

Application of Surfactants as Corrosion Inhibitor for Different Metals and Alloys: A Review.

SheerinMasroor and Mohammad Mobin

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, 202 002 (India), e-mail:masroor.sheerin@gmail.com.

Abstract—The inclination of this review is to find the application of surfactants as corrosion inhibitors on different metals and alloys. After an introduction and brief addition of inhibitors types, the article shows the different type of surfactants which are applied to different metals. The principle mechanisms of corrosion inhibition by conventional and novel surfactants are also considered. Literature surveys are added for the last few decades. As seen herein, the most used of surfactant as corrosion inhibitor is for mild steel, much research is to be needed for other metals.

Index Terms— Surfactants, Iron, Aluminium, Steel, Zinc, Inhibition

1. INTRODUCTION

Corrosion is commonly called as degradation of metals when they come in contact with external encompassing media. It can also be define as “autonomous susceptibility of metals to go back from a refined, “metallic” state to their primitive “ore” state. Since ancient times corrosion has affected not only the quality of daily lives of people, but also their technical progress. Generally speaking corrosion relates itself with metals deterioration, but the annihilation of non-metallic materials as a result of exposure to the environment cannot be ignored to count itself in corrosion. The corrosion product we see on the surface of metals is mostly the rust. Till now there are various different methods of corrosion exclusion and control like selection of appropriate materials for specific corroding circumstances[1]. Changing the metal surface by the use of protective coatings [2], i.e., cathodic and anodic protection [3] and the use of inhibitors. Every technique has its own complication and purposes, but the best way is to use inhibitors, which is the most prevalent, effective and economic methods to protect metallic surfaces from getting corroded in aggressive media in closed systems.

1.1 Inhibitors

The best way to quench corrosion is the utilization of inhibitors which are further divided into various categories depending upon their combination and application.

Adsorption type inhibitors

First and most applied among them are adsorption type corrosion inhibitors; these constitute largest class of inhibitors and comprise mostly organic compounds which adsorb on the metal surface and suppress metal dissolution and reduction reaction [4].

Vapor phase inhibitors

The secondary among them are Vapor phase corrosion inhibitors. Their are mostly effective when applied with closed system [5].

Inorganic inhibitors

Next inorganic inhibitors are heavy metal ions which form a layer over metal surface to prevent corrosion [6].

Organic inhibitors

This section contains large number of organic substances containing O, S, N and P[7]. Generally organic inhibitors works by adsorbing on the metal surfaces to obstruct its degeneration. As per recorded in the previous literature the effect of surfactants has been examined and it was observed that the protection efficiency increases with the number of carbon atoms present in the molecule [8].

Anodic inhibitors

The work action of anodic type inhibitors is that they curtail the the anodic area by acting on the anodic sites by forming protective oxide film over the surface and polarizing the anodic reaction [9]. This causes large anodic shift in the corrosion potential plot, leading to passivation. Sometimes they are called as passivators.

Cathodic inhibitors

These are used by confining the processes of cathodic reduction to balance the reaction at the anode or selectively precipitating on cathodic areas to restrict the diffusion of reducing species to the surface.

Green corrosion inhibitors

There are diverse form of natural products which have low toxicity and act as good corrosion inhibitors. This is because they don't have heavy metal or any toxic compounds [10-13]. Aanalysis of the literature published on green corrosion inhibitors during 1950-2010 [14], affirm that the number of

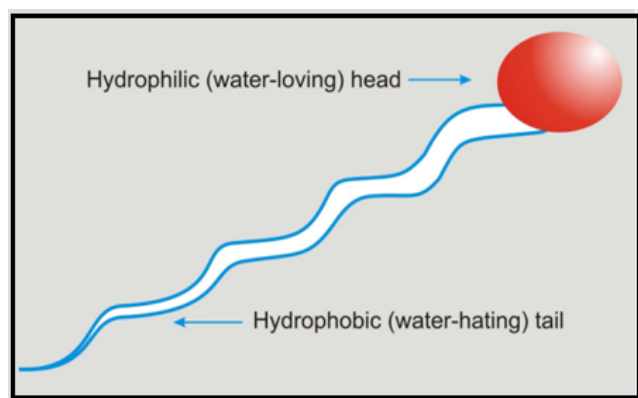
articles published on corrosion inhibitors during the period 2001-2010 has been doubled compared to 1991-2000.

Despite of having the number of investigations on corrosion inhibitors only 5% of the literature published during the last decade concerns green inhibitors. In the recent years, the extracts of *Azadirachta indica*, *Fenugreek* leaves, *Zanthoxylum armatum*, *Opuntia*, *Nyctaginia*, *Ocimum viridis*, *Phyllanthus amarus*, *Chamomile*, *Halfbar*, and *Murrayakoenigii* were studied as corrosion inhibitors in sulphuric and/or hydrochloric acid medium [15-21].

In addition with plant extracts, polymers are also acting as green corrosion inhibitors, because they form complexes with metal and its surface. There are number of polymers which acts as good corrosion inhibitors and some of them are, starch, polyethylene glycol, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl pyridine, polyethylenimine[22-28].

1.2 Surfactants as inhibitors

As the name specifies its characteristics, surfactants are some surface active agents which alter the surface and interfacial property when mixed in a medium by depressing surface tension. The nature of interfaces may differ accordingly, like liquid/liquid (e.g. oil/water), solid/liquid and gas/liquid (e.g. air/water) type [29-32]. Surfactants are mostly organic molecule comprising of two parts, one lyophilic (solvent-loving) group and other lyophobic (solvent-fearing) group in the molecule. If the medium in which the surfactant is to be used is water or an aqueous solution, then the respective terms 'hydrophilic or water loving' and 'hydrophobic or water hating' are used, which is represented somewhat as in Figure 1. It is concluded that surfactants are molecule having havingatleast one polar and one non polar group.



