

REVIEW OF ACTION OF CATIONIC AND ANIONIC SURFACTANTS ON CORROSION INHIBITION OF STEEL IN ACIDIC MEDIUM

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ABSTRACT

The use of a cationic surfactant, namely, cetyltrimethylammonium bromide (CTAB) as a corrosion inhibitor of carbon steel, and a mixed surfactant, i.e., a mixture of cationic and anionic surfactants, CTAB and sodium dodecyl sulfate (SDS) as corrosion inhibitor of mild steel and in acidic medium have been reviewed here. The results have been evaluated by weight loss method. The results show that CTAB acts as a good inhibitor against the corrosion of carbon steel in 1M and 2M HCl solutions, and the maximum inhibition efficiency (IE) is about 87% in 2M HCl solution. The IE increases with the inhibitor concentration, while it decreases with increasing the hydrochloric acid concentration more than 2M, temperature and immersion time. Meanwhile, CTAB and SDS, in a concentration of about 50ppm each has an inhibition efficiency of 83% on mild steel. It has also been noted, that as the medium is changed from acidic to basic, the inhibition IE increases. The protective film consists of Fe²⁺-SDS complex. Furthermore, Scanning Electron Microscopy (SEM) is used to examine the surface morphology of the carbon steel samples, both in absence and presence of each inhibitor at optimum conditions.

Keywords: Anionic Surfactants, Cationic Surfactants, Corrosion Inhibition, Steel, Weight Loss

Method.

I. INTRODUCTION

Corrosion of materials usually takes place in the presence of oxygen and moisture and involves two electrochemical reactions, oxidation occurs at anodic site and reduction occurs at cathodic site. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. Surfactants can be used alone as corrosion inhibitors or in combination with other compounds to improve their performance. In aqueous solution the inhibitory

action of surfactant molecules may be due to the physical (electrostatic) adsorption or chemisorption onto the metallic surface, depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface. The investigation of surfactants adsorbed on metal surfaces is extremely important in electrochemical studies such as corrosion inhibition, adhesion, lubrication, and detergency. The effective type of corrosion inhibitors for these applications is film-forming inhibitors. Out of the different types of surfactants, the use of common cationic surfactants like CTAB and anionic surfactants like SDS, which can be produced by relatively less expensive methods have been undertaken with convincingly positive results [12],[13] [14].

II. CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB) [1]:

Carbon steel strips of size (2.5cm x 5 cm x1 cm) were acquired. Strips were mechanically polished with different grades of emery papers and degreased with acetone. AR grade HCL was used as the acidic medium, to prepare the solutions, all with triply distilled water. CTAB used was BDH made. Inhibition efficiencies (IEs) for different concentrations of the inhibitor were calculated from weight loss values in the absence and presence of the inhibitor at temperature of 20, 40, and 60°C. The analysis was done by using weight loss method and the following formulae were used to calculate the corrosion rate (Cr), surface coverage (θ) and inhibition efficiency ($\eta\%$) were determined using [2]:

$$Cr = \frac{w_o - w_i}{At} \quad (1)$$

$$\theta = \frac{w_o - w_i}{w_o} \quad (2)$$

$$\eta \% = \frac{w_o - w_i}{w_o} \times 100 \quad (3)$$

where, w_i and w_o are the weight loss values (mg) in presence and absence of inhibitor, respectively. A is the total area of the specimen in cm^2 and t is the immersion time in minutes.

III. EFFECT OF INHIBITOR CONCENTRATION AND TEMPERATURE ON INHIBITION EFFICIENCY [1]:

The variation of the inhibition efficiencies obtained from the weight loss with different inhibitor concentrations in 1M and 2M HCl at different temperatures (20, 40, and 60°C) are shown in Figs. 1, 2 and 3:

From the results, we can see that as the concentration of the inhibitor increases from 25 to 300 ppm, the inhibition efficiency increases at 20, 40 and 60°C. The maximum inhibition efficiency for CTAB inhibitor was found to be

about 87% in 2M HCl solution. The inhibition was estimated to be 72% at 20°C even at very low concentrations (25 ppm), and at 300 ppm its protection was more than 80% (20^o- 40°C). The inhibition efficiency decreases with an increase in corrosion temperature at the same inhibitor concentration Figs. 1, 2 and 3, indicating that the high temperature might result in desorption of the inhibitor molecules from the C-steel surface [3],[4],[5].

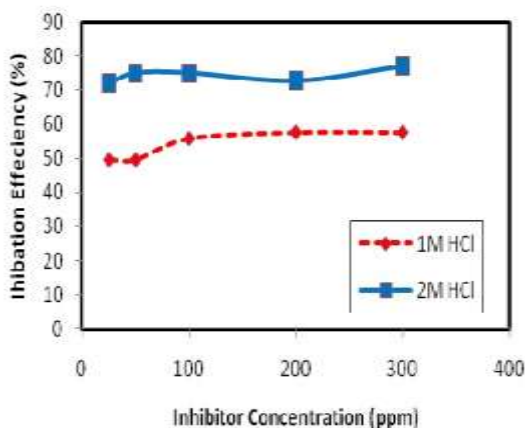


Fig. 1: Inhibition efficiency as a function of inhibitor concentration in 1 and 2M HCl at 20°C [1]

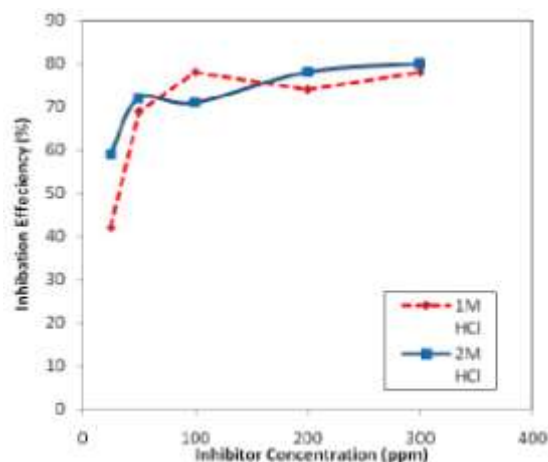


Fig. 2: Inhibition efficiency as a function of inhibitor concentration in 1 and 2M HCl at 40°C [1]

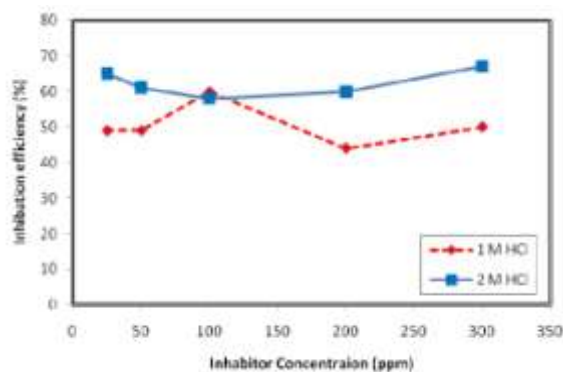


Fig. 3: Inhibition efficiency as a function of inhibitor concentration in 1 and 2M HCl at 60°C [1]

IV. EFFECT OF IMMERSION TIME [1]

The effect of immersion time on corrosion inhibition of different concentrations of CTAB on the corrosion of C-steel in 1M and 2M HCl at 20, 40 and 60°C keeping the inhibitor concentration at 300 ppm was also studied. The variation is shown in Figs. 4, 5 and 6:

The inhibition efficiency is higher than 55% when the immersion time is only 0.5 hours, which indicates that the adsorption rate of CTAB on the C-steel surface is relatively high. The figures show that CTAB inhibits the corrosion of C-steel for all immersion time at all concentrations of CTAB. Increasing immersion time resulted in increasing IE. The most suitable results were obtained in 2M HCl at 20⁰C giving an efficiency of up to 87% at 2 hours of immersion time. The high inhibition efficiency with longer immersion time could be attributed to the formation of a protective film on the C-steel surface, which is time dependent. It has been stated that stable two dimensional layers of inhibitor molecules are formed on metal surfaces on longer immersion times [6].

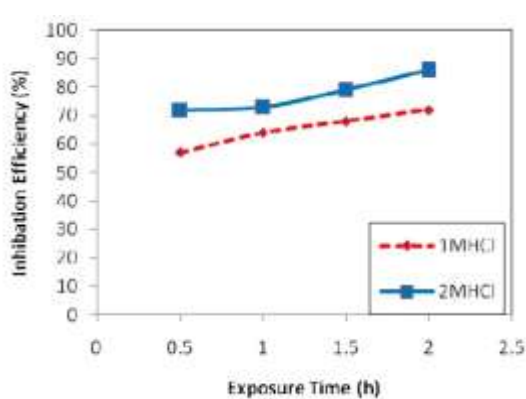


Fig. 4: Effect of exposure time in 1 and 2M HCl at 20⁰C [1]

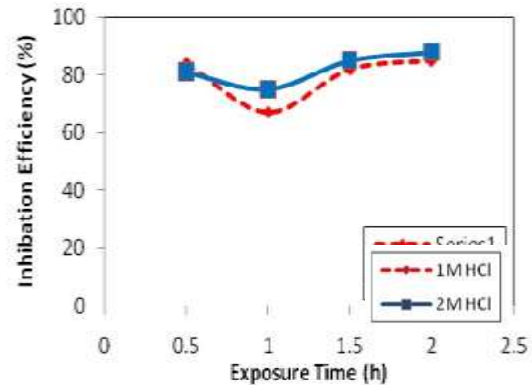


Fig. 5: Effect of exposure time in 1 and 2M HCl at 40⁰C [1]

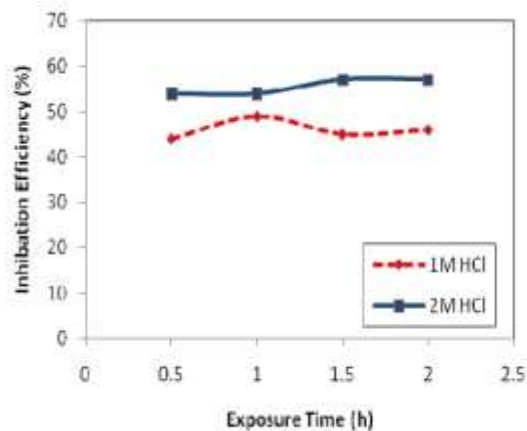


Fig. 6: Effect of exposure time in 1 and 2M HCl at 60⁰C [1]

V. ADSORPTION ISOTHERM [1]

The action of corrosion inhibitors is attributed to adsorption of organic molecules on the metal surface, and the inhibition efficiency is directly proportional to the surfactant coverage [7]. According to Langmuir adsorption model, the relationship between surface coverage (θ) and inhibitor efficiency ($\eta\%$) is defined as:

$$\theta = \frac{\eta}{100} \quad (4)$$

Assuming the adsorption of CTAB on C-steel surface obeys Langmuir adsorption isothermal equation, then we have the relation:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

where, C is the concentration of inhibitor and K the adsorptive equilibrium constant [3],[8],[9]. The relationship between C/θ and C at 25°C is shown in Fig. 7. The linear regressions between C/θ and C show that all the linear correlation coefficients (r) in case of 1M and 2M HCl solutions are equal to 1 and also, all the slopes are very close to 1 which indicates that the adsorption of CTAB inhibitor onto C-steel surface corresponds with the Langmuir adsorption isotherm.

The adsorptive equilibrium constant, K in case of 2M HCl is more than K in case of 1M HCl which indicates that the adsorption of CTAB molecules on C-steel surface in 2M HCl media is easier than that 1M HCl solution. These results supports the conclusion that maximum inhibition corresponds to the formation of a monolayer of the additive on the active sites of the metal surface.

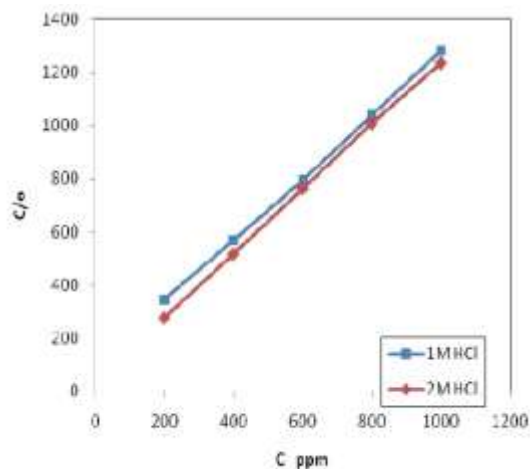


Fig. 7: The relationship between C/θ and C at 25°C in 1M and 2M HCl [1]

VI. CTAB AND SODIUM DODECYL SULPHATE (SDS) [10]:

For the analysis, the same methods employed for only CTAB were used, except in this case, instead of carbon steel, mild steel was used. The assumption that the adsorption of SDS molecules follow the Langmuir adsorption isotherm was made, and equation (5) was used to calculate and plot the graph of C/θ vs. C between 25 and 65⁰C. Fig. 8 gives the graph obtained [11].

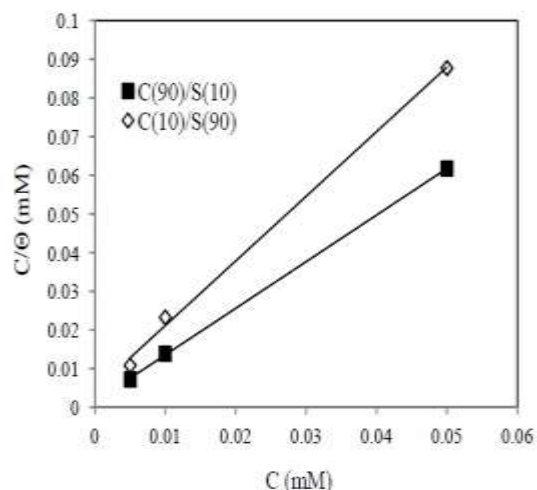


Fig. 8: Langmuir adsorption plots for mild steel in 2M HCl in different concentrations of mixed surfactants

From the graphs, we could observe that the slopes were close to 1, showing that in addition to CTAB, SDS can be also used as an independent surfactant [10].

VII. INFLUENCE OF PH ON THE IE OF SDS [12],[15]:

It was observed that the addition of a base like NaOH increased the inhibition efficiency of the added SDS surfactant. This is due to the fact that in acidic medium the protective film is broken by the acid. When pH is increased, IE slightly increases for SDS system. This is due to the fact that ionization of SDS is increased by the presence of OH⁻ in solution, and hence coordination of SDS with Fe²⁺ of the steel surface is enhanced, effectively forming SDS-Fe²⁺ on the metal surface. It was also observed that the use of SDS-Zn²⁺ inhibitor system increased corrosion inhibition greatly. The formulation consisting of 50 ppm of SDS and 5 ppm of Zn²⁺ has 83% IE, thus proving that a mixed inhibitor mostly always has a better IE than a single inhibitor.

This is illustrated in Fig.9, in which inhibition efficiency ($\eta\%$) is plotted against pH.

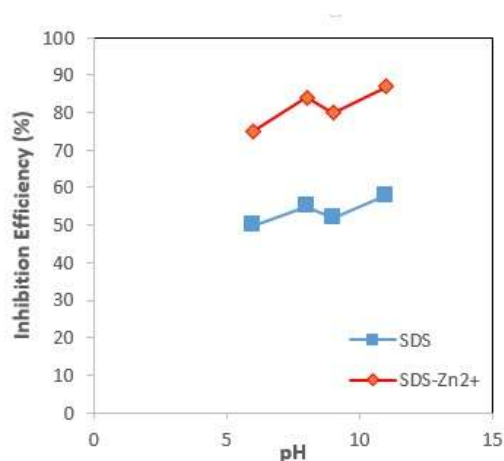


Fig. 9: Influence of pH on IE of SDS and SDS-Zn²⁺ system [12]

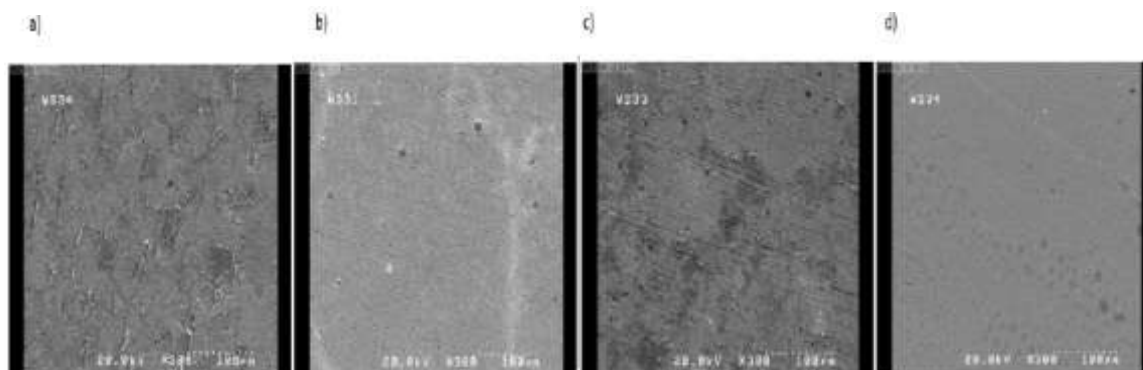


Fig. 10: SEM images for the mild steel surface in 2 M HCl (a) without surfactant, (b) with 0.05mM of CTAB, (c) with 0.05mM of SDS and (d) with 0.05mM of 90:10 CTAB/SDS [10]

VIII. CONCLUSION

From the experiments conducted we can say that CTAB acts as a good inhibitor for the corrosion of C-steel in 1M and 2M HCl solutions, and the maximum inhibition efficiency is about 87% in 2M HCl solution. The inhibition efficiency values increase with the inhibitor dose, but decrease with the temperature. Increasing the immersion time resulted in increasing the inhibition efficiency. The adsorption of CTAB on C-steel surface obeys the Langmuir adsorption isotherm.

The usage of SDS and CTAB as a mixed inhibitor, increases the corrosion inhibition of mild steel when compared to using a single surfactant. The use of SDS-Zn²⁺ inhibitor system increased corrosion inhibition greatly. The

formulation consisting of 50 ppm of SDS and 5 ppm of Zn^{2+} has 83% IE. At lower pH, IE decreases, while at higher pH IE increases.

From the above data, we can conclude that all surfactants can be used as a cheaper alternative for the protection of metals. Furthermore, a good inhibition efficiency can be achieved for a very small dosage of the surfactants.

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