

Synergistic effect of halides and surfactants on the corrosion inhibition of thiazolo thiadiazole derivative for mild steel in acid medium

J.Saranya^(a), P.Sounthari^(a), A. Zarrouk^(b), S.Chitra^{(a)*}

^(a)Department of Chemistry, PSGR Krishnammal College for Women, Coimbatore, India

^(b)LC2AME, Faculty of Science, First Mohammed University, PO Box 717, 60 000 Oujda, Morocco.

Abstract

The synergistic action caused by halide ions (Cl^- , Br^- and I^-) and surfactants (cetyltrimethyl ammonium bromide and sodiumlaurylsulphate) on the corrosion inhibition of mild steel in 1M H_2SO_4 by thiazolo thiadiazole derivative namely 5-phenyl-5H-thiazolo[4,3-b][1,3,4]thiadiazole-2-amine (PTA) was studied using weight loss method at 303 K. It was found that the addition of iodide ions and surfactants enhance the inhibition efficiency to a considerable extent. Adsorption of the inhibitor alone and in combination of halide ions and surfactant was found to obey Temkin adsorption isotherm. The synergism parameter (S1) is defined and evaluated from the inhibition efficiency values. This parameter for the different concentrations of halide ions and surfactants from weight loss method is found to be greater than unity indicating that the enhanced inhibition efficiency of the inhibitor caused by the addition of halides and surfactants is due to synergism.

* Corresponding author:

rajshree1995@rediffmail.com

Received 26 Sept 2016,

Revised 09 Dec 2016,

Accepted 03 Mar 2017

Keywords: iodide ion, surfactant, isotherm, weight loss, corrosion rate

1. Introduction

Mild steel is one of the important iron-containing alloys used in different applications and is susceptible to corrosion due to its thermodynamic instability especially in aggressive media. 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 important factor is the 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, to diversify the application of inhibitor in acidic media [1]. The addition of halides or surfactants to some inhibitor solutions results in a synergistic effect. Halide ions have proven to be good corrosion inhibitor intensifiers in acidic or basic media for both steel and aluminium and the halide ions themselves act as corrosion inhibitors. Several studies have explained the role of synergism in the corrosion inhibition mechanism of mild steel in acidic medium with halide ions [2-4]. This synergism is due to increased surface coverage as a result of ion-pair interactions between organic cation and halide anion. The halide ions present in an inhibiting solution adsorb on the corroding electrode surface by creating oriented dipoles and facilitate the adsorption of inhibitor cations on the dipoles [4]. However, the influence of surfactants on the corrosion behaviour of organic molecules is very scanty. There remain relatively few works directed toward the synergistic effect of surfactants with the different organic compounds [5,6]. The corrosion inhibition by surfactant molecules is related to the surfactants ability to aggregate at interfaces and in solution. The effectiveness of surfactant inhibitor can be studied on the basis of their micellar properties in a particular medium. The adsorbed molecules form monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration and prevent the acid attack at the surface and thus reduce the corrosion attack [7,8]. The surfactant can be used either alone or in mixture with other compounds to improve their performance as inhibitors. The present work was undertaken to investigate the corrosion inhibition behaviour of the inhibitor namely 5-phenyl-5H-thiazolo[4,3-b][1,3,4]thiadiazole-2-amine (PTA) separately and in combination with very low concentration (1 mM) of the halides like Cl^- , Br^- and I^- , surfactants like sodium laurylsulphate (SLS) and N-N'cetyltrimethylammoniumbromide (CTAB) on mild steel in 1M H_2SO_4 solution by weight loss measurements.

2. Experimental methods

2.1 Inhibitor

The inhibitor was synthesized in the laboratory following the procedure described by Asif et al[9]. The name and structure of the inhibitor is shown below:

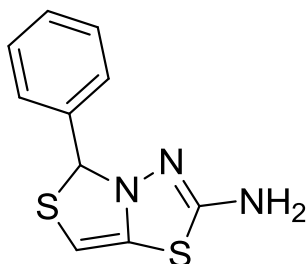


Figure 1. 5-phenyl-5H-thiazolo[4,3-b][1,3,4]thiadiazole-2-amine (PTA)

2.2 Preparation of stock solutions

The solution of 1M H_2SO_4 was prepared by dilution of AR grade 98% H_2SO_4 .

2.3 Evaluation of the inhibition efficiency of the studied inhibitors with halide ions/surfactants

Gravimetric measurements were carried out according to the ASTM standard procedure. The inhibition efficiency and surface coverage were calculated from the weight loss results using the formulas,

$$\text{Inhibitor Efficiency (IE \%)} = \frac{(W_b - W_i)}{W_b} \times 100$$

where W_b is the weight loss without inhibitor/halide/surfactant; W_i is the weight loss with halides/surfactants
 Surface Coverage, $\theta = \%IE \times 100$

