

CHAPTER - 8

SYNERGISTIC EFFECT OF HALIDE IONS AND SURFACTANTS ON CORROSION INHIBITION OF MILD STEEL IN SULPHURIC ACID

8.1 INTRODUCTION

Synergism is a combined action of a compound greater in total effect than the sum of individual effects. It has become one of the most important factors in inhibition process and serves as a basis for all modern corrosion inhibitor formulation. Synergism of corrosion inhibitors is either due to interaction between components of the inhibitors or due to interaction between the inhibitor and one of the ions present in aqueous solution.

Synergistic inhibition studies for corrosion inhibitors for metals have been advocated as an effective means of decreasing the amount of inhibitor usage, diversifying the application of the inhibitor and improving the inhibitive force of the inhibitor in the presence of a secondary species. Interestingly, addition of halide salts to acid solutions containing any organic compound has been reported to result in a synergistic effect thereby inhibiting iron corrosion¹. Recently, several studies have been reported to explain the role of synergism on the mechanism of corrosion inhibition of mild steel in H₂SO₄ medium²⁻⁷. This synergistic effect may be due to the increased surface coverage, as a result of ion-pair interactions between an organic cation and the halide ion. Halide ion present in an inhibiting solution first adsorbs on the corroding surface by creating oriented dipoles and thus it facilitates the adsorption of inhibitor cations on the dipoles³. In literature, it has been reported that the synergism order in presence of different halides^{8,9} is I⁻ > Br⁻ > Cl⁻. The highest synergistic effect was found to be associated with iodide ions, due to their large size and ease of polarizability, hence can be easily chemisorbed on the metal surface¹⁰.

Surfactant is a wide spread class of organic inhibitors that has been used for achieving such protection. Surfactants exert their inhibition action *via.*, the adsorption on the metal surface, the polar or ionic group (hydrophilic head) attaches to the metal surface and its tail (hydrophobic part) exposed to the solution. Ionic and non-ionic surfactants have been reported to be potent corrosion inhibitors for metals like copper, aluminium and mild steel^{11, 12}. Moreover, surfactants are very beneficial reagents and

their presence at very low quantity in any medium provides desirable properties in all industries such as petrochemical, food, paints and coating industry¹³. Most acid inhibitors are known for their specificity of action. However, the combinations of inhibitors with surfactants are more likely to provide multiple effects required for effective corrosion inhibition.

8.2 REVIEW OF LITERATURE

The previous work done with halide ions and surfactants have been analyzed and summarized below

Mohammed *et al.*, examined the inhibitive effect of non-ionic surfactant namely nonylphenoxy poly(ethyleneoxy) ethanol (NPPE) on carbon steel corrosion in oil field formation of water. The effect of NPPE has been studied at the temperature range 303 - 333 K using electrochemical polarization technique. Potentiodynamic polarization studies revealed that NPPE acted as mixed type inhibitor. Addition of halide salts synergistically increased the inhibition efficiency of NPPE in the order $KCl < KBr < KI$. Adsorption of NPPE followed Langmuir isotherm model¹⁴.

Shaju *et al.*, investigated the synergistic effect of KI using polynuclear Schiff base namely anthracene-9(10H)-one-3-amino propanoic acid (A903AP) on mild steel corrosion in 0.5M H_2SO_4 by weight loss measurements, electrochemical impedance spectroscopy and potentiodynamic polarization studies. The addition of iodide ions synergistically enhanced the inhibition efficiency of the polynuclear Schiff base. The adsorption of A903AP and A903AP + KI obeyed Freundlich and Langmuir isotherms respectively. Thermodynamic parameters (K_{ads} and ΔG_{ads}^0) calculated from adsorption isotherm showed that both physisorption and chemisorption were involved in the inhibition process. Synergistic mechanism was proposed for the studied polynuclear Schiff base¹⁵.

Khamis *et al.*, studied the inhibitive effect of cationic surfactants cetyl pyridinium chloride (CPC) and cetyl pyridinium bromide (CPBr) on mild steel corrosion in 0.5M H_2SO_4 by potentiodynamic polarization studies. The obtained results showed that addition of chloride ions to any of the surfactants significantly influenced the protection efficiency. The adsorption of surfactants and surfactants + chloride ions obeyed Temkin adsorption isotherm. The value of S_0 (synergistic parameter) was greater

than unity, which revealed the synergistic nature of surfactants with chloride ions and indeed co-operative adsorption was followed¹⁶.