The surfactants are broadly classified according to the nature of hydrophilic head groups and are categorized below into five categories:

- **Anionic surfactants:** These surfactants contain hydrophilic head-group containing negative charge. e.g., Sodium dodecyl sulfate (SDS), Sulphate- OSO_2O^- , Sulphonate- SO_2O^- , Ether sulphate- $(\text{OCH}_2\text{CH}_2)_n\text{OSO}_2\text{O}^-$, Ether phosphate- $(\text{CH}_2\text{CH}_2\text{O})_n\text{P}(\text{O})\text{O}^-$, Ether carboxylate- $(\text{CH}_2\text{CH}_2\text{O})_n\text{CO}_2^-$, Carboxylate- $\text{C}(\text{O})\text{O}^-$.
- **Cationic surfactants:** Hydrophilic head-group contains a positive charge. e.g., cetyltrimethylammonium bromide (

CTAB), Primary ammonium N^+H_3 , Secondary ammonium $\text{N}^+(\text{R})\text{H}_2$, Tertiary ammonium $\text{N}^+(\text{R})_2\text{H}$, Quaternary ammonium $\text{N}^+(\text{R})_3$

- **Amphoteric (zwitterionic) surfactants:** When a single surfactant molecule exhibit both anionic and cationic dissociations, it is called amphoteric or zwitterionic. e.g., betaines, aminoacids, Amine oxide $\text{N}^+(\text{R})_3\text{O}^-$, Betaine $\text{N}^+(\text{R})_3(\text{CH}_2)_n\text{C}(\text{O})\text{O}^-$, Aminocarboxylates $\text{N}^+\text{H}(\text{R})_2(\text{CH}_2)_n\text{C}(\text{O})\text{O}^-$.
- **Nonionic surfactants:** Non-ionic surfactants have a hydrophilic head group that is uncharged. e.g., Triton X-100, Brij 58, Polyoxyethylene (an 'ethoxylate') $(\text{OCH}_2\text{CH}_2)_n\text{OH}$, Acetylenic $\text{CH}(\text{OH})\text{C}\equiv\text{CH}(\text{OH})^-$, Monoethanolamine $\text{NHCH}_2\text{CH}_2\text{OH}$, Diethanolamine $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$.
- **Gemini surfactants:** Gemini Surfactants are further divided into three groups: (i) Ionic gemini surfactants, (ii) Nonionic gemini surfactants and (iii) Heterogemini surfactants. The ionic Gemini surfactants are further classified into cationic gemini surfactants and anionic gemini surfactants. E.g., Butane diyl-1,4-bis(dimethyl tetradecyl ammonium bromide) (14-4-14), Hexane diyl-1,6-bis(dimethyl tetradecyl ammonium bromide) (14-6-14), Butane diyl-1,4-bis(dimethyl hexadecyl ammonium bromide) (16-4-16), Pentane diyl-1,5-bis(dimethyl hexadecyl ammonium bromide) (16-5-16), Hexane diyl-1,6-bis(dimethyl hexadecyl ammonium bromide) (16-6-16)

1.3 Principle of adsorption of surfactants

The working action of surfactants is by adsorbing on the metal surface; forming a layer or depositing onto the surface. The extent of adsorption depends on the type of attractions between surfactant molecule and the metal surface and the force of attraction exist between both. These forces of attraction can be due to Vanderwaal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between surfactant and metal surface, adsorption can be classified into two types: Chemical Adsorption or Physical Adsorption.

In chemisorptions, the surfactants adsorb chemically on the metal surface so energy exchange is involve in this process which vary from small to large amount. The chemical adsorption requires charge sharing or charge transfer from the surfactants molecules to the metal surface [33]. Chemisorptions leads to take place with formation of unilayer of surfactant over the metal surface. It has high enthalpy of adsorption. Also this type of adsorption increases with temperature.

While in physical adsorption of surfactants, the adsorption likely to be occur when the force of attraction which was developed between surfactant and metal surface are weak Vanderwaal forces of attraction, the process is called physical adsorption or physisorption. In this phenomenon adsorption takes place with formation of multilayer of surfactant on the metal surface. The enthalpy of adsorption i.e. ΔH adsorption lies in between 20-40KJ/mol, which is low so these reaction can be reversed. As the temperature increases, process of

Physisorption decreases, which favours Le-Chatelier's Principle. In this type of adsorption intermolecular forces such as van der Waals forces come into play when surfactant molecules adsorb. It decreases with increase in temperature. It is an exothermic process [34].

2. RESULTS AND DISCUSSION

2.1 Surfactants as corrosion inhibitor for different metals

The use of surfactant as corrosion inhibitor for different metals has been reviewed, some of which is given as:

Iron

M. El Achouri and his co-workers synthesized three gemini surfactants from the series of alkanediyl- α,ω -bis-(dimethylalkyl ammonium bromide) and tested as corrosion inhibitors for iron in acidic medium (HCl) using gravimetric, electrochemical polarisation and electrochemical impedance spectroscopy (EIS) measurements. Results obtained show that the surfactants studied are good cathodic inhibitors and act on the cathodic hydrogen reaction without modifying its mechanism. EIS results show that the changes in the impedance parameters (R_T and C_{dl}) with concentration of surfactants studied is indicative of the adsorption of molecules of surfactant leading to the formation of a protective layer on the surface of iron. The effect of the temperature on the iron corrosion in both 1M HCl and 1M H_2SO_4 with addition of various concentrations of 1,2-ethane bis-(dimethyl tetradecyl ammonium bromide) in the range of temperature 20–60°C was studied [35].

Lin Niu et al studies on the corrosion inhibition of iron in acidic medium using alkyl quaternary ammonium halides [36]. They concluded that the structure of alkyl group and the type of halide ions present along with in these inhibitors greatly influence the inhibition efficiency. The corrosion inhibition of iron in 0.5 M H_2SO_4 solutions by alkyl quaternary ammonium halides inhibitors has been studied and its inhibition efficiency was calculated by potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements. The correlation between inhibition efficiency and molecular structure of the alkyl quaternary ammonium halides compounds was investigated. Data obtained from EIS measurements are analyzed to model the corrosion inhibition process through appropriate equivalent circuit models.

El Achouri and his team members have synthesized gemini surfactants of the type 1,2-ethanediyl bis-(dimethylalkyl ammonium bromide) and studied their inhibitive effect on the corrosion of iron in HCl, and revealed that these compounds are good inhibitors of iron corrosion and reach their maximum inhibition efficiency near their CMC [37].

