Chapter 7

CHAPTER-7

SYNERGISTIC INFLUENCE OF SURFACTANTS ON THE CORROSION INHIBITION PERFORMANCE OF BENZODIAZEPINES FOR MILD STEEL IN 1M H_2SO_4

7.1 Introduction

Several reports indicate that the efficiency of inhibitors can be improved by the addition of other compounds which act in synergism. It is one of the most important effects in inhibition process and serves to formulate efficient inhibitor compounds. The overall effect produced by the mixture of inhibitor constituents is considerably greater than the sum of the effects achieved by each inhibitor. Synergism of corrosion inhibitors is reported to be due to (i) interaction between the constituents of the mixture or (ii) interaction between the inhibitor and one of the ions of the other constituent produced in aqueous solution[1]. The advantage of synergism is that the amount of organic inhibitor can be decreased or an environmental friendly, but less effective corrosion inhibitor can be used more effectively. Several reports are available on the use of halide ions to enhance the inhibition performance of a vast majority of organic compounds[2-6]. However reports on influence of surfactants on the corrosion inhibition behavior of organic compounds are scanty[7].

Surfactants or surface active compounds are organic compounds that possess spatially distinct polar (hydrophilic) head and non-polar (hydrophobic) tail group. Due to the presence of hydrophilic and hydrophobic domains, surfactants exhibit unusual properties and found multifarious industrial application ranging from mundane (washing cloth) to very sophisticated preparation of microchips[8]. Surfactants have been effectively used as corrosion inhibitors as their molecules possess strong adsorption ability to the metallic surfaces. The adsorbed molecules form monolayer or bilayer hemimicelles or admicelles depending on the surfactant concentration and reduce corrosion rate. Surfactants can be classified as ionic (cationic, anionic), zwitterionic or non-ionic depending on the nature of their head groups. Anionic surfactants are very good corrosion inhibitors because they can adsorb on to positively charged metallic surfaces in a direct and more effective way than other types of compounds.

Keeping the above facts in view, an attempt has been made to study the effect of addition of two surfactants viz., cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) on the inhibition efficiency of the benzodiazepines (DPBD and TMBD) for mild steel corrosion in 1M H_2SO_4. Weight loss method was used under varied conditions. A brief review on the previous reports in the synergistic effects of surfactants and organic inhibitors is presented.

7.2 Review of literature

The corrosion of copper alloys in sulphuric acid by benzotriazole derivatives was investigated by weight loss and polarization measurements. The effect of non-ionic, cationic and anionic surfactants on the inhibition efficiency of benzotriazole was studied by **Ullah *et al*** [8]., the inhibition efficiency was found to increase with the sodium dodecylsulphate (SDS), cetyl trimethyl ammonium bromide (CTAB) and X-Triton. Surface morphology of the inhibited specimen was confirmed by scanning electron microscope.

Mobin *et al* [9]., investigated the synergistic effect of CTAB and SDS on the corrosion inhibition of mild steel in 0.1M H_2SO_4 by the amino acid L-methionine (LMT) using weight loss measurements and potentiodynamic polarization measurements. It was found that the mixed effect of the inhibitor and CTAB is more effective than the mixture of LMT and SDS. It has been proposed that the inhibitor is adsorbed on the metal surface obeying Langmuir adsorption isotherm.

Corrosion inhibition properties of stainless steel 316 by thiourea based inhibitor and its synergistic effect with cetyl trimethyl ammonium bromide, sodium dodecyl sulphate (SDS) and non-ionic triton X-100 has been studied by weight loss method was studied by **Ullah *et al*** [10]., it was found that surfactants enhanced the corrosion inhibition performance of thiourea.

Lalitha *et al*., [11] studied the influence of 1, 2, 4-triazole derivatives and ionic surfactants CTAB and SDS on the corrosion control of copper in acidic solution. From the investigations it was concluded that a mixed effect of triazoles and surfactant exhibited a marked synergistic effect. Inhibition studies of CTAB and *o*-phenylenediamine have shown

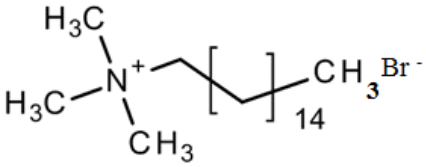
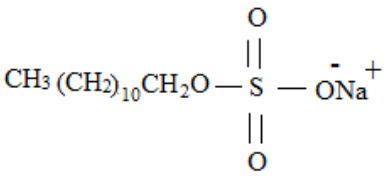
that they were effective inhibitors for corrosion of carbon steel in HCl. It was found that the inhibition efficiency was due to polymolecular film formed by the physical adsorption of the inhibitors on the metal surface.

Rajendran *et al*.,[12] investigated the effect of cationic surfactant CTAB on the inhibition efficiency of calcium gluconate against mild steel corrosion in a neutral aqueous environment containing chloride ion. It was found that addition of various concentration of CTAB to the above system enhanced the inhibition efficiency to 99%.