Kumar Harish *et al.*, investigated the role of some surfactants namely ammonium decyl sulphate (ADS), ammonium lauryl sulphate (ALS), ammonium hexadecyl sulphate (AHDS) and ammonium dodecyl benzene sulfonate (ADDBS) on carbon steel corrosion in 1M HCl. The obtained results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. Adsorption of all the surfactants followed Freundlich adsorption isotherm. Potentiodynamic studies revealed mixed type of inhibition. It was found that addition of KI to the surfactant molecules showed synergistic effect towards the carbon steel corrosion. Moreover, the results obtained by polarization methods were in good agreement with the results made by weight loss measurements¹⁷.

Fouda *et al.*, investigated the effect of cationic surfactants namely cetyl trimethyl ammonium bromide (CTAB) and dodecyl trimethyl ammonium chloride (DTAC) on C-steel corrosion in 0.5M HCl using weight loss measurements, electrochemical impedance spectroscopy measurements and electrochemical frequency modulation. The efficiency of the cationic surfactant was dependent on the hydrophobic chain length and the used doses of the surfactants. Inhibition efficiency of the surfactants followed the order CTAB > DTAC. Adsorption of the investigated surfactants fitted Langmuir model and polarization data confirmed the mixed nature of the surfactants. Density functional theory (DFT) was used to study the structural properties of the surfactants. Mixed mode of adsorption was proposed for the investigated surfactants¹⁸.

Eduok *et al.*, reported the inhibiting effects of leaves and stem extracts of *sida acuta* and synergistic effect of iodide ion additive on mild steel corrosion in 1M H₂SO₄ using weight loss and hydrogen evolution techniques performed at 30 - 60°C. The extract from the leaves was found to inhibit mild steel corrosion to a large extent, compared to the stem extract both in the absence and presence of iodide ions. Adsorption of extracts alone and combination of extracts + KI were found to obey Freundlich model. In all the techniques, synergism parameter was found to be greater than unity showing that the enhanced inhibition efficiency of both the extracts was due to synergistic effect. Physical adsorption mechanism was proposed from a decrease in inhibition efficiency with an

increase in temperature. Results obtained from thermodynamic and activation parameters confirmed the inhibition mechanism¹⁹.

Xiumei Wang *et al.*, explored the influence of chloride ion on the corrosion inhibition of 1,4-bis(benzimidazolyl)butane (BBB) in 0.25M H₂SO₄ using weight loss, electrochemical methods and discussed the synergistic inhibition mechanism. The results revealed that BBB together with chloride ion was more effective than single BBB for mild steel corrosion. Polarization curves showed that single BBB and BBB-NaCl mixture were mixed type inhibitors. The adsorption of BBB-NaCl mixture was stronger than that of BBB and obeyed Langmuir's adsorption isotherm. The results obtained from weight loss and electrochemical results were in good agreement²⁰.

Mosarrat Parveen *et al.*, studied the inhibitive effect of three aminoacids namely L-cystine (LCY), L-methionine (LMT), L-histidine (LHS) and surfactants namely sodium dodecyl sulphate (SDS), cetyl trimethyl ammonium bromide (CTAB) for mild steel corrosion in 0.1M H₂SO₄. Weight loss measurements, potentiodynamic polarization measurements, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques were employed to know the performance of the studied compounds. The results of the studies provided better insight into the adsorption and corrosion inhibition mechanism of inhibiting formulations consisting of amino acids and surfactants. The adsorption mechanism for amino acids and amino acid-surfactant mixture fitted Langmuir model. The studied inhibitive formulations acted as mixed type. The high inhibitive effect of amino acid surfactant mixtures were confirmed by SEM and AFM studies. Synergism was more pronounced in N-containing amino acid surfactant mixture than S-containing compounds²¹.