3. Results and Discussion

3.1 Synergistic effect of halide ions (Cl^- , Br^- and I^-) at different concentrations of the studied inhibitors

In attempts to explain the different synergisms obtained for the Cl^- , Br^- and I^- ions, several authors have attributed this to their differences in electronegativity, nucleus radius and bonding with steel. Solmazet al., [10] attributed the different behaviour of halide ions to the difference in radii. Due to its larger ionic radius, the I^- ion has higher hydrophobicity when compared to the other two halide ions. As a result, I^- ion with a radius of 1.35 Å is more predisposed to adsorption than the Br^- ion with a radius of 1.14 Å or the Cl^- ion with a radius of 0.90 Å. According to Umoren and Solomon [11], the variation in synergism is not only due to the difference in atomic radii, which increases in the order $I^- > Br^- > Cl^-$, but also to the different electronegativity of the halide ions, which increases in the order $Cl^- > Br^- > I^-$. Frenier and Andreozzi [12] attributed the difference in the synergism of halide ions to the mild steel bonding, where halide ions adsorb through an electron pair and the strength of the surface bond depends on the basicity of the electrons in the frontier orbital or the highest occupied molecular orbital (HOMO). Chloride is an accelerator because it is easily removed during the anodic dissolution process, while iodide is tightly bound. Malowan has found that mixtures of iodide ions and organic amines are found to be good inhibitors for the inhibition of corrosion of steel in phosphoric acid [13]. Using the electrical double layer capacity measurements, Conway [14], Hackerman [15], Schmid [16], Frumkin [17] and Kolotyrykin [18] have investigated the adsorption of anions on metal surfaces and detected the synergistic influence of anions. From capacity potential curves, Murakawa et al., have found the relative degree of adsorption of Cl^- and ClO_4^- ions [19]. Several investigations on the synergistic influence on the corrosion of various metal surfaces have been reported in the literature [20-22]. Eduok et al., have noticed the synergistic inhibition effect between leaves and stem extracts of *Sidaacuta* and iodide ion for mild steel corrosion in 1M H_2SO_4 solutions [23]. Shaju et al., have studied the synergistic effect of KI on corrosion inhibition of mild steel by polynuclear Schiff base in sulphuric acid. It has been found that the adsorption of inhibitor and the adsorption of inhibitor + KI on the mild steel surface obey Freundlich and Langmuir isotherms respectively. The thermodynamic parameters calculated from the adsorption isotherms showed that both physisorption and chemisorption are involved in the inhibition process [24]. Hazaziet al., have observed that the inhibition efficiency increased with the concentration of triazole derivative in H_2SO_4 and upon adding (Cl^- , Br^- and I^-) the inhibition efficiency increased considerably [25]. Ali et al., have investigated the new insights into the synergetic effect between halide ions and diamine-based corrosion inhibitor for HCl. The results revealed that the synergetic effect of chloride ions (Cl^-) and bromide ions (Br^-) failed at high temperatures, high acid concentrations and longer soaking times, and tended to induce more corrosion under those conditions. In contrast, iodide ions (I^-) maintained good intensifying properties with the synthesized diamine corrosion inhibitor at all examined conditions. The value of the synergism parameter was found to be greater than unity for iodide ions at all examined conditions and varied from unity to less than unity for Cl^- and Br^- ions, depending on test conditions [26].

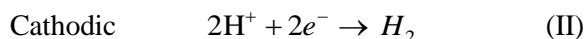
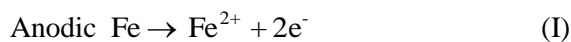
The inhibition activity of the studied inhibitor in the absence/ presence of halides added as corrosion inhibitor intensifiers were investigated for mild steel in 1M H_2SO_4 solution. The anions such as Cl^- , Br^- and I^- were introduced

into the aggressive medium, *viz.* 1M H₂SO₄ as their potassium salts and the effect of these anions on the corrosion inhibition of mild steel was studied using weight loss method. From the Table 1, it is clear that, the inhibition efficiency increased with increase in concentration of the inhibitor and was greatly enhanced on addition of the halide ions. The stronger synergistic influence noticed for the Cl⁻ ions of HCl medium in comparison to the weak influence shown by the SO₄²⁻ ions of the H₂SO₄ medium is due to the irreversible chemisorption of Cl⁻ ions on to the metal surface as proposed by Frumkin [27], Iofa [28] and supported by Damaskin et al., [29] and some researchers [30-41]. Now, the same mechanism of synergism can be attributed for the synergism exhibited by the externally added halide ions into sulphuric acid medium as investigated in the current chapter. As per this mechanism, the steel surface is originally positively charged at the open circuit potential (~500 mV/SCE) in H₂SO₄ due to the weak adsorption of the highly solvated SO₄²⁻ ions from the aggressive medium. Under these conditions, the cationic protonated inhibitor molecules are not adsorbed strongly. Only the neutral inhibitor molecules hold onto the anionic metal active centres. When the halide ions are added, they strongly chemisorb on the metal surface by entering into the metallic part of the double layer and thereby shift the potential of zero charge ϕ_n towards more positive potentials. As a result, the metal surface at the open circuit potential becomes negatively charged. Once the surface is rendered negatively charged, the cationic inhibitor molecules are strongly attracted to the metal surface and are effectively adsorbed. Damaskin et al., have supported this concept by stating that when the added anions form a part of charge of the metal surface the resultant dipoles shift ϕ_n towards more value that is positive and consequently the metal surface become negatively charged. The surface of iron with adsorbed halide ions can be regarded as a surface of different composition *i.e.*, the surface has a definite proportion of iron halide and hence definitely has a more positive ϕ_n than pure iron.