M'hamed Touilet all studied [38] the corrosion-inhibition efficiency of three surfactants, *N*-decyl-1,2,4-triazole, *N*-undecyl-1,2,4-triazole, and *N*-dodecyl-1,2,4-triazole and their corresponding protonated molecules were

analysed computationally using density functional theory and second-order Møller-Plesset calculations. The corrosion-inhibition properties and the strength of the affinity of the iron-surfactant molecules were estimated by using a most accepted cluster model. The iron-surfactant complexes were constructed by attaching the triazole ring to the iron surface modeled by one and five iron atoms, respectively. Relations between molecular properties and corrosion-inhibition efficiency were calculated by using linear regression and quantitative structure-activity relationship. This analysis yielded significant correlations between the corrosion-inhibition activity of the studied molecules with molecular properties such as the highest occupied molecular orbital, the lowest unoccupied molecular orbital, dipole moments (μ), and the total atomic charges. Fukui indexes were also calculated for assessing correlations between them and experimental corrosion-inhibition efficiencies. Polarized continuum model was used to observe solvent effects. The effects of the acidity medium and the local reactivity of the triazole derivatives with iron were also obtained. The calculated binding energy of 276 kJ/mol for the Fe_5 -*N*-dodecyl-1,2,4-triazole cluster shows that the surfactant molecules bind strongly to iron surfaces, which is favourable with experimental data.

Steel

T. Vasudevan and team revealed the influence of *N*-hexadecyl benzyl dimethyl ammonium chloride or cetyl benzyl dimethyl ammonium chloride on the corrosion of mild steel in 5 N and 5.5 N solutions of H_2SO_4 and HCl has been studied using techniques such as gravimetric and gasometric measurements, potentiodynamic polarization, linear polarisation studies and small amplitude cyclic voltammetric studies. Inhibition efficiencies have been obtained both from gravimetric and gasometric measurements. The effectiveness of the inhibitor was also seen keeping solution at 8 N. Potentiodynamic polarisation studies reveal that the inhibitor acts as an anodic in H_2SO_4 and as a mixed inhibitor in HCl solutions by measuring the values of polarisation resistance (R_p) and the double layer capacity (C_{dl}). Also the effect of temperature on corrosion inhibition has been studied and activation energies for both the acids have been evaluated. It was proposed that the inhibition of corrosion of mild steel in both the acids can be attributed to micelle formation. Temkin adsorption isotherm was followed by inhibitor to adsorb on the mild steel surface from both the acids [39].

Mohammad Mobin and Sheerin Masroor [40] synthesized three surfactants from series of gemini surfactants, butanediyl 1,4-bis(dimethyl cetyl ammonium bromide), pentanediyl 1,5-bis(dimethyl cetyl ammonium bromide) and hexanediyl 1,6-bis(dimethyl cetyl ammonium bromide) from Alkanediyl- α,ω -bis(dimethyl cetyl ammonium bromide) in laboratory, which were confirmed by using Nuclear Magnetic Resonance (NMR) spectroscopy. The all three surfactants were tested as corrosion inhibitors for mild steel in 20% formic acid. The impact of surfactants on mild steel corrosion inhibition was investigated by measuring the corrosion rate and inhibition efficiencies of mild steel in their absence and presence. The techniques applied includes weight loss measurements,

solvent analysis of iron ions into the test solution and potentiodynamic polarization measurements. Scanning Electron Microscopy was used to see the surface morphology of the corroded steel samples in presence and absence of surfactants. The effectiveness of gemini surfactants was revealed by calculating inhibition efficiency range which is 76.66-97.41%. The effect of spacer length on the inhibition efficiencies was very less and it increases with increase in surfactant concentration and temperature. The adsorption of gemini surfactants on the steel surface was found to obey Langmuir adsorption isotherm. All results obtained were consistent with each other.

Furthermore two year later, M. Mobin & Sheerin Masroor [41] synthesized and investigated the adsorption and corrosion inhibition behavior of Schiff base-based cationic gemini surfactant bis[p-(N,N,N-tetradecyldimethyl-ammonium bromide)benzylidene]thiourea i.e., 14-S-14 on mild steel in the same medium as was used earlier by them which is 20% formic acid in the temperature range of 30°C to 60°C using gravimetric and potentiodynamic polarization measurements, solvent analysis of iron ions. The synthesized Schiff base inhibitor was characterized using nuclear magnetic resonance spectroscopy (NMR), and thin layer chromatography (TLC). Scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive x-ray analysis (EDAX) were employed to see the surface morphology of the corroded mild steel sample. Experimentally kinetic/thermodynamic parameters were calculated which explained the adsorption and corrosion inhibition mechanism of the inhibitor. The inhibition efficiency of the Schiff base compound was found to vary with inhibitor concentration, immersion time, and temperature. Langmuir adsorption isotherm was followed.

Tween-20, Tween-40, Tween-60, Tween-80 and Ol(EO)₂₀ which were nonionic in nature, investigated as corrosion inhibitor in acid chloride solution by Osman and Shalaby. They concluded their finding by studying adsorption behaviour and gravimetric method [42]. Non ionic compounds acts as very good inhibitors. The high inhibition efficiency was observed around their critical micelle concentrations, which increases with the number of carbon atoms in the chain length of each molecule.

Another non-ionic surfactant polyoxyethylene (80) monopalmitate [Pa(EO)₈₀], in addition with cationic hexadecyltrimethylammonium bromide (HTABr) and anionic sodium dodecyl sulphate were tested as corrosion inhibitor in sea water on carbon steel by Shalaby and team [43]. They concluded that the inhibition efficiency increased with the increase in concentration of surfactant and reached a maximum value near at their critical micellar concentration.

Ghebremichael co-workers used commercial surfactants like alkylphenolethoxylate-2000 and alkylphenylethoxylate-400 as corrosion inhibitor for mild steel in H₂SO₄. The inhibition efficiencies were in good agreement [44].

Bereket and Yurt in 2002 investigated the corrosion inhibition efficiencies of quaternary ammonium salts. They acts as mixed inhibitors for the corrosion of low carbon steel in

acidic solutions and the inhibition efficiency is maximum around and above the critical micellar concentrations [45].

Saeed and Ali synthesized different bisquaternary ammonium salts by reacting N,N,N',N'-tetraallyl-1,6-hexanediamine with allyl chloride, propargyl chloride, benzyl chloride, and 1-bromododecane (yield >90 per cent). The corrosion inhibition efficiency of the synthesized compounds was determined in 1M HCl by weight loss method. Electrochemical results are in good agreement with weight loss. Approximately same results were obtained from both techniques. Temkin's adsorption isotherm was followed [46].