Khamis *et al.*, investigated the synergistic effect of N-hexa decyl pyridinium bromide (PyC₁₆Br) and different halide ions on mild steel corrosion in 0.5M sulphuric acid by electrochemical methods, X-ray diffraction studies (XRD) and scanning electron microscopy (SEM). They discussed the synergistic effect of halide ions with the PyC₁₆Br molecule towards the inhibition of mild steel corrosion. The values of S₀ were found to be greater than unity which confirmed the high protection efficiency due to the co-operative adsorption between halides and PyC₁₆Br. XRD and SEM studies confirmed the corrosion product phases and surface morphology of the mild steel specimen²².

Zaafarany examined the inhibitory effect of three cationic surfactants of olyel-amido derivatives on mild steel corrosion in HCl solution. The inhibition efficiency was evaluated by weight loss, galvanostatic polarization measurements and potentiodynamic anodic polarization techniques. Inhibition efficiency was found to increase with increase in the number of polyethylene diamine units. The inhibition values obtained by the three cationic surfactants followed the order compound I > compound II > compound III. The inhibitive effect of cationic surfactants was explained on the basis of adsorption mechanism. Moreover, the adsorption process followed Freundlich model. Some thermodynamic parameters were computed and discussed. The studied olyel-amido derivatives provided a very good protection towards pitting corrosion of steel by shifting the pitting potential in the noble direction²³.

Geethanjali *et al.*, studied the synergistic effect of amodiaquine (AMQ) using metal cations (Na^+ , Mg^{2+}) and halides (Cl^- , Br^- , I^-) on the corrosion of mid steel in 0.5M H_2SO_4 by weight loss methods and electrochemical techniques. They inferred that addition of AMQ at fixed concentrations of cations and halides enhanced the protection efficiency of mild steel. The synergism parameter values S_θ showed that corrosion inhibition performance of AMQ + anion + cation mixtures have been found to be synergistic in nature. Polarization studies also revealed mixed mode of inhibition. The results obtained in weight loss measurements were in good agreement with electrochemical measurements²⁴.

Tarik Attar *et al.*, investigated the effectiveness of potassium iodide (KI) as corrosion inhibitor on carbon steel (XC38) corrosion in 0.5M H_2SO_4 by weight loss measurements. The effect of temperature was studied in the range 293 - 323 K. The adsorption of KI on carbon steel obeyed Temkin adsorption isotherm. Some thermodynamic parameters were computed. Physical and chemical adsorption mechanisms were proposed²⁵.

Hazazi studied the synergistic effect of sulfachloropyridazine (SCP) by halides and/or copper ions in 0.5M H_2SO_4 solution by electrochemical impedance and potentiodynamic polarization measurements. Halides and copper ions enhanced the corrosion inhibition of mild steel by SCP with preferential effect on the anodic branch.

Adsorption of SCP in the absence and presence of copper ions obeyed Langmuir isotherm²⁶.

In this chapter an attempt was made to study the synergistic effect of the synthesized isoxazolines/hydroxy pyrazolines inhibitors with the addition of 1 mM halide ions (KCl, KBr and KI) and surfactants (cetyl trimethyl ammonium bromide and sodium lauryl sulphate) to 1M H₂SO₄ solution on mild steel.

8.3 EXPERIMENTAL WORK

(i) Synergistic effect of halide ions

The synergistic studies have been carried out in combination with 1 mM KCl/1 mM KBr/1 mM KI and inhibitors. Weight loss measurements were carried out with mild steel specimens immersed in 1M H₂SO₄, 1M H₂SO₄ containing 1 mM KCl/1 mM KBr/1 mM KI and 1M H₂SO₄ containing isoxazolines/pyrazolines and 1 mM KCl/ KBr/ KI.

Synergism parameter

The synergism parameter was calculated by using the equation²⁷

$$S = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \longrightarrow 8.1$$

where, $I' = I_1 + I_2$; I_{1+2} = measured inhibition efficiency of the anions plus organic cations; I_1 = Inhibition efficiency of anions (halides); I_2 = Inhibition efficiency of cations (inhibitors). If synergistic effect exists between the inhibitors, S value will be greater than 1.