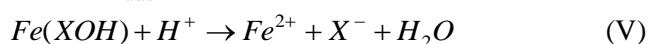
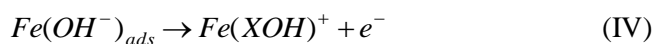
There is a proposal in the literature that the adsorption of halide ions on metal surface raises the hydrogen overpotential and thereby retards the corrosion reaction. The retardation of hydrogen evolution corrosion reaction by means of increasing the hydrogen overpotential in the simultaneous presence of organic cations and halide ions has been confirmed by the observation that this effect is found to decrease in the order iron ($\Delta\eta=240$ mV) > Co ($\Delta\eta=100$ mV) > Ni (65-70 mV) [29]. This gradation is apparently due to the decrease in the adsorption of halide ions and in the shift of the ϕ_n into the positive region in the sequence from iron to nickel. The most probable reason for this sequence may be the progressive filling of the 3d sub level with electrons in the same series: Iron (3d⁸) < Cobalt (3d⁹) < Nickel (3d¹⁰). It is interesting to find from literature that Iofa et al., [28] have observed an increased adsorption of organic cations (tribenzylamine) in the presence of organic anions (benzene sulphonic acid) instead of halide ions in 1N H₂SO₄. However, the mechanism of adsorption of organic anions is different from the adsorption mechanism of halide ions. Iofa et al., have suggested that adsorbed sulphonic acid anions apparently enter only into the ionic part of the double layer while the halide ions have entered into the metallic part of the double layer. While this may be the reason why the adsorption of organic anions decrease the hydrogen overvoltage, adsorption of I⁻ ions raises the hydrogen overvoltage while present individually. However, in simultaneous presence of cations and anions the hydrogen overpotential increases in both cases.

A review of literature also reveals that halide ions also influence the absorption of neutral organic substances like hexyl alcohol and camphor and organic compounds of anionic type. Probably, in presence of halide ions, the surface of iron is rendered hydrophobic in addition to undergoing a change of surface charge, which obviously leads to some increase in the adsorption of neutral organic substance. In the case of organic anions, both the factors seemed to have influenced the adsorption. On the other hand in the case of organic cations the influence of surface charge should have predominated as discussed earlier [32]. The synergistic influence of the added halide ions on the inhibition of mild steel corrosion by inhibitors can be explained on the basis of a concept proposing the direct participation of halide ions

in the mechanism of corrosion. According to this concept, corrosion of steel in acidic solution is the sum of the following reactions.



However, each of these reactions proceeds through many consecutive steps depending on the pH and type of anion present in the solution. There are two main theories for inhibition based on the work of Heusler [42] and Bockris [43]. Both the theories indicate the participation of anions of the solutions directly. The anodic dissolution of steel in aqueous solution is known to be significantly facilitated by hydroxyl ions that form intermediate catalytic complexes on the metal surface [35]. Halide ions, at some concentrations, may replace hydroxyl ions adsorbed on the surface of the metal, thus leading to a reduction in the catalytic effect of the hydroxyl ions as follows



where X represents the halide ions. The effect is more pronounced with I⁻ and is initiated by the specific adsorption of the anion onto the metal surface. The greater influence of the iodide ion is often attributed to its large ionic radius, high hydrophobicity and low electronegativity, compared to the other halide ions [44,45]. Adsorption of halide ions on the metal surface affects the above kinetics of dissolution of steel [46-48].

3.2 Cause for the exceptionally high synergistic influence of I⁻ and the order of synergism noticed

Analysis of the inhibition efficiency and the values of synergistic parameters data presented in Table 1 reveal that the synergistic influence of halide ions follows the order I⁻ > Br⁻ > Cl⁻. This observed order suggests that I⁻ has highest synergistic influence among the halide ions. During the study of the adsorption and inhibiting action of organic cations and of organic compounds of onium type on metals of iron group, similar trend has been noticed by several investigators [38-41]. This behaviour can be attributed to the more stable chemisorption of I⁻ ions because of the easy deformability of their electron shells. Differential capacity curves derived by Iofa et al., have demonstrated the high absorbability of tribenzylamine in presence of I⁻ ions on zone refined iron. The polarization studies made by Iofa et al., also indicate the strong retardation of hydrogen evolution and dissolution of iron, in the simultaneous presence of tributyl ammonium sulphate (TBAS) and I⁻ ion [41].