Rajendran and coworkers have investigated the influence of the cationic surfactant N-cetyl-N,N,N-trimethylammonium bromide along with Zn²⁺-1-hydroxyethane-1,1-diphosphonic acid complex on mild steel. The metal was protected by the layer of film which comprise of Fe²⁺-HA complex, Fe²⁺-CTAB complex and Zn(OH)₂ [47]. Also, they also used the Zn²⁺-ATMP systems in controlling the corrosion of carbon steel in aqueous environment [48] and the Zn²⁺-calcium gluconate [49].

In the same year as that was done by Rajendran et al (2000) corrosion behaviour of N-cetyl-N,N,N-trimethylammonium bromide, along with synergistic influence of Zn²⁺ and calcium gluconate on carbon steel by Manjula and co-workers [50].

Soror and El-Ziady investigated the effect of cetyltrimethyl ammonium bromide (CTAB) on the corrosion of carbon steel in two acidic medium, i.e., H₂SO₄ and HCl. The techniques used were weight loss, Tafel polarization, linear polarization and open circuit potential. The corrosion inhibition efficiencies was obtained by weight loss method. The variation of temperature at different strength of acids was also observed. The cationic surfactant acts as good inhibitor in both mediums. The open circuit potential plots were shifted to less negative potential compared to the blank [51].

In 2002, Free checked cetylpyridinium chloride (CPC) and cetyltrimethylammonium bromide (CTAB) as the corrosion inhibition for mild steel in acidic medium. The surfactants acts as inhibitor by aggregating at interfaces in solution [52].

Lin Wang and his team confirmed experimentally the corrosion inhibition behavior of two compounds, 2-mercaptothiazoline and cetylpyridinium chloride as effective inhibitors for low carbon steel over a different strength of aqueous phosphoric acid solution [53].

Migahed [54] experimented in the laboratory to saw the effectiveness of cationic surfactant such as 1-dodecyl-4-methoxypyridinium bromide by electrochemical methods as corrosion inhibitor for mild steel in 2M HCl. The percentage inhibition efficiency of surfactant was increased with the increase of the surfactant concentration until critical micelle concentration (cmc) is reached. The potentiostatic polarization measurements showed that this surfactant suppressed both cathodic and anodic processes of mild steel corrosion in 2 M HCl. Langmuir adsorption isotherm was followed and acts as mixed type inhibitor. The data was also obtained from

impedance spectroscopy (EIS) and analyzed to model the corrosion inhibition process through equivalent circuit. The adsorption equilibrium constant (K_{ads}) along with free energy of adsorption (ΔG_{ads}) were calculated from adsorption isotherm [54].

Osman alone examined the corrosion inhibition of steel in H_2SO_4 by hexadecyltrimethylammonium bromide over the temperature range 30-60°C at different inhibitor concentrations ranging from 0.5×10^{-3} to 2.5×10^{-3} M by the gravimetric method. Langmuir's adsorption isotherm fits the experimental data for the studied compound. Thermodynamic parameters for dissolution and adsorption were calculated and observed as good inhibitor [55]. Migahed, Azzam and Al-Sabagh have synthesized anionic surfactant named as *p*-myristyloxy carbonyl methoxy-*p*'-sodium carboxylate-azobenzene. The effectiveness of the surfactant as corrosion inhibitor has been studied by both chemical and electrochemical techniques at 25 °C and concluded as mixed inhibitor. The corrosion of metal was decreased in presence of inhibitor significantly. The surface tension, the critical micelle concentration (cmc) and some surface active parameters were calculated at 298 K. The calculated corrosion values showed that, the inhibition of mild steel corrosion is due to the adsorption of the inhibitor molecules on the surface and follows Langmuir adsorption isotherm. The surface analysis of mild steel samples in absence and presence of the inhibitor was examined using scanning electron microscopy [56].

The synergistic effect of anionic, cationic and non-ionic surfactant like Sodium dodecyl sulfate, Cetyltrimethylammonium bromide and Triton X-100 was seen by Rafiquee et al over the corrosion inhibition characteristics of 2-aminophenyl-5-mercapto-1-oxa-3,4-diazole on mild steel in HCl solution. In his experiment he concluded best synergistic influence was seen by nonionic surfactant Triton X-100. Weight loss measurements showed that the inhibition efficiency increased with the increasing surfactant concentration and attained a maximum value around 0.2 mol dm^{-3} . In presence of synergistic effect of surfactant, the compound obeyed Langmuir's adsorption isotherm. The obtained values of thermodynamic parameters for adsorption reveal a strong interaction between the synthesized compound and mild steel surface. The spontaneous adsorption of inhibitors was revealed by negative values of G_{ads} on the mild steel surface. The surfactants showed mixed-type inhibition by potentiodynamic polarization studies [57].

Al-Sabagh and his coworker member's have prepared twelve new ethoxylated monoalkyl bisphenol surfactants having general formula as $E(X) B(Y) M(R)$, where $E(X)$ is the degree of ethyleneoxide units, the $B(Y)$ is the bisphenol based on acetophenone (BAC), cyclohexanone (BCH) or acetone (BA) and R is the alkyl chain of fatty acids. They were tested as corrosion inhibitors in 2 M HCl for carbon steel. From their experiment data, it was concluded that corrosion inhibition efficiency increases with increase in the degree of unsaturation, ethoxylation and alkyl chain length, and that minimum inhibition efficiency was exhibited by bisphenol BCH and maximum by bisphenol BAC [58].

The activity of four gemini surfactants namely N-trimethyl butane-diyl-1, 2-ethane-bis-ammonium bromide, N-hexane-diyl-1,2-ethane-bisammonium bromide, N-dodecane-diyl-1, 2-ethane-bis-ammonium bromide as corrosion inhibitors for steel in 1N HCl and 1N H_2SO_4 was investigated by Sharma and Quraishi. All four surfactants showed variation in corrosion inhibition efficiencies with nature, concentration, temperature, immersion time and acid strength [59].

Migahed and his team synthesized another group of fourethoxylated fatty alkyl amine surfactants and tested them as corrosion inhibitors for carbon steel in 1M HCl. The corrosion inhibition efficiency for each inhibitor increased with increasing concentration until the critical micelle concentration (CMC) was reached. The surface morphology was obtained by scanning electron microscopy of the carbon steel samples to be examined [60].