(ii) Synergistic effect of surfactants (SLS and CTAB)

The surfactant effect was studied by the addition of 1mM sodium lauryl sulphate/ 1mM cetyl trimethyl ammonium bromide to 1M H₂SO₄ containing various concentrations of the inhibitors and mild steel specimens for a duration of 3 hours. From the weight loss the inhibition efficiency was calculated.

8.4 RESULTS AND DISCUSSION

The goal of this work was to investigate the synergistic behaviour of halide ions (KCl/KBr/KI) and surfactants (CTAB/SLS) and to evaluate the synergism parameter by weight loss measurements.

8.4.1 Synergistic effect of halide ions

Despite the broad spectrum of organic/naturally occurring compounds as corrosion inhibitors, the final choice of the appropriate inhibitor for a particular application is restricted by several factors. One factor is the vast variety of possible corrosion systems coupled with the specificity of action of most acid inhibitors which often necessitates the use of a combination of additives to provide multiple effects required for effective corrosion inhibition. This has resulted in studies to identify co-operative (synergistic) effects among corrosion inhibiting species. Synergism is an effective method to improve the inhibitive performance, to decrease the amount of usage and to diversify the application in acidic media.

The present work was focussed on the evaluation of the synergistic effect of halide ion in combination with the inhibitors isoxazolines and hydroxy pyrazolines on the corrosion inhibition of mild steel in 1M H₂SO₄. The inhibitors studied in chapters 5 and 6 were not taken for the study since they exhibited maximum inhibition efficiency even at a concentration of 1 mM. The percentage inhibition efficiency obtained from weight loss method by the addition of 1 mM KCl/KBr/KI to the isoxazolines/hydroxy pyrazolines are presented in Tables 8.1 and 8.2. The percentage inhibition efficiency for 1 mM KCl/KBr/KI are 10.6, 26 and 69 respectively. From the tables 8.1 and 8.2, it is evident that for both the series of inhibitors, the percentage inhibition efficiency increased on addition of halide ions and each anion plays a certain effect on decreasing the corrosion rate process according to the following order^{28, 29} $I^- > Br^- > Cl^-$.

It is generally accepted that the presence of halide ions in acidic media synergistically increases the inhibition efficiency of some organic compounds. It is thought that the halide ions are able to improve adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition by synergism results from

increased surface coverage arising from ion-pair interactions between the organic cations and the anions.

The strong chemisorption of iodide, bromide and chloride ions on the metal surface are responsible for the synergistic effect of these anions in combination with cations of the inhibitor. The cation is then adsorbed by columbic attraction on the metal surface where these ions are already adsorbed by chemisorption. Stabilization of adsorbed anions with cations lead to greater surface coverage and therefore greater inhibition is observed^{30,31}.

It has also been reported³² that the inhibitive effect increases in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, which seems to indicate that the radii of halide ions may have an important role to play. For example, the iodide ion (radius: 135 pm) is more predisposed to adsorption than is the bromide ion (radius: 114 pm) or the chloride ion (radius: 90pm).

The steel surface is originally positively charged in 1M H_2SO_4 . When I^- ion is added to the inhibiting solution they are strongly chemisorbed by forming chemical bonds leading to the formation of iron iodide. The chemisorption of I^- ions shifts ϕ_n of the metal to more positive potential than in the case of Cl^- and Br^- and renders the surface highly negatively charged on the highly negatively charged metal surface, the protonated cationic inhibitor molecules are physisorbed due to electrostatic interaction. This interaction is higher for I^- than Cl^- and Br^- due to higher magnitude of negative charge on the metal surface. Hence, the observed order is $\text{I}^- > \text{Br}^- > \text{Cl}^-$.