Table 1: Synergistic effect of 1 mM KCl/KBr/KI on the inhibition efficiency of the studied inhibitor PTA on mild steel in 1M H₂SO₄ by weight loss method at 303 K

Conc. (mM)	Inhibition efficiency (%)				S1 (KCl)	S1 (KBr)	S1 (KI)
	Without KCl, KBr, KI	With KCl	With KBr	With KI			
0.01	31.16	40.37	51.16	70.16	1.04	1.12	1.43
0.02	32.09	42.64	53.49	72.65	1.00	1.09	1.40
0.03	32.95	43.51	56.32	73.15	1.03	1.05	1.40
0.04	33.49	45.19	59.46	76.91	1.05	1.00	1.34
0.05	34.76	49.66	61.26	77.89	1.03	1.01	1.34

Subramaniam et al., [46] have used the anions Cl^- , Br^- , I^- , SCN^- , NO_3^- and $\text{S}_2\text{O}_3^{2-}$ for understanding the effect of introduction of various anions on the inhibition efficiency of 1,1'-methylene bispyridinium sulphate and have found that I^- and SCN^- ions exhibit synergism and NO_3^- and $\text{S}_2\text{O}_3^{2-}$ exhibit antagonism. Cl^- and Br^- ions are found to have little effect and the inhibitors have shown good efficiency even in their absence. This has been attributed by these authors to the surprisingly negatively charged mild steel surface at the open circuit potential (-490 mV/SCE with $\phi_n = 400$ mV/SCE) even in the absence of adsorbable anions like Cl^- and Br^- , which is the condition favourable, for the adsorption of cations. Probably the type of steel used by Subramaniam et al., would have exhibited such different characteristics. Effect of anions on enhancing corrosion inhibition has also been studied by Hackerman et al., who have suggested that the halide ions in general and especially iodide ions affect the steel dissolution by a strong interaction with the metal surface, possibly through chemisorptions [47]. Anion adsorption is found to be greater for iodide and bromide than chloride. This suggests that the radii and electronegativity of the halides play a significant role in the adsorption process. Hence, the following conclusions can be made for the highest synergistic influence observed for the I^- ions in the current work.

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

3.3 Synergism considerations of the halide ions

The interaction of the studied inhibitors and halides can be described by a synergism parameter S_1 [48], which is defined as:

$$S_1 = \frac{1 - I_{1+2}}{1 - I_1} \quad (1)$$

where I_{1+2} = measured inhibition efficiency of the anions plus organic cations; $I_{1+2} = I_1 + I_2$; I_1 = Inhibition efficiency of the anions (halides); I_2 = Inhibition efficiency of the cations (inhibitors). I_1 has been determined by immersing mild steel in 1M H_2SO_4 containing 1 mM of $\text{Cl}^-/\text{Br}^-/\text{I}^-$ and calculating the weight loss in each case (percentage inhibition efficiency = 10.6, 26 and 69 respectively). S_1 approaches unity when no interaction between the inhibitor molecules exists, while $S_1 > 1$ indicates a synergistic effect. In the case of $S_1 < 1$, antagonistic behaviour prevails which may be attributed to competitive adsorption. The values of synergism parameter for the various concentrations of the studied inhibitors were calculated from the gravimetric data at 303 K and the results are given in Table 1. From the Table 1, it is clear that the values of S_1 are greater than unity in the presence of halides with inhibitor suggesting that the enhanced %IE caused by the addition of halide ions to the inhibitors (which is in the order of $\text{Cl}^- < \text{Br}^- < \text{I}^-$) may be only due to synergistic effect. This is due to the greater tendency of halide ions to be adsorbed on the surface. It can also be concluded that the iodide ion is strongly adsorbable and facilitates the adsorption of organic cations, thereby leading to an inhibition synergism. The order indicates that the radii and electronegativity of the halides play an important role in the adsorption process.

3.4 Adsorption isotherm for the studied inhibitors with halides

The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface. The resulting adsorbed layer constitutes a barrier that isolates the metal surface from the action of the corrosive anions present in solution. The adsorption can be physical in nature, which involves electrostatic interaction between the adsorbed molecules and the metal surface, or chemical, in which case there is charge sharing or transfer between the adsorbed molecules and the metal surface. In discussing the adsorption isotherms, the degree of surface coverage values obtained from weight loss measurements using the equation ($\theta = \% \text{ IE}/100$) assuming a direct relationship between surface coverage and inhibition efficiency were employed. Attempts were made to fit (θ) values to the thermodynamic-kinetic model of Freundlich, Temkin, Langmuir, and Flory-Huggins isotherms. The correlation coefficient (R^2) values were used to determine the best fit isotherm. By far the best results were obtained for the Temkin adsorption isotherm. The characteristics of the Temkin adsorption isotherm are given by the equation,

$$\exp(-20C) = KC \quad (2)$$

where a is molecule interaction parameters, θ is the degree of surface coverage, ' C ' is the concentration of the inhibitor and K is the equilibrium constant of the adsorption process. Figure 2 shows the plot of θ against $\log C$ for the studied inhibitors at 303 K. Linear plots were obtained indicating that the experimental data obtained from the weight loss measurement fits the Temkin adsorption isotherm. In fact, Temkin isotherm characterizes chemisorption of uncharged molecules on a heterogeneous surface. The linear correlation coefficients, molecular interaction parameters ' a ' and the adsorption coefficients deduced from the Temkin adsorption isotherm plot (Figure 2) is listed in Table 2. From the Table 2, it is seen that the linear correlation coefficient, R^2 is close to unity. Hence, adsorption of the inhibitor in combination with halides followed the Temkin adsorption isotherm. The equilibrium constant of adsorption process K is related to the free energy of adsorption,

$$K = \frac{1}{55.5} \exp \left[\frac{-\Delta G_{ads}^\circ}{RT} \right] \quad (3)$$