The protection efficiency was found to be 97% of the cationic surfactant cetylpyridinium chloride on low carbon steel by Atia and Saleh in 1 M H_2SO_4 . Electrochemical technique was used to evaluate the surfactant at varied concentration and temperature. The Tafel plot obtained has a shift of corrosion potential in the cathodic region for surfactant. Adsorption isotherm followed was Bockris-Swinkels in temperature range of 30–60 °C. Chemisorption type adsorption was obtained on the steel surface by the cetylpyridinium chloride [61].

In 2010, Farhat and her coworkers synthesized and examined three gemini surfactants, N-hexane-diyl-1,2-ethane-bisammonium bromide, N-dodecane-diyl-1,2-ethane-bis ammonium bromide, N-hexadecane-diyl-1,2-ethane-bis ammonium bromide as novel corrosion inhibitors for mild steel in 20% formic acid. Electrochemical method was used to find the corrosion inhibition efficiencies of these gemini surfactants. The surface morphology were investigated by scanning electron microscopy (SEM). Their inhibition efficiency is in accordance to their order of critical micelle concentrations. The adsorption pattern of all the gemini surfactants was found to follow Langmuir adsorption isotherm. The electrochemical impedance spectroscopy results predicted that the change in the impedance values (R_t and C_{dl}) with concentration of gemini surfactants was due to the formation of a protective layer on the surface of mild steel [62].

Further in 2004, Min et al. studied the corrosion inhibitive action of green surfactant Alkyl polyglucoside on 907 carbon steel in natural seawater. The techniques employed were weight-loss measurements and potentiodynamic polarization curves measurements respectively. The green surfactant acts as good corrosion inhibitor in natural seawater. The synergistic influence was also obtained when the green surfactant was used with calcium gluconate and zinc sulfate, which greatly improved the corrosion inhibition efficiency, at very low level of surfactant. The used corrosion inhibitor was found to control both the anodic and cathodic processes. The inhibitor acts as mixed type [63].

Recently two commercially used cationic surfactants Cetylpyridinium bromide and Cetyltrimethylammonium bromide was experimented as corrosion inhibitor for carbon steel in 1 M HCl. The techniques employed are weight loss, Tafel polarization, electrochemical impedance spectroscopy, and electrochemical frequency modulation techniques. Scanning electron microscope was used to analyze surface morphology. The obtained results showed that the inhibition efficiency increases with increasing concentration of the surfactants, reaches at 94% at concentration 150 ppm. The protection of carbon steel by these two surfactants was due to the synergistic effect between bromide anions and positive quaternary ammonium ions. Langmuir adsorption isotherm was followed by the molecules of both surfactants [64].

Stainless steel

The pitting corrosion protection of 304 stainless steel from 0.1 M NaCl solutions was done by organic surfactant, N-lauroylsarcosine sodium salt by Zhenqiang and his co-workers in 2003. The neutral pH was maintained throughout. The technique applied was combination of surface chemical techniques with electrochemical ones. It was examined that N-lauroylsarcosine sodium salt increases the pitting corrosion resistance of 304 stainless steel and reach maximum at salt concentration of 30 mM. The surfactant adsorbs on 304 stainless steel by dual layer coverage on metal surface. The relationship between pitting inhibition and adsorption density of surfactant suggests that it does not adsorb preferentially on the pit nucleation sites and complete inhibition requires that the whole surface be covered completely by it. The inhibition mechanism of surfactant proposed is due mainly by blocking effect of a negatively charged surfactant's adsorption layer [65].

R. Fuchs-Godec in 2007, formulated the corrosion inhibition efficiencies of two non-ionic surfactants from Triton-X series, Triton-X-100 and Triton-X-405 on stainless steel of the type X4Cr13 in H₂SO₄. The results showed that these surfactants act as good inhibitors in 2 mol L⁻¹ H₂SO₄ solution, the variation of inhibition efficiency strongly depends on the electrode potential [66].

Two year later again R. Fuchs-Godec in 2009 showed corrosion inhibition characteristics of cationic (Myristyltrimethylammonium bromide), zwitterionic (Palmitylsulfo-betaines), and non-ionic surfactant (TRITON-X-405) with synergistic effect mixed with 1 mM of KBr, as corrosion inhibitors for ferritic stainless steel (SS) (type X4Cr13) in aqueous solutions of 2 M H₂SO₄ by using potentiodynamic polarisation measurements. All the three surfactants under study was acting as mixed-type inhibitors as revealed by polarisation data. The adsorption of surfactants on the stainless steel surface is in agreement with the Flory-Huggins adsorption isotherm [67].

Fuchs-Godec and Pavlović comparatively showed synergistic effect between one of the member of the non-ionic surfactant, Triton-X-405 and bromide ions from KBr or C₄H₁₂Ni in the forms of inorganic or organic salts for the corrosion inhibition of stainless-steel of the type X4Cr13 in

2.0 M H₂SO₄. The techniques employed are potentiodynamic and electrochemical impedance spectroscopy measurements. The potentiodynamic and electrochemical data showed that they are in good agreement with the Flory-Huggins adsorption isotherm. The obtained results indicates that KBr or C₄H₁₂Ni had a good synergistic effect with Triton-X-405 in 2.0 M H₂SO₄. The effect was more effective on adding C₄H₁₂Ni, and at concentrations above the CMC of the used mixtures, which had been determined via corrosion-kinetic parameters [68].

Aluminium

Two alloys of aluminium containing copper (Al+6%Cu) and Silicon (Al+6%Si), along with aluminium (Al) alone were checked for corrosion inhibition by Sayed Abdel Rehim et al. They used anionic surfactant dodecyl benzene sulphonate for the study in 1 M HCl in the temperature range of 10-60°C. The experimental results obtained were from the techniques such as weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) and concluded that the used surfactant acts as inhibitor for all the three aluminium samples. The inhibitor molecules adsorbs on the aluminium and alloy metal surface without modifying the mechanism of corrosion process. The surfactant acts as cathodic inhibitor on the metal surface predominately. The corrosion inhibition efficiency increases on increasing the surfactant concentration, but has antagonistic effect with temperature. Maximum corrosion inhibition was obtained around surfactant's critical micelle concentration. The order obtained for inhibition efficiencies are in the order: (Al+6%Si) > (Al+6%Cu) > Al. The adsorption isotherm which fits was Frumkin adsorption isotherm with all the experimental data [69].

