of synthesized HPAE-PEG600 for steel corrosion in 1 M hydrochloric acid was investigated by potentiodynamic polarization and electrochemical impedance spectroscopic methods. The electrochemical impedance spectroscopic study revealed that HPAE-PEG600 adsorbed on the metal-electrolyte interfaces and acts as interface corrosion inhibitors. A substantial increase in the values of charge transfer resistance (R_{ct}) was observed in the presence of HPAE-PEG600. The R_{ct} values increases from 5.9 Ohm (69.49%) to 10.4 Ohm (82.17%) on increasing HPAE-PEG600 concentration from 50 to 250 ppm. During the polarization study it was observed that presence of HPAE-PEG600 in the corrosive test solution causes significant change in the values of anodic and cathodic Tafel slopes without affecting the values of corrosion potential too much. This observation suggest that HPAE-PEG600 is an effective and mixed type inhibitor.

The ethylenediamine cored imidazoline based dendrimeric polymer with four terminal imidazole rings, tetra-imidazoline (DDTI) was synthesized and investigated as good corrosion inhibitor for carbon steel in CO₂ medium using weight loss, PDP, EIS and SEM methods [37]. Results manifested that the DDTI acts as good corrosion inhibitor for carbon steel and showed the optimum inhibition efficiency of 98.29% at 400 mg L⁻¹ concentration. Results further showed that DDTI forms multi-layered film over the metallic surface which isolates the surface from corrosive environment and save from corrosion. The interfacial nature of the DDTI was determined by EIS study in which significant increase in the values of charge transfer resistance (R_{ct}) was observed in the presence of the DDTI. The adsorption of the DDTI follows the most common Langmuir adsorption isotherm. The large negative values of standard Gibbs' free energy for adsorption (ΔG^0) showed that DDTI has strong tendency of spontaneous and chemical adsorption on the metal surface. For DDTI the values of ΔG^0 ranges from -40.0 kJ mol⁻¹ to -45.77 kJ mol⁻¹. The morphology of the metal surfaces have also been tested using SEM analysis where the huge smoothness in the surface morphology of the metal surface

was obtained in the presence of different concentrations of DDTI. This increased surface smoothness revealed that DDTI inhibit metallic corrosion through adsorption mechanism. Polarization study revealed that DDTI affected both the values of anodic as well as cathodic Tafel slopes, however, anodic Tafel slopes values were more affected as compared to the cathodic Tafel slopes values suggesting that DDTI is a predominantly anodic type inhibitor.

In another study [38], our research group has tested the inhibition effect of two ammonia based PAMAM dendrimers namely, DEND-G₀ and DENG-G₁ on mild steel corrosion using weight loss, electrochemical, SEM, EDX, AFM and DFT studies. Results showed that both the tested dendrimers act as efficient inhibitors for mild steel corrosion in hydrochloric acid solution. Inhibition performance of the dendrimers was tested at different concentrations ranging from 10 to 60 ppm, however after 50 ppm concentration there was no much change in the inhibition performance which suggested that 50 ppm (mg L⁻¹) was the optimum concentration. The weight loss investigation showed that inhibition efficiencies of the both dendrimers enhances on increasing their concentrations. Among the dendrimers taken under consideration, DENG-G₁ exhibited slightly higher inhibition efficiency as compared to DENG-G₀ which is might be resulted due to higher molecular which in turns causes high surface coverage for DENG-G₁ as compared to the DEND-G₀ which have slightly lower molecular size and lesser numbers of heteroatoms. Several adsorption isotherms were tested in order to find best for the both tested dendrimers, among which Langmuir isotherm gave the best fit. The values of K_{ads} for DENG-G₀ vary from $19.0 \times 10^3 \text{ M}^{-1}$ to $5.34 \times 10^3 \text{ M}^{-1}$, while for DENG-G₁ K_{ads} values vary from $36.31 \times 10^3 \text{ M}^{-1}$ to $7.13 \times 10^3 \text{ M}^{-1}$ from varying temperature from 308 to 338 K. The high value of K_{ads} suggested that investigated dendrimers have strong tendency of adsorption. The values of standard Gibbs' free energy was evaluated at different temperature for both the dendrimers using formula $\Delta G_{ads}^{\circ} = -RT \ln(55.5K_{ads})$. The calculated ΔG° values vary from -34.28 to $-35.52 \text{ kJ mol}^{-1}$ for DENG-G₀, while for DENG-G₁, ΔG° values vary from -37.18 to -35.24 . The negative sign of the ΔG° for both the dendrimers suggested that they are spontaneously adsorbed over the mild steel surface.