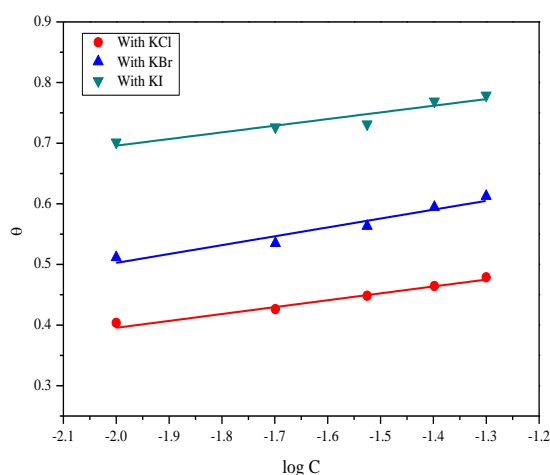


Figure 2. Temkin adsorption isotherm for the studied inhibitor (PTA) for mild steel in 1M H₂SO₄ without and with halides

where 55.5 is the moles of water in mol dm⁻³. The free energy of adsorption ΔG_{ads}° were evaluated using equation (3) and are presented in Table 2.

Table 2: Temkin adsorption parameters of adsorption of the inhibitor PTA on the mild steel surface at room temperature

Name of the inhibitor	R ²	K _{ads} L mol ⁻¹	Slope	-ΔG _{ads} ^o kJ mol ⁻¹
PTA+Without halides	0.9948	404.60	0.0478	25.24
PTA+WithKCl	0.9921	622.61	0.1136	26.33
PTA+WithKBr	0.9899	794.95	0.1462	26.95
PTA+With KI	0.9960	915.33	0.1097	27.30

Generally, the values of $-\Delta G_{ads}^{\circ}$ up to 20 kJ mol⁻¹ are consistent with electrostatic interaction between the charged metal and charged molecules [49,50], which signifies physical adsorption, while the values more negative than 40 kJ mol⁻¹ involve charge sharing or transfer from the inhibitor molecules to the metal to form a coordinate type of bond, which signifies chemical adsorption [51,52]. In the present case, $-\Delta G_{ads}^{\circ}$ lies between 20 kJ mol⁻¹ and 40 kJ mol⁻¹. It can be concluded that, the adsorption of molecules on the mild steel surface from 1M H₂SO₄ solution takes place through both physical and chemical processes simultaneously.

3.5 Synergistic effect of surfactants (SLS and CTAB) at different concentrations of the studied inhibitors

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 amphiphile 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, zwitter ionic 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) Cetyl-N,N,N-trimethyl ammonium bromide (C₁₉H₄₂BrN)

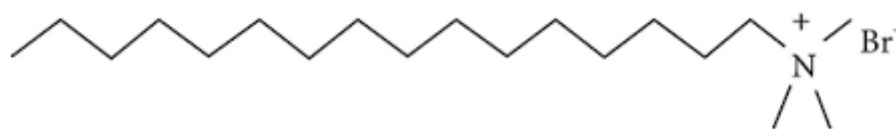


Figure 3. Structure of cetyl-N,N,N-trimethyl ammonium bromide

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 with CTAB and SLS in combination with inhibitors is presented below: Lalitha et al., [53] have investigated the influence of 1,2,4-triazole derivatives and ionic surfactants CTAB and SLS on the corrosion control of copper in acidic solution and reported on the marked synergistic effect of the triazolein combination with the surfactants. Inhibition studies of CTAB and o-phenylenediamine 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 surface

[54]. 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., [55]. 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., [56] 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 beetroot extract and Zn²⁺. Addition of CTAB did not change the excellent inhibition efficiency of beetroot-Zn²⁺ system.

A perusal of literature shows that only limited work has been done on the synergistic influence of CTAB on the corrosion of mild steel in acid medium. The synergistic influence of CTAB in combination with quinoxaline, pyran and thiazolo thiadiazole derivatives was evaluated by weight loss method and the results are presented in Table 3. Observation of the percentage inhibition efficiency in Table 3 clearly proves the synergistic effect of CTAB on the inhibitors. With 1 mM CTAB, the percentage inhibition efficiency of the inhibitors has tremendously enhanced. The inhibitive effect of surfactants in combination with the 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 onto 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. Therefore, bromide ion acts as an adsorption mediator of an adsorption composite film in which bromide ions are sandwiched between metal and positively charged part of the inhibitor [57].