Monticelli, Brunoro, Frignani and F. Zucchi used four surface active substances like sodium salts of N-dodecanoyl-N-methylglycine, dodecyl sulphate, N-dodecanoyl-N-methyltaurine and dodecylbenzenesulfonate, on aluminium of the type AA 6351 in 0.01 M NaCl to check their corrosion inhibition efficiencies. Their inhibition efficiencies obtained were calculated by performing experiments like gravimetric measurements, electron probe micro-analysis, potentiodynamic, potentiostatic and galvanostatic tests and electrochemical impedance spectroscopy, which showed that these substances act by adsorption on the aluminium surface oxide and displacement of adsorbed chloride ions [70].

Again the corrosion inhibition was seen for the aluminium by the anionic surfactants such as Dodecyl Sulphonic Acid Sodium Salt, Dodecyl Benzene Sulfonic Acid Sodium Salt and Sodium Dodecyl Sulfate. The acidic medium used was HCl. Langmuir equation was followed. In addition of taking weight loss measurements, the thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy were calculated. The changes of the contact angles of aluminum sheets with and without surfactants were determined [71].

Sheerin and Mobin observed experimentally the effect of non-ionic surfactant, Triton X-100 as corrosion inhibitor for

Aluminium in 1 M HCl and the synergistic influence of 1,4-bis(N-tetradecyl-N,N dimethyl ammonium) butane dibromide was also reported by them in the temperature range of 30-60°C. The method used was weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy. Surface study was obtained by scanning electron spectroscopy. The highest inhibition efficiency was found to be 75.99% at Triton X-100 concentration of 1×10^{-3} (M) on temperature 30°C. The synergistic influence (94.62%) was greatly seen on adding, gemini surfactant 1,4-bis(N-tetradecyl-N,N dimethyl ammonium) butane dibromide with concentration 10^{-7} M. The adsorption of inhibitors on aluminium surface obeyed Langmuir's adsorption isotherm. Thermodynamic parameters were also calculated [72].

The effect of some surfactants as corrosion inhibitors for aluminium in 1 M HCl was observed by Elewady and his group. They used weight loss and galvanostatic polarization techniques to obtain results. The inhibition efficiency from corrosion was found to increase with increasing surfactant concentration and decreased on increasing temperature. The reason behind the result may be to the fact, that the rate of corrosion of Al is higher than the rate of adsorption of surfactant on the aluminium surface. The used surfactant act as mixed type. The adsorption of these surfactants on the aluminium surface was according to Freundlich adsorption isotherm. The inhibiting action of these surface active agents were considerably enhanced by the addition of KI, due to the increase of the surface coverage and therefore indicate the joint adsorption of these compounds and iodide ions. Thermodynamic parameters and activation processes were determined. Results obtained from the two techniques are in good agreement [73].

Zhang and his co-worker members synthesized four new gemini surfactants in the series of hexanedyl-1,6-bis-(diethyl alkyl ammonium bromide), with general formula $C_mC_6C_m(ET)_2Br$ ($m = 10, 12, 14, 16$), and used them as corrosion inhibitors of aluminium in 1 M HCl solution at 25 °C using gravimetric, gasometric measurements and SEM techniques. Langmuir adsorption isotherm was obeyed. The adsorption of synthesized gemini surfactants at the aluminium/solution interface can be highly considered and the values of ΔG_{ads} could be attributed to the high adsorption ability of the surfactant molecules on the aluminium surface. The inhibition is done by the formation of protective film due to the synergistic influence between bromide anions and cationic quaternary ammonium ions, which increases the efficiency. On the basis of the variation of inhibition efficiency with the surfactant concentrations, the adsorption modes of the gemini surfactants $C_mC_6C_m(ET)_2Br$ at the aluminium/solution interface were proposed [74].

Copper

The corrosion inhibitive properties of four surfactants from cationic, anionic and nonionic groups, i.e., cetyltrimethylammonium bromide, sodium dodecyl sulfate, sodium oleate and polyoxyethylenesorbitanmonooleate, were studied for the copper in aerated 0.5 M H_2SO_4 medium by Houyi and group. These surfactants act as the mixed-type

inhibitors and decrease the corrosion rates by arresting the copper exposed surface through electrostatic adsorption or chemisorption. For the surfactant's used inhibition efficiency was increased with the exposure time to aggressive solutions, reached a maximum and then decreased gradually, which may be due to the change in orientation of adsorbed molecule on the copper surface. Out of four used surfactant's, cetyltrimethylammonium bromide inhibited most effectively for the copper corrosion among the four surfactants. The copper surface was found to be positively charged in H_2SO_4 solutions at the corrosion potential, which is best condition for electrostatic adsorption of cationic surfactant [75].

Lalitha, Ramesh and Rajeshwari have experimented the existence of synergistic effect between cetyltrimethylammonium bromide and sodium dodecyl sulfate with triazoles (1,2,4 triazole, 3-amino 1,2,4-triazole, 3-amino 5-mercapto 1,2,4 triazole and 3-amino 5-methylthio 1,2,4 triazole) for the corrosion inhibitions of copper in acidic medium. Electrochemical parameters from potentiodynamic polarization method like corrosion potentials, corrosion current density, corrosion rates and inhibition efficiencies were determined. The results obtained showed that the all triazoles give best inhibition and anionic surfactant, sodium dodecyl sulfate protects the surface better than the cationic surfactant, cetyltrimethylammonium bromide [76].

Abd-El-Maksoud concluded that hexadecylpyridinium bromide and hexadecyltrimethylammonium bromide, act as mixed inhibitors for iron and copper in H_2SO_4 and HCl. The potential of the zero charge of the metal and the adsorption ability of chloride and sulfate ions on the metal surfaces leads to better corrosion inhibition. The method applied were potentiodynamic polarization and Tafel extrapolation. Hexadecylpyridinium bromide was having more corrosion inhibitive property comparable hexadecyltrimethyl ammonium bromide in both acids. The mechanism of adsorption could be explained on the basis of the charge located on the nitrogen atom on the two compounds [77].