8.4.2 Significance of synergism parameter

The synergistic inhibition effect was evaluated using a parameter ‘S’ as defined by the relation

$$S = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \longrightarrow 8.2$$

where I_{1+2} is the measured inhibitor efficiency of the anions plus organic cations, I_1 and I_2 is the inhibition efficiency of anions (halides) and of cations (inhibitors) (Tables 8.1 and 8.2). The inhibition efficiency for 1 mM KCl is 10.6, KBr is 26 and KI is 69. This parameter was evaluated from the inhibition efficiency values obtained from the weight loss measurements. Accordingly, when S approaches unity, no interaction takes place between the inhibitor molecules and the halide ions, while the value of $S > 1$ points to a

synergistic effect as a result of a co-operative adsorption. In the case of $S < 1$ the antagonistic interaction prevails, which may be attributed to competitive adsorption³³. The synergistic parameter calculated for the three halide ions are given in Tables 8.1 and 8.2. From the values, it is clear that for different concentrations of the isoxazolines/pyrazolines the value of 'S' is greater than unity. This indicates that the improved corrosion inhibition efficiency caused by the addition of halide ions to the isoxazolines/pyrazolines have been only due to synergistic effect. Further the 'S' value increases in the order $Cl^- < Br^- < I^-$ giving highest synergistic influence for I^- which is in accordance with the findings noted in literature³⁴.

8.4.3 Adsorption isotherm

Adsorption of inhibitors on the corroding surfaces never reaches the real equilibrium and tends to an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady state has a tendency to become a quasi-equilibrium state. Therefore, it is reasonable to consider the quasi-equilibrium adsorption in a thermodynamic manner using the appropriate equilibrium isotherms³⁵. The adsorption isotherm can provide basic information on the nature of processes between the inhibitor and metal surface.

The degree of surface coverage (θ) for various concentrations of inhibitors (isoxazolines/pyrazolines) and inhibitors in combination with halides have been used to explain the best isotherm to determine the adsorption process. In order to study the different types of adsorption isotherm models, the obtained data were tested graphically by fitting to various isotherms like Temkin, Flory-Huggin and Langmuir in (Figs. 8.1 a-d - 8.6 a-d). Tables 8.3 and 8.4 shows the slope value and linear regression coefficient value for all the adsorption isotherm models in the presence of inhibitors (isoxazolines/pyrazolines) and inhibitors in combination with halides. Among the various isotherms mentioned above, the best description was obtained for Langmuir adsorption isotherm.

The plot of C/θ against C , at 303 K gave a straight line with a correlation coefficient of 0.99 for mild steel in 1M H_2SO_4 in the presence of inhibitors alone and in combination with halides (Figs 8.5 a-d for isoxazolines and 8.6 a-d for pyrazolines). Moreover, a slope value close to unity was obtained for all inhibitors and inhibitors in

combination with halides suggesting the adsorption on mild steel interface in all cases obeyed Langmuir adsorption isotherm. This further confirmed that in 1M H₂SO₄ solution the tested halides interacted with isoxazolines/pyrazolines and adsorbed on the mild steel surface as single entity.

The adsorption equilibrium constant K_{ads} is related to the standard free energy of adsorption ΔG_{ads}° by

$$\Delta G_{ads}^{\circ} = -RT \ln(55.5K_{ads}) \quad \longrightarrow \quad 8.3$$

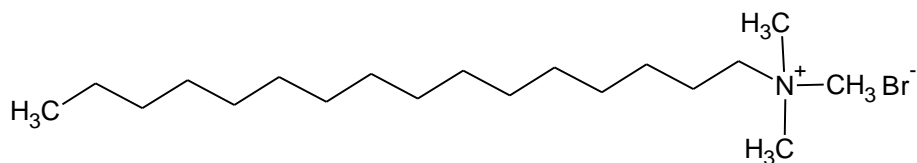
where 55.5 is the molar concentration of water, R is the molar gas constant and T is the temperature in Kelvin³⁶. Table 8.4 presents the thermodynamic parameters obtained from weight loss measurements of mild steel in 1M H₂SO₄ in the presence of inhibitors and inhibitors in combination with halide ions at 303 K for 3 hours. The values of ΔG_{ads}° were negative indicating the spontaneity of the process. The value of ΔG_{ads}° upto -20 kJ mol⁻¹ is an indication of the electrostatic interaction of the charged molecule and the charged surface of the metal (physisorption) while ΔG_{ads}° is more negative than -40 kJ mol⁻¹ implies that inhibitor molecules are adsorbed strongly on the metal surface through coordinate type bond (chemisorption)^{37,38}. In the present study, the ΔG_{ads}° values obtained for isoxazolines and hydroxy pyrazolines ranges between - 19.90 to - 28.18 kJ mol⁻¹ and - 21.20 to - 28.13 kJ mol⁻¹ respectively, which are lower than -40 kJ mol⁻¹ but higher than -20 kJ mol⁻¹. This indicates that the adsorption is neither typical physisorption nor typical chemisorption but it is a complex mixed type. That is the adsorption of inhibitor molecules and halide ions on the metal surface involves both physisorption and chemisorption (comprehensive adsorption).