(ii) SLS-Sodium lauryl sulphate(NaC₁₂H₂₅SO₄)

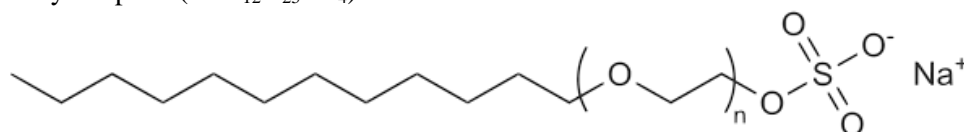


Figure 4. Structure of sodium lauryl sulphate

No work has been reported so far on the synergistic effect of SLS in combination with inhibitors for mild steel. Hence, 1mM SLS was added to various concentrations of the studied inhibitors in 1M H₂SO₄ and the percentage inhibition efficiency was evaluated by weight loss techniques. The results presented in Table 3 clearly confirm the synergistic effect exhibited by SLS. Addition of 1mM SLS has changed the percentage inhibition efficiency to a maximum extent. The increase in % IE of the studied inhibitors in the presence of SLS can be explained as follows: SLS interact with the studied inhibitor molecule, help and direct them to adsorb to the mild steel surface more firmly. The possible interactions between SLS and inhibitors are SLS head group and positively charged 'N' of, hydrophobic hydrocarbon chains of SLS and side chain of DP/DQD/PCN/PTA. These interactions are responsible for the adherence of the inhibitors on the mild steel surface. Additionally, the surfactant SLS also adhere to the mild steel surface unoccupied by the inhibitor molecules [58].

3.6 Synergism considerations of the surfactants

The values of the synergism parameter S1 for various concentrations of the studied inhibitors in combination with 1 mM of surfactants (SLS and CTAB) are calculated from the gravimetric data using the relationship (equation 1). The results are given in Table 3. The values are all greater than unity. This is an indication that the enhanced inhibition efficiency resulting from the addition of surfactants to the inhibitor is synergistic in nature and proved that, addition of a very small concentration of surfactants can improve the adsorption of inhibitors on the mild steel.

3.7 Adsorption isotherm for the studied inhibitors with surfactants

The adsorption of ionic surfactants on oppositely charged metal surface could be taking the following path:

- At low surfactant concentrations, the adsorption is due to electrostatic interaction between individual isolated charged monomeric species and the oppositely charged metal surface.
- Surfactant species begin to form surface aggregates, colloids (surface colloids), including hemi-micelles, admicelles, etc., due to adjacent interactions between hydrocarbon chains.
- When the metal surface is electrically neutralized by the adsorbed surfactant ions, the electrostatic attraction is no longer operative and adsorption takes place due to adjacent attraction alone with a reduced slope.
- When the surfactant concentration reaches critical micelle concentration, the surfactant monomer activity becomes constant, any further increase in concentration contributes only to the micellization in solution, and it does not change the adsorption density. The adsorption in this region is mainly through adjacent hydrophobic interaction between the hydrocarbon chains.

In steps c and d, surfactant molecules adsorb with a reversed orientation (head groups facing the bulk solution) resulting in a decrease in the hydrophobicity of the particles in this region. pH plays a very significant role in controlling adsorption of ionic surfactants. Thus the adsorption of anionic surfactants is higher on positively charged surfaces (pH below isoelectric point (IEP)) than on negatively charged surfaces while the cationic surfactants adsorb more on negatively charged surfaces [59,60]. Molecular structure of surfactant does influence its adsorption behaviour markedly.

Table 3. Synergistic effect of 1 mM SLS/CTAB on the inhibition efficiency of the studied inhibitor PTA on mild steel in 1M H₂SO₄ by weight loss method at 303 K

Conc. mM	Inhibition efficiency (%)			S1 (SLS)	S1 (CTAB)
	Without SLS and CTAB	With SLS	With CTAB		
0.01	31.16	70.54	79.02	1.66	1.48
0.02	32.09	73.49	82.46	1.60	1.43
0.03	32.95	76.15	86.73	1.56	1.36
0.04	33.49	78.77	88.15	1.51	1.35
0.05	34.76	84.84	90.41	1.42	1.33

Several adsorption isotherms were assessed and the Temkin adsorption isotherm was found to be the best description of the adsorption behaviour of the investigated surfactants, which obeys equation 1. Figure 5 shows that the dependence of the fraction of the surface coverage (C/θ) as a function of the concentration (C) of the studied inhibitors

in the presence of SLS and CTAB. ΔG_{ads}° were calculated according to the equation 2 and the values are given in Table 4. The regression coefficient R^2 (close to unity) suggests a good relation between C/θ and C . The calculated values of ΔG_{ads}° for all the studied inhibitors in the presence of SLS and CTAB are between -20 kJ mol^{-1} and -40 kJ mol^{-1} . This suggests a comprehensive adsorption (physical and chemical adsorption) [61-63].

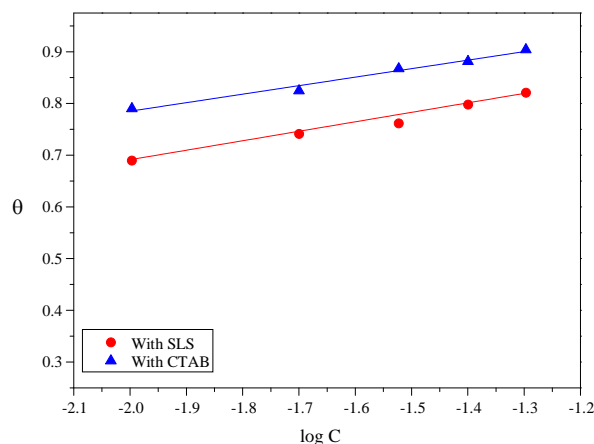


Figure 5. Temkin adsorption isotherm for the studied inhibitor (PTA) for mild steel in 1M H₂SO₄ without and with surfactants

Table 4. Temkin adsorption parameters of adsorption of the inhibitor PTA on the mild steel surface at room temperature

Name of the inhibitor	R^2	K_{ads} $L \text{ mol}^{-1}$	Slope	$-\Delta G_{ads}^{\circ}$ kJ mol^{-1}
PTA+Without surfactants	0.9958	575.6	0.0837	26.13
PTA+With SLS	0.9956	1058.3	0.0427	27.67
PTA+With CTAB	0.9941	1113.6	0.0134	27.81

3.8 Comparison of % IE of CTAB and SLS

Inhibition efficiency of CTAB is higher than SLS because

- ✓ Br^- is a borderline base attached with a borderline acid (Fe^{2+} surfaces) and soft acid (bulk Fe metal surfaces) more than the harder, 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 is adsorbed more tightly on the mild steel surface.

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

4. Conclusions

1. The inhibitor PTA showed good performance as corrosion inhibitor for mild steel in 1M H₂SO₄, which is further improved in presence of halides (Cl⁻, Br⁻ and I⁻) surfactants (SLS and CTAB).
2. The effect of halides and surfactants on the corrosion inhibition behaviour of the studied inhibitor appears to be synergistic in nature.
3. The data obtained from weight loss measurements confirm the corrosion inhibition by adsorption mechanism and fit well the Temkin adsorption isotherm.
4. The value of ΔG_{ads}° confirm mixed type of adsorption involving both physisorption and chemisorption.

References

1. P.C. Okafar, Y. Zheng, *Corros. Sci.* 51 (2009) 850-859.
2. E.E. Oguzie, C. Unalgbu, C.N. Ogukwe, B. N. Okolue, A.I. Onuchakwu, *Mater. Chem. Phys.* 84 (2004) 363-368.
3. A.S. Fouda, G.E. Bader, M.N. El-Haddad, *J. Korean Chem. Soc.* 52 (2008) 124-132.
4. E.E. Oguzie, Y. Li, Y. F.H. Wang, *J. Colloid Interface Sci.* 310 (2007) 90-98.
5. M.Z.A. Rafiquee, N. Saxena, S. Khan, M.A. Quraishi, *Mater. Chem. Phys.* 107 (2008) 528-533.
6. M. Mobin, M.A. Khan, M. Parveen, *J. Appl. Polym. Sci.* 121 (2011), 1558-1565.
7. M.A. Migahed, A.M. Al-Sabagh, *Chem. Eng. Commun.* 196 (2009) 1054-1075.
8. M.L. Free, *Corrosion.*, 58 (2002) 1025-1030.
9. K. Asif, M. Himaja, V. Mali Sunil, K. Jagadeesh Prathap, S. Sikarwar Mukesh., *Int. Res. J. Pharm.* 2 (2011) 153-158.
10. R. Solmaz, E. Mert MS, G. Kardas, B. Yazici, M. Erbil, *Acta Physico-Chimica Sinica*. 24 (2008) 1185-1191.
11. S.A. Umoren, M.M. Solomon, *Arab. J. Sci. Engg.* 35 (2010) 115-129.
12. W.W. Frenier, P.A. Andreozzi, *Proceedings of the Electrochemical Society*. 86-87 (1986) 123-129.
13. J Saranya, P Sounthari, K Parameswari, S Chitra, *Measurement*. 77 (2016) 175-186.
14. P.Sounthari, T.Kavitha, A.Kiruthika, J.Saranya, S.Chitra, K.Parameswari, H. Yuvaraj, *Mater. Focus*. 3 (2015) 455-464.
15. N. Hackerman, E.S. Snavel, J.S. Payne, *J. Electrochem. Soc.* 113 (1966) 677-689.
16. G.M. Schmid, N. Hackerman, *J. Electrochem. Soc.* 109 (1962) 243-249.
17. A.N. Frumkin, B.B. Damaskin, *J. Electroanal. Chem.* 3 (1962) 36-47.
18. J.M. Kolotyrkin, *J. Electrochem. Soc.* 108 (1961) 209-215.
19. T. Murakawa, N. Hackerman, *Corros. Sci.* 4 (1964) 387-396.
20. A. Alagta, I. Felhosi, J. Telegdi, I. Bertoti, K. Erika, *Corros. Sci.* 49 (2007) 2754-2766.
21. U. Rammelt, S. Koehler, G. Reinhard, *Corros. Sci.* 50 (2008) 1659-1663.
22. X. Li, S. Deng, H. Fu, *Corros. Sci.* 51 (2009) 1344-1355.
23. U.M. Eduok, S.A. Umoren, A.P. Udoh, *Arab. J. Chem.* 5 (2012) 325-337.
24. K.S. Shaju, K. Joby Thomas, Vinod P. Raphael, Aby Paul, *ISRN Corrosion*. (2012) Article ID 25878, 8 pages, doi:10.5402/2012/425878.
25. O.A. Hazazi, A. Fawzy, M. Awad, *Int. J. Electrochem. Sci.* 9 (2014) 4086-4103.
26. Ali A. Al-Taq, Dr. Shaikh A. Ali, Jaffer A. Saleem, Habeeb H. Al-Haji, *Saudi Aramco Journal of Technology* (Fall 2014).
27. V. I. Vigdorovich, L. E. Tsygankova, *Prot. Met.* 43 (2007) 628-636