Villamil and team in 1999 saw, the corrosion inhibitive effect of sodium dodecyl sulfate on the copper corrosion used 0.5 M H_2SO_4 solution. The results have been obtained from electrochemical and in situ Raman spectroscopic measurements. It has been shown that sodium dodecyl sulfate is a corrosion inhibitor for copper on all range of potentials studied and presents a synergetic effect on the inhibitive action of benzotriazole. It was concluded that sodium dodecyl sulfate inhibits the H^+/H_2 reaction on the copper electrode below or above the critical micelle concentration. The surfactant film obeys a Langmuir adsorption isotherm. The spectroscopic results have shown that the sodium dodecyl sulfate adsorbs on the copper surface with both moieties, the hydrophobic and hydrophilic, interacting with the copper surface [78].

Four years later in 2003, Villamil again experimented the effect of anionic surfactant, sodium dodecyl sulfate on the corrosion of copper has been studied in the absence and presence of benzotriazole in H_2SO_4 . The technique applied

were electrochemical impedance and surface tension measurements maintained at room temperature. In addition of providing synergistic effect on the inhibitive action of benzotriazole, sodium dodecyl sulfate also provide a slight inhibition of copper corrosion, when stationary copper electrode is used. Sodium dodecyl sulfate decreases significantly the inhibitive effect of benzotriazole on the copper corrosion in H_2SO_4 media under hydrodynamical conditions. The interaction of benzotriazole and sodium dodecyl sulfate was also observed at H_2SO_4 solution/air interface. The presence of benzotriazole increases the sodium dodecyl sulfate effect on the decreasing of surface tension values [79].

Hong et al [80] experimented the two environmentally benign anionic surfactants namely sodium dodecyl sulphate and ammonium dodecyl sulphate as dissolution inhibitors for Copper CMP (Chemical mechanical planarization) using a standard slurry (1 wt % glycine with 5wt % H_2O_2 at pH = 4.0). Combined measurements of open circuit potentials and contact angles with those of copper removal rates showed both sodium dodecyl sulphate and ammonium dodecyl sulphate were found to be superior to those of benzotriazole, a traditional inhibiting agent used for Copper CMP.

Sodium dodecyl sulfate was found to be an effective corrosion inhibitor for copper in acidic solution. The experiment performed by polarization technique revealed that Sodium dodecyl sulfate was a good anodic inhibitor at low anodic overvoltage and the adsorption of the inhibitor followed the Langmuir isotherm. The critical micelle concentration of Sodium dodecyl sulfate in 0.5 M H_2SO_4 is 8×10^{-4} M [81].

Houyi Ma et al. [82] have investigated the inhibitive action of cetyltrimethylammonium bromide, sodium dodecyl sulfate, sodium oleate and Tween-80 on the corrosion behaviour of Copper by electron impedance spectroscopy. All surfactants acted as the mixed-type inhibitors and lowered the corrosion reactions by blocking the copper surface through electrostatic adsorption or chemisorption. The inhibitor efficiency increased with the exposure time to aggressive solutions, reached a maximum and then decreased, which implies the orientation change of adsorbed surfactant molecules on the surface. Cetyltrimethylammonium bromide inhibited most effectively on the copper corrosion among the four surfactants, because the cetyltrimethylammonium bromide attributed to the synergistic effect between bromide anions and positive quaternary ammonium ions. $C_{16}H_{33}N(CH_3)_4^+$ ions may electrostatically adsorbed on the copper surface forming a film with primarily adsorbed bromide ions. On the basis of the variation of impedance behaviors of copper in the surfactant-containing solutions with the immersion time, the adsorption model of the surfactants on the copper surface was proposed.

Nickel

Rong Guo et al have studied the effects of an anionic surfactant, sodium dodecyl sulphate and some alcohols (ethanol/n-butanol) on the inhibition of the corrosion of

Nickel. The techniques involved are weight loss, the voltammetry and the impedance in SDS/ $C_2H_5OH/H_2O/HCl$ system and SDS/ $n-C_4H_9OH/H_2O/HCl$ system, respectively. The inhibition efficiency of surfactant SDS for nickel increases with the increase of sodium dodecyl sulphate content. The corrosion rate of nickel metal first increases to the maximum and then starts decreasing with the increase of alcohol content. The addition of alcohols like butanol and ethanol can increase the corrosion rate of nickel in acidic medium of HCl solution, which shows that the corrosion rate can be adjusted by ethanol, also the effect of ethanol on the inhibition efficiency is less than that of n-butanol. The orders of the corrosion rates as obtained from the electrochemical corrosion rate constant and the electrochemical exchange current of nickel corrosion in different media are given as $HCl(aq) > \text{surfactant} + \text{alcohol} + HCl(aq) > \text{surfactant} + HCl(aq) > \text{surfactant} + \text{alcohol}(aq) > \text{surfactant}(aq)$ [83].

M. Abdallah and A.Y. El-Etre tested four easily available and commercial non-ionic surfactants like tween 80, 60, 40 and 20 as corrosion inhibitors for corrosion of nickel metal in 1.0 M H_2SO_4 solution. Three techniques involved are weight loss measurements, potentiostatic polarization and cyclic voltammetry techniques in this study. The all tween acts as mixed inhibitor, as revealed by potentiodynamic polarization. It was observed that the adsorption of only tween 20 and 40 follows Langmuir adsorption isotherm. The values of free energy of adsorption for them were calculated. It was found that the adsorption process is spontaneous and increases, for different surfactants, in the same direction as inhibition efficiency. The cyclic voltammetry results shows that there is existence of only one anodic peak corresponding to the dissolution reaction of nickel electrode. The current of this dissolution peak was used also for corrosion rate measurements and in evaluation of inhibition efficiencies of the used compounds [84].

The corrosion of metal Ni in acidic medium, HCl solution can be inhibited in three types of typical surfactant systems. The order of the inhibition efficiency as obtained from different and the corrosive active energy is CTAB > Triton X-100 > SDS. The adding butanol as co-surfactant mixture, which can be used as inhibiting adjuster, and can control and change the corrosive rate of Ni in HCl(aq) solution. The order of the corrosive rate in different medium is $HCl(aq) > \text{surfactant} + \text{butanol} + HCl(aq) > \text{surfactant} + HCl(aq) > \text{surfactant} + \text{butanol}(aq) > \text{surfactant}(aq)$ [85].

Zinc

Bereket, Gulec and Yurt have investigated the inhibition efficiencies of six quaternary ammonium salts, three cationic surfactants and two non-ionic surfactants on the corrosion of zinc in 2 M KOH. The inhibiting properties was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy and linear polarization methods. Inhibition efficiencies were found because of the physical adsorption of the cathodic sides of zinc electrode [86].

Viorel and team used organic inhibitors such as sodium dodecyl sulphate, sodium dodecyl benzenesulphonate

and natrium 1,4-bis(2-ethylhexyl) sulphosuccinate for corrosion inhibition of Zinc in neutral aqueous NaCl solutions and in alkaline aqueous KOH solution. The effect of these surfactants as a corrosion inhibitor for the corrosion of zinc electrode in neutral solutions of NaCl was studied by measuring the current during hydrogen evolution. The obtained results show that these surfactants inhibit the hydrogen evolution and were capable of inhibiting corrosion inhibiting of zinc electrode. In alkaline KOH solutions the adsorption of these surfactants can effectively decrease the passivation of zinc surface during the electrochemical dissolution of zinc and so greatly improve the discharge capacity of zinc anode in alkaline batteries [87].

Deyab tested Polyoxyethylene (40) nonylphenyl ether a nonionic surfactant as an inhibitor for zinc corrosion in 7.0 M KOH. The techniques applied are potentiodynamic polarization together with electrochemical impedance spectroscopy measurements. The surface analysis of zinc has been examined with scanning electron microscopy and confirmed by infrared spectroscopy. The results show that Polyoxyethylene (40) nonylphenyl ether surfactant has inhibition capability and increases with the concentration of surfactant. The maximum inhibition efficiency has been obtained near to critical micelle concentration of Polyoxyethylene (40) nonylphenyl ether surfactant (CMC = 0.25 mM). The battery containing Polyoxyethylene (40) nonylphenyl ether surfactant exhibits better performance. Polyoxyethylene (40) nonylphenyl ether surfactant works as a mixed type inhibitor by physical adsorption. This adsorption obeys Freundlich adsorption isotherm [88].

The influence of surfactant (sodium dodecylsulfate and *N,N*-dimethyldodecan-1-amine oxide) and synergism on Zn corrosion inhibition in 0.1 M HCl aqueous solutions has been determined at room temperature by Abdel-Rahem and co-workers. They used solutions of single and mixed surfactants consisting of sodium dodecylsulfate(I) and *N,N*-dimethyldodecan-1-amine oxide (II) in water and in 0.1-M HCl were also prepared at room temperature. Critical micelle concentration data were formulated through surface tension measurements as a function of mixing composition. A regular solution model was considered to analyze CMC values. Different parameters such as interaction parameter (β), the composition of mixed micelles (x) and the activity coefficients (f) were calculated by a regular solution model for all amphoteric-anionic mixed systems. β values showed synergism for the binary mixtures of these solutions in the absence and presence of 0.1 M HCl at all investigated surfactants compositions. The weight loss data revealed corrosion inhibition activity obeyed the following order: binary (0.75 II + 0.25 I) > binary (0.50 II + 0.50 I) > single II > single I, suggesting an enhancement in the corrosion inhibition activity of II in the presence of a proper amount of I. Conductivity time measurements show a same trend as that obtained by a weight loss method at (0.50 II + 0.50 I). The results were illustrated on the basis of synergistic interaction between the mixed surfactants [89].

Alloys

Karpagavalli and Rajeswari have reported the application of inhibiting action of 2-mercaptobenzothiazole and cetyltrimethyl ammonium bromide on the corrosion of brass in groundwater. The techniques used are open circuit potential and potentiodynamic polarization. The results showed that the corrosion inhibition occurred by blocking the reaction sites on the surface of brass via chemisorption of the inhibitors. The adsorption of both the inhibitors on brass surface in groundwater is found to obey Langmuir isotherm. The results also indicate that 2-mercaptobenzothiazole functions predominantly as an anodic inhibitor whereas cetyltrimethyl ammonium bromide and the combination of 2-mercaptobenzothiazole and cetyltrimethyl ammonium bromide behave as mixed type inhibitors [90].

The adsorption behaviour of surfactant dodecylamine on alloy made up of Copper and Nickel in 0.2 M NaCl was studied using electrochemical and atomic force microscopy. It acts as cathodic type of inhibitor. The corrosion inhibition tendency increases as the concentration increased from 0.0005 to 0.005 M, the monolayer adsorbed film of inhibitor tended to become more ordered and denser so that corrosion inhibition efficiency tended to increase. Another study differential capacity curve experiments indicated that the adsorbed dodecylamine film changed the structure of the double-electric layer and made the potential of zero charge shift to the positive direction [91].

Monticelli et al. have experimented on the corrosion inhibition efficiency of some sodium salts of *N*-dodecanoyl-*N*-methylglycine, dodecyl sulfate, *N*-dodecanoyl-*N*-methyltaurine and dodecylbenzenesulfonate for aluminium alloy (AA 6351) in 0.01M NaCl. They concluded best results from them [92].

Some researchers saw the effect of temperature on the corrosion behavior of iron-based alloy in 1N H₂SO₄ by electrochemical techniques. The inhibitor was an anionic surfactant (sodium dodecyl benzene sulfonate) at various concentrations. The obtained results show that the temperature increase decreases the performance of the alloy, in the acidic medium. Otherwise, the surfactant inhibits the alloy dissolution in the H₂SO₄, through its adsorption on the alloy surface without modifying the mechanism of corrosion process. They concluded that the highest inhibition effect is obtained at a concentration above its critical micelle concentration. Langmuir adsorption isotherm fits well with the experimental data [93].

Anforéticos surfactants were tested as corrosion inhibitors for copper-iron alloys in 1M HCl solution. The techniques applied were weight loss, electrochemical polarization, impedance measurements and atomic absorption spectroscopy. The name of surfactants used were aspartamatos b-N-alkyl- (amino ethylene) molecular formula: H₂N- (CH₂)₂ - HN-CH-COOH (R = C₁₀ - C₁₄). I CH₂ CONH-R. These surfactants act like that type of inhibitors "hybrid", i.e. anodic and cathodic affect reactions without changing its mechanisms. The inhibitory nature of these surfactants may occur via hydrophobic effect and locking. The corrosion inhibitory action increases with increasing length of

the alkyl group (R). These surfactants are adsorbed onto the surface of the alloy according to the Frumkin isotherm model. The presence of these surfactants in aggressive environment contributes to increasing the apparent activation energy [94].

3. CONCLUSION

The literature survey given in this review concluded that much more research to be done for checking surfactants as corrosion inhibitor on other metals.

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