8.4.4 Synergistic effect of surfactants (SLS/CTAB)

Surfactants or surface active compounds are a class of compounds that decrease prominently the interfacial tension or interfacial free energy of the interfaces. They are amphiphilic in character *i.e.*, they possess hydrophilic and hydrophobic regions, having a long hydrocarbon tail and a relatively small ionic or polar head group. They may be ionic, zwitterionic or non ionic depending on the nature of the head group. They have a tendency to accumulate at the interface of immiscible fluids, resulting in decrease of free energy, hence lowering the surface tension. The promising potential application of

surfactants as corrosion inhibitors has been studied widely for last few years. A number of researchers have reported a reduction in steel corrosion in acidic media by means of surfactants. Addition of surfactants to acidic media is an efficient and quite cheap method for rust protection of metal surfaces

(i) CTAB: Cetyl-N, N, N-trimethyl ammonium bromide



Molecular Formulae = C₁₉H₄₂BrN ; Molecular weight = 364.45

CTAB is not only a cationic surfactant but also a quaternary ammonium salt with long hydrocarbon chain, whose homologues are used as inhibitors and biocides. A brief review on the previous work alone with CTAB in combination with inhibitors is presented below

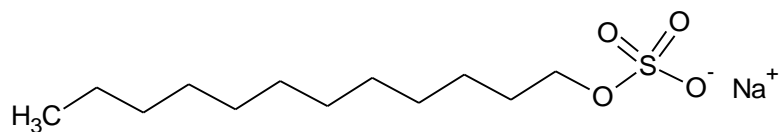
Lalitha et al.,³⁹ have investigated the influence of 1,2,4-triazole derivatives and ionic surfactants CTAB and SDS on the corrosion control of copper in acidic solution and reported on the marked synergistic effect of the triazole in combination with the surfactants. Inhibition studies of CTAB and ortho phenylene diamine have shown that they are effective inhibitors for the corrosion of carbon steel in HCl. The inhibition was due to a polymolecular film formed by the physical adsorption of the inhibitors on the metal surface⁴⁰. The influence of CTAB on the inhibition efficiency of calcium gluconate (CG)-Zn²⁺ system in controlling corrosion of mild steel in a neutral aqueous environment containing 60 ppm Cl⁻ was evaluated by **Rajendran et al.**,⁴¹. Addition of various concentrations of CTAB to the above system improved the inhibition efficiency from 86% to 99%. Presence of CTAB facilitates the transport of CG and Zn²⁺ from the bulk of the solution to the metal surface. **Foss et al.**,⁴² evaluated the inhibition efficiency of an aqueous extract of beet root in controlling the corrosion of carbon steel in well water in the absence and presence of Zn²⁺. A synergistic effect existed between beet root extract and Zn²⁺. Addition of CTAB did not change the excellent inhibition efficiency of beet root-Zn²⁺ system. A perusal of literature shows that no work has been done on the

synergistic influence of CTAB and isoxazolines/hydroxy pyrazolines on the corrosion of mild steel in acid medium.

In this chapter, the synergistic influence of CTAB in combination with isoxazolines/hydroxy pyrazolines was evaluated by weight loss method and the results are presented in Tables 8.5 and 8.6. The percentage inhibition efficiency of 1 mM CTAB in 1 mM H₂SO₄ is 75. Observation of the percentage inhibition efficiency in Tables 8.5 and 8.6 clearly proves the synergistic effect of CTAB on the inhibitors with 1 mM CTAB and the percentage inhibition efficiency has tremendously enhanced. The inhibitive effect of surfactants + inhibitor in 1M H₂SO₄ cannot be considered as an electrostatic adsorption and covalent bonding chemisorption. This action is attributed to the effect of bromide ion of CTAB. Moreover, the molecular weight of CTAB is large (C₁₆H₃₃-N⁺(CH₃)₃Br⁻), thus CTAB can easily adsorb on the mild steel surface by van der Waal's force. In addition, the main hydrophilic part ⁺N(CH₃)₃ of CTAB may attack the mild steel surface while the main hydrophobic part (-C₆H₃₃) may extend to the solution phase. Furthermore CTAB may chemisorb at mild steel-solution interface *via.*, chemical bond between positively charged nitrogen atoms and negatively charged mild steel surface as follows:

In strong acidic solution, CTAB as a cationic surfactant, ionizes and carry a positive charge whereas bromide ion is negatively charged. As a result, the specific adsorption of bromide ion occurs on the mild steel surface, ionized CTAB easily reaches mild steel surface and the dipoles of the surface compound are oriented with their negative ends towards solution, preventing the acid solution attack directly on mild steel surface. So, bromide ion acts as an adsorption mediator of an adsorption composite film in which bromide ion are sandwiched between metal and positively charged part of the inhibitor⁴³.

(ii) SLS-Sodium lauryl sulphate



Molecular Formulae = Na C₁₂H₂₅SO₄; Molecular weight = 288.37

No work has been reported so far on the synergistic effect of SLS in combination with inhibitors. Hence, 1 mM SLS was added to various concentrations of the inhibitors isoxazolines/hydroxy pyrazolines in 1M H₂SO₄ and the percentage inhibition efficiency was evaluated by weight loss technique. The percentage inhibition efficiency of SLS in 1mM H₂SO₄ is 58.5. The results presented in Tables 8.5 and 8.6 clearly confirm the synergistic effect exhibited by SLS. The percentage inhibition efficiency at 1.5 mM concentration of the inhibitors is in the range 27 - 88 % for isoxazolines and 45 - 86 % for hydroxy pyrazolines. Addition of 1 mM SLS has changed the percentage inhibition efficiency to 79 - 91 for isoxazolines and 91 - 98 for hydroxy pyrazolines.

The increase in % IE of the studied inhibitors in the presence of SLS can be explained as follows: SLS interacts with the isoxazolines/hydroxy pyrazolines molecules, help and direct them to adsorb to the mild steel surface more firmly. The possible interactions between SLS and isoxazolines/hydroxy pyrazolines are SLS head group (SO₄²⁻) and positively charged metal surface 'N' of isoxazolines/hydroxy pyrazolines, hydrophobic hydrocarbon chains of SLS and side chain of isoxazolines/hydroxy pyrazolines. These interactions are responsible for the adherence of isoxazolines/hydroxy pyrazolines to the mild steel surface. Additionally, the surfactant SLS also adhere to the mild steel surface unoccupied by isoxazolines/hydroxy pyrazolines molecules⁴⁴.

8.4.5 Comparison of % IE of CTAB and SLS

Synergistic influence of CTAB is higher than SLS:

- Br⁻ is a borderline base attached with a borderline acid (Fe²⁺ surfaces) and soft acid (bulk Fe metal surfaces) more than the harder SO₄²⁻ according to Pearson classification of acids and bases.
- The alkyl chain of CTAB is longer than SLS. Hence greater will be the forces of attraction between the alkyl chains of adjacently adsorbed head group ions.
- Br⁻ ions are more hydrophobic, with large ionic radius and low electronegativity. Thus it gets adsorbed more tightly on mild steel surfaces.

This study helps to minimize the usage of higher concentrations of inhibitors since higher percentage inhibition efficiency is obtained by addition of minimum quantity of surfactants to minimum concentration of inhibitors.

8.5 CONCLUSIONS

- The addition of halide ions and surfactants (CTAB & SLS) to the synthesized isoxazolines and hydroxy pyrazolines enhances the inhibition efficiency.
- The order of inhibition efficiency was found to be $I^- > Br^- > Cl^-$ for halide ions and $CTAB > SLS$ for surfactants.
- The effect of halides and surfactants on the corrosion inhibition behaviour of the studied inhibitors appears to be synergistic in nature.
- The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well with Langmuir adsorption isotherm.
- The value of ΔG_{ads}° confirm mixed type of adsorption involving both physisorption and chemisorption.

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