The ΔG° values for both the dendrimers are more than -40 kJ mol^{-1} and less than -20 kJ mol^{-1} suggesting that both the dendrimers adsorbed on the metallic surface by physiochemisorption mechanism. The values of activation energy (E_a), enthalpy of adsorption (ΔH^*) and entropy of adsorption (ΔS^*) were also derived for studied dendrimers by the weight loss experiments at different temperatures ranging from 308 to 338 K. The values of E_a were higher for DENG-G₀ ($55.47 \text{ kJ mol}^{-1}$) and DENG-G₁ ($65.42 \text{ kJ mol}^{-1}$) as compared to the E_a value of blank ($28.48 \text{ kJ mol}^{-1}$). The superior values of E_a for inhibited solution indicate that in presence of dendrimers metallic dissolution has become difficult due to formation of energy barrier. Similar interpretation was derived from the increased values of ΔH^* and ΔS^* in the presence of dendrimer as compared to in their absence.

The investigated dendrimers were also subjected to electrochemical studies using EIS and PDP methods. The EIS and PDP studies carried out only at their optimum concentration *i.e.* at 50 mg L^{-1} (ppm) concentration. EIS study revealed that both the dendrimers enhance the value of charge transfer resistance in their presence and acted as interface type of corrosion inhibitors. Presence of the single semicircle in the Nyquist plots of the inhibited and uninhibited mild steel specimens suggests that corrosion of mild steel in the tested solution involves single charge transfer mechanism. The values of R_{ct} were $173.7 \Omega \text{ cm}^2$ and $259.2 \Omega \text{ cm}^2$ for DENG-G₀ and DENG-G₁, respectively at 50 mg L^{-1} concentration. The increased value of R_{ct} and decreased value of C_{dl} *i.e.* double layer capacitance suggested that dendrimers adsorb on the metal–electrolyte interfaces and thereby form the protective film which protect metals from corrosion.

The EIS study was further supported by PDP study, where significant decrease in the corrosion current densities was observed in the presence of dendrimers. Presence of dendrimers at their optimum concentrations affect the anodic and cathodic Tafel curves without significant change in the values of corrosion potential (E_{corr}) suggesting that both the dendrimers are behaved as mixed type corrosion inhibitors. Moreover, the shape of polarization curves for inhibited and uninhibited metal specimens are similar which again suggests that both the investigated dendrimers inhibit corrosion by adsorbing on the metal surface without changing the mechanism of metal dissolution. The weight loss, EIS and PDP analyses were supported by scanning electron microscopy (SEM) study. The corroded mild steel specimens after 3 hrs immersion time were analysed under SEM method at 500x magnification. The metal surface corroded in absence of dendrimers showed very high surface roughness due to free acid attack. However, in the presence of dendrimers at 50 mg L^{-1} concentration the surfaces become smoother which attributed due to formation of the protective film by dendrimers. The finding of SEM analysis was supported by EDX and AFM studies. The authors observed that AFM images of inhibited metal specimens are relatively smooth as compared to the uninhibited metal specimen. Increased intensity for nitrogen and oxygen in the EDX spectra of inhibited mild steel as compared to uninhibited metal specimen showed that dendrimers inhibit corrosion by adsorption mechanism.

The experimental results of weight loss, electrochemical (EIS and PDP) and surface (SEM, AFM and EDX) was supported by DFT based quantum chemical calculations. The DFT analysis were performed on the protonated and neutral forms of the dendrimers. A good agreement between DFT and experimental results were observed. Several DFT based parameters such as energy of frontier molecular orbital (E_{HOMO} and E_{LUMO}), energy band gap (ΔE) global hardness (η) and softness (σ) and dipole moment (μ) were derived and discussed in order to correlate the sequence of inhibition efficiency derived from experimental means. Both the tested dendrimers have high value of E_{HOMO} and low value of E_{LUMO} which suggested that they have strong adsorption and interactions tendency with the metallic surface. The values of E_{HOMO} and E_{LUMO} are accordance to the experimentally determined inhibition efficiency. The DENG-G₁ has lesser value of ΔE as compared to the

DENG-G₀ suggesting that DENG-G₁ is more reactive as showed better adsorption tendency as compared to the DENG-G₀.

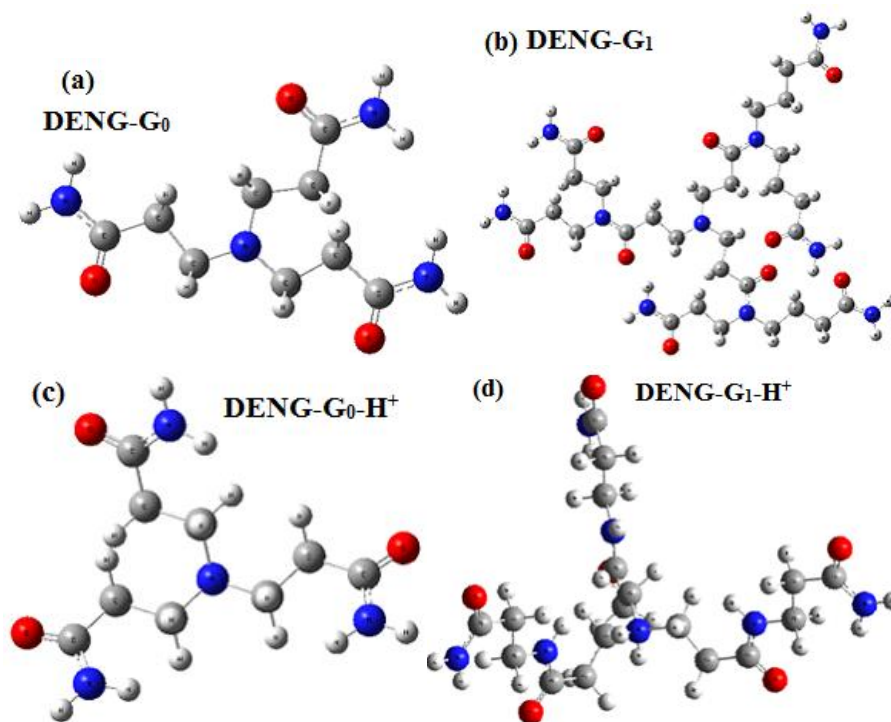


Figure 3. Optimized structure of neutral as well as protonated forms of dendrimers: (a) DEND-G₀, (b) DEND-G₁, (c) DENG-G₀-H⁺ and (d) DENG-G₁-H⁺.

The higher dipole moment value for DENG-G₁ as compared to the DENG-G₀ indicated that DENG-G₁ has more tendency of polarizability and will cover larger surface area as compared to the DENG-G₀. The global hardness values for DENG-G₁ and DENG-G₀ were 0.130 Hartree and 0.280 Hartree, respectively. These results showed that DENG-G₁ is chemically more resistant and therefore showed fewer interactions with the mild steel surface as compared to the DENG-G₀. Similar conclusion can be derived from the value of global softness (σ); DENG-G₁ has higher value of global softness and therefore is more reactive as compared to the DENG-G₀ with lower value of global softness. The optimized and frontier molecular orbital pictures (HOMO and LUMO) of the tested dendrimers are shown in Figures 3 and 4. From the frontier molecular orbital diagrams it was observed that HOMO and LUMO electrons densities are distributed over the entire part of the dendrimer molecules indicating that almost whole part of the molecules donate to the metal surface as well as accept electrons from the metal surface.

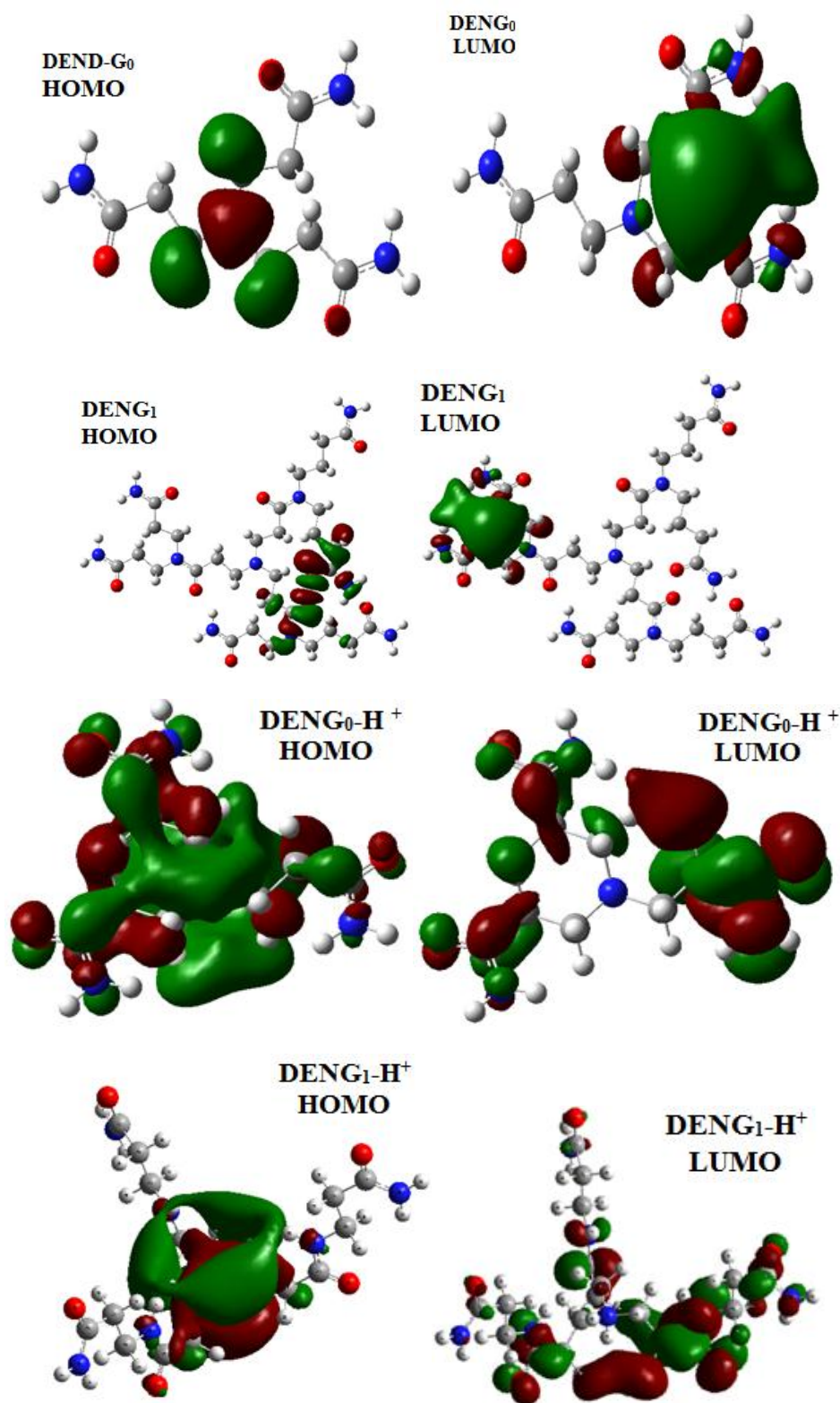


Figure 4. Frontier molecular orbitals of neutral and protonated forms of DEND-G₀ (a) and DEND-G₁ (b).

3. Dendrimers as scale inhibitors

Apart from the above use as solution phase corrosion inhibitors, the dendrimers have been extensively used as scale inhibitors particularly for silica. Demadis [39] studied the inhibition properties of a PAMAM dendrimer with generations 0.5, 1, 1.5, 2 and 2.5 for silica scale growth. Experimental results showed that scale inhibition tendency of the PAMAM dendrimers mainly influence by the nature and number of the peripheral groups. The PAMAM dendrimer becomes effective as low as 40 ppm concentration by forming the silica–PAMAM composite. The loss in the inhibition performance was observed over the time due to co-precipitation and entrapment in the silica matrix. The results showed that presence of the terminal $-\text{NH}_2$ groups are responsible for the high scale inhibitory property of the PAMAM dendrimer. The anti-scaling property of the PAMAM dendrimers in combination with carboxymethylinulin (CMI) has also been investigated other group of authors [40]. The inhibitory effect of the PAMAM is again attributed due to formation of PAMAM-silica insoluble composite on the surface. Neofotistou and Demadis [41] studied the anti-scaling behaviour of a PAMAM dendrimer by a combined effect of $-\text{COOH}$ and $-\text{NH}_2$ groups.

4. Conclusion

From the ongoing discussion it can be concluded that dendrimers are ideal polymeric candidates to replace tradition organic corrosion inhibitors due to their ease synthesis, high solubility in the polar solvents, and presence of polar functional groups as the periphery through which they can easily adsorb on the metallic surfaces. The dendrimers are polymeric materials and therefore associate with very high molecular weight with several adsorption centres and high surface area due to their nano-sized nature. Generally, dendrimers inhibits metallic corrosion by adsorbing and forming the insoluble metal-dendrimer film which separates metal from corrosive surrounding. The adsorption of the dendrimers on metallic surface often obey the Langmuir adsorption isotherm. Literature survey reveals that dendrimers mostly acted as interface inhibitors i.e. adsorb at metal–electrolyte interfaces in which their terminal functional groups act as adsorption centres. PAMAM is the most common dendrimer which has been investigated as metal corrosion inhibitors. Most of the investigated dendrimers acted as mixed type corrosion inhibitors. The inhibition efficiency of the dendrimers have been investigated using several experimental such as weight loss, EIS, PDP, AFM, SEM and EDX as well as computational such as MD and DFT methods. The anti-scaling behaviour of few PAMAM dendrimers have also been studied particularly for silica. Literature results showed that PAMAM dendrimers become effective anti-scalants by forming insoluble silica–PAMAM dendrimers.

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