28. Z.A. Iofa, *Vestn. Mosk. Gos. Univ.* 2 (1956) 139-145.
29. B.B. Damaskin, O.A. Petrii, V.V. Batrakov, *Adsorption of Organic Compounds on Electrodes*, Plenum Press, New York, London, (1971) 245.
30. R. Saratha, C. Marikkannu, S. Sivakamasundari, *Bull. Electrochem.* 18 (2002) 141-144.
31. B.E. Conway in "Transactions of the Symposium on Electrode Processes", John Wiley and Sons NY (1961).
32. N. Hackerman, E.S. Snavel, J.S. Payne, *J. Electrochem. Soc.* 113 (1966) 677-682.
33. G.M. Schmid, N. Hackerman, *J. Electrochem. Soc.* 109 (1962) 318-325.
34. I. Cornet; E.A. Barrington; G.U. Behrning, *J. Electrochem. Soc.* 108 (1961) 947-953.
35. Z.A. Iofa, V.V. Batrakov, Cho Ngok Ba, *Electrochim. Acta.* 9 (1964) 1645-1653.
36. Z.A. Iofa, *Dokl. Akad. Nauk SSSR*, 119 (1958) 971-974.
37. Z.A. Iofa, L.A. Medvedeva, *Dokl. Akad. Nauk SSSR*, 69 (1949) 213-216.
38. Z.A. Iofa, V.V. Batrakov, Cho Ngok Ba. *Zashchita Metallov.*, (1965) 56-58.
39. R.M. Hudson, C.J. Warning, *Mat. Prot.* 6 (1967) 52-59.
40. R.M. Hudson, C.J. Warning, *Corros. Sci.* 10 (1970) 121-134.
41. K.F. Hager, M. Rosenthal, *Corrosion.* 6 (1950) 344-346.
42. K.E. Heusler, *J. Electrochem. Soc.* 62 (1958) 529-532.
43. J.O.M. Bockris, B. Drazic, A.R. Despic, *Electrochim. Acta.* 4 (1961) 325-361.
44. C. Jeyaprabha, S. Sathiyarayanan, S. Muralidharan, G. Venkatachari, *J. Braz. Chem. Soc.*, 17 (2006) 61-67.
45. E.E. Oguzie, Y. Li, F.H. Wang, *J. Colloid Interf. Sci.* 310 (2007) 90-98.
46. G. Subramaniam, K. Balasubramanian, P. Sridhar, *Bull. Electrochem.* 6 (1980) 225-229.
47. K. Aramaki, M. Hackerman, *J. Electrochem. Soc.* 116 (1969) 568-574.
48. A.S. Fouda, H.A. Mostafa, F. El-Taib, G.Y. Elewady, *Corros. Sci.* 47 (2005) 1988-2004.
49. S.J.A. Iofa, E. Ljachoreskaya, K. Schortfor, *Acad. Sci.* 84 (1952) 548-573.
50. R. Geethanjali, S. Leelavathi, S. Subhashini, R. Rajalakshmi, *Chem. Sci. Trans.* 2 (2013) 1296-1303.
51. E.A. Noor, *Int. J. Electrochem. Sci.* 2 (2007) 996-1017.
52. L. Tang, X. Li, Y. Si, G. Mu, G. Liu, *Mater. Chem. Phys.* 95 (2006) 29-38.
53. P.C. Okafor, E.E. Ebenso, U.J. Ekpe, U. J. Ibok, M.I. Ikpi, *Trans. Soc. Adv. Electrochem. Sci. Technol.* 38 (2003) 338-343.
54. E.E. Ebenso, *Mater. Chem. Phys.* 79 (2003) 58-70.
55. A. Lalitha, S. Ramesh, *Electrochem. Acta.* 51 (2005) 47-55.
56. B. Ramesh Babu, A.K. Parande, P.L. Ramasamy, *Can. J. Chem.* 84 (2006) 1658-1666.
57. S. Rajendran, B.V. Apparao, N. Palaniswamy, *Electrochim. Acta.* 44 (1998) 533-537.
58. M. Foss, E. Gulbrandsen, J. Sjöblom, *Corros. Sci.* 65 (2009) 3-14.
59. A.S. Fouda, K. Shalabi, G.Y. Elewady, H.F. Merayyed, *Int. J. Electrochem. Sci.* 9 (2014) 7038 - 7058.
60. Mosarrat Parveen, Mohammed Mobin, *Int. J. Sci. Eng. Res.* 4 (2013) 162-167.
61. A.X. Fan, P. Somasundaran, N.J. Turro, *Langmuir.* 13 (1997) 506-510.
62. F. Bentiss, M. Lagrenée, *J. Mater. Environ. Sci.* 2 (2011) 13-17.
63. E. Khamis, F. Belluci, R.M. Latanision, E.S.H. El-Ashry, *Corrosion.* 47 (1991) 677-686.