A perusal of literature shows that no work has been done on the synergistic influence of CTAB, SDS and benzodiazepines on the corrosion of mild steel in acid media. Therefore an attempt has been made in this research work to study the influence of CTAB and SDS on the inhibitory property of two benzodiazepines (CTAB and SDS) on the corrosion of mild steel in 1M H_2SO_4 by weight loss method.

7.3 Results

Molecular structures of the surfactants used are

Surfactant	Structural formula	Molecular Formula	Molecular weight
CTAB		$C_{16}H_{33}N(CH_3)_3$-Br	364.45
SDS		$C_{12}H_{25}SO_4Na$	288.37

The corrosion of mild steel in 1M H_2SO_4 and inhibition in presence of surfactants and varying concentrations of benzodiazepines (DPBD and TMBD) was studied at 303 ± 1K. the concentration of the benzodiazepines was varied between 20 ppm – 100 ppm and the concentration of surfactants was kept constant as 20 ppm. The results are recorded in

Tables 7.1 and 7.2. Surfactants CTAB and SDS (20 ppm) alone displayed inhibition efficiency of 33% and 29% respectively. Similarly 100 ppm of DPBD and TMBD showed 67.42% and 54.89% inhibition efficiency (Table 4.3, Chapter 4). But the combination of DPBD with surfactants in the ratio 100 ppm: 20 ppm increased the corrosion inhibition performance to greater than 80% and 70%. This shows that there is synergism between the two constituents. The synergism parameter $S_{\circ}$ was calculated using the equation proposed by Aramaki and Hackerman,

$$S_{\circ} = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

Where $\theta_{1+2} = (\theta_1+\theta_2) - \theta_1\,\theta_2$ where θ_1= surface coverage by surfactant; θ_2= surface coverage by inhibitor, θ'_{1+2} = surface coverage of mixture of surfactant and organic inhibitor.

The $S_{\circ}$ values are also given in Tables 7.1 and 7.2. $S_{\circ}$ approaches 1 when there is no interaction between inhibitor and surfactant. $S_{\circ} > 1$ indicate synergistic effect, $S_{\circ} < 1$ shows antagonistic behavior which may be attributed to competitive adsorption. The values are all greater than 1 for both CTAB and SDS which suggest synergistic inhibition. Maximum value of 2.01 is observed for the combination 100 ppm DPBD and 20 ppm CTAB which is an effective combination for combating corrosion of mild steel in 1M H_2SO_4.

7.4 Adsorption isotherms

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reaction. In the present study, Langmuir isotherm was found to be suitable as shown by the linearity of the plot of C/θ vs. C (Figure 7.1 and 7.2) for the adsorption of DPBD/ TMBD in the combination with surfactants in 1M H_2SO_4 at 303 ± 1K. The values of adsorption parameters deduced from the isotherm such as linear regression coefficient (R^2), slope and adsorptive equilibrium are presented in the Table7.3. The plots are linear but the R^2 values deviate from unity which may be explained as due to the interaction between the adsorbed species. The high values of K_{ads} indicate that the benzodiazepine - surfactant mixture is strongly adsorbed on the mild steel.

7.5 Effect of immersion time, temperature and concentration of acid

Generally high temperature, high acid concentration and longer period of immersion induce more corrosion of metallic materials. Hence an attempt has been made to test the inhibitor plus surfactant for formulation at various experimental conditions. The weight loss of mild steel immersed in 1M H_2SO_4 containing 100 ppm of the benzodiazepine and 20 ppm surfactants was determined for various time intervals from 1-6 hours and the inhibition efficiency was calculated. As is seen in Table 7.4 and 7.5, the efficiency increased up to 3 hours afterwards it decreased and reached 30%.

The synergistic inhibition performance was evaluated at various temperatures from 303K-333K. The values in Table 7.6 show that the efficiency decreased by about 10% for every 10 ◌C rise in temperature but the values are higher (by 10-15%) compared to that in the absence of surfactants.

The effect of acid concentration on the performance of the inhibitor – surfactant mixture is given in Table 7.7. As the concentration of acid increased, the efficiency decreased drastically. This may be attributed to the degradation and desorption of the inhibitors at the higher concentration of the corrosive acid.

7.6 Discussion

Adsorption of surfactants on solid surfaces is governed by a number of forces such as covalent bonding, electrostatic attraction, hydrogen bonding or non-polar interactions between adsorbed species. Tammam *et al* [13]., have reported that the adsorption of cetylpyridiniumbromide (CP^+ Br^-) molecule can be enhanced by the electrostatic attraction between the CP^+ and the induced negative sites resulting from the adsorption of Br^- ion on the iron surface, which is positively charged in acid medium i.e. the Br^- modifies the surface charge of the iron surface. A similar explanation was reported by Parveen *et al* [14] for the synergistic corrosion inhibition by amino acids and surfactants such as CTAB and SDS. According to them, the polar head groups of the surfactants interact with polar groups (COO^- and NH_3^+) of amino acids and direct them to adsorb on the steel surface more firmly.

In the present study the enhancement of corrosion inhibition may be explained in light of the above reports. The Br^- of CTAB gets adsorbed on the positively charged steel surface, making the surface negatively charged. Hence the CTA^+ ions get attracted and adsorbed. The CTA^+ ions bind with the nitrogen atoms of the benzodiazepines via lone pair of electrons and attract towards the surface and help to get adsorbed firmly.

In the case of SDS, direct interaction with the diazepines is unfavorable due to repulsion between the anion DS^- (after ionization of Na^+) and lone pair of electron on nitrogen. However in acid solutions some of the molecules get protonated. These protonated organic cations can interact with adsorbed DS^- ions and favor greater adsorption. Mobin and Alam Khan[15] have offered a similar explanation to explain synergistic inhibition of PVA and SDS.

The interaction between the adsorbed organic molecule and adsorbed surfactant was also confirmed from the adsorption isotherm. Further, the hydrophobic, long hydrocarbon chain of the surfactant offers complete coverage of the steel surface forming a functional blanket and protects the surface from acid attack even in small concentration.

References

1. Afolabi A S, *Leonardo El J Pract Technol.,* **11** (2007) 143.
2. Qian B, Wang J, Zheng M, Hou B, *Corros. Sci*., **75** (2013) 184.
3. Arukalam I O, *Carbohydr. Polym.* **112** (2014) 291.
4. Khamis A, Saleh M M, Awad M I, El-Anadouli B E, *J. Adv. Res*., **5** (2014) 637.
5. Chidiebere M A, Oguzie E E, Liu L, Ying L, Fuhui Wang L, *Ind. Eng. Chem. Res*., **53** (2014) 7670.
6. Umoren S A, Pan C, Li Y, Wang F H, *J. Adhes. Sci. Technol*., **28** (2014) 31.
7. Rafiquee M Z A, Saxena N, Khan S, Quraishi M A, *Mat. Chem. Phys*. **107** (2008) 528.
8. Ullah S, Shariff A M, Bustam M A, Nadeem M, Naz M Y, Ayoub M, *Int. J. Electrochem. Sci.,* **10** (2015) 8321.
9. Mobin M, Parveen M, Rafiquee M Z A, *Arab J Chem*., (2013) http://dx.doi.org/10.1016/j.arabic.2013.04.006.
10. Ullah S, Nadeem M, Shariff A M, Ahmad F, Shahid S A, Sagir M, Malik M R R, Mushtaq M, *Adv. Mater. Res*., **917** (2014) 28.
11. Lalitha A, Ramesh S, Rajeswari S, *Electrochim. Acta*., **51** (2005) 47.
12. Rajendran S, Apparao B V, Palaniswamy N, *Anti Corros. Method. M.,* **47** (2000) 11.
13. Tammam R H, Fekry A M, Saleh M M, *Int. J. Electrochem. Sci.,* **11** (2016) 1310.
14. Parveen M, Mobin M, *Int. J. Sci. Eng Res*., **4** (2013) 167.
15. Mobin M, Alam Khan M, *Chem. Eng. Commun.* **20** (2013) 1149.

Tables

Table 7.1 Effect of CTAB on the inhibition efficiency of various concentrations of the inhibitors in 1M H_2SO_4 obtained by weight loss measurements at $303 \pm 1K$

Name of the inhibitor	Inhibitor concentration(ppm)	Inhibition efficiency (%)	Surface coverage (Θ)	Synergistic factor (S_o)
DPBD	BLANK	33.05	0.3305	
	20	76.02	0.7602	1.20
	40	80.82	0.8082	1.39
	60	84.40	0.8440	1.54
	80	87.14	0.8714	1.77
	100	89.00	0.8900	2.01
TMBD	20	60.30	0.6030	1.12
	40	65.50	0.6550	1.15
	60	69.30	0.6930	1.18
	80	73.50	0.7350	1.22
	100	78.40	0.7840	1.24

Table 7.2 Effect of SDS on the inhibition efficiency of various concentrations of the inhibitors in 1M H_2SO_4 obtained by weight loss measurements at $303 \pm 1K$

Name of the inhibitor	Inhibitor concentration(ppm)	Inhibition efficiency (%)	Surface coverage (Θ)	Synergistic factor (S_o)
DPBD	BLANK	29.51	0.2951	
	20	70.08	0.7008	1.12
	40	75.80	0.7580	1.17
	60	79.05	0.7905	1.22
	80	83.33	0.8333	1.44
	100	86.30	0.8630	1.71
TMBD	20	56.23	0.5623	1.02
	40	61.30	0.6130	1.05
	60	64.62	0.6462	1.08
	80	68.50	0.6850	1.10
	100	72.10	0.7210	1.11

Table 7.3 Langmuir adsorption isotherm parameters for benzodiazepines at 303 ± 1K

Compound	Surfactant	K_{ads} (M^{-1})	R^2	Slope
DPBD	CTAB	5 X 10^4	0.9994	1.1227
	SDS	2.5 X 10^4	0.994	1.1825
TMBD	CTAB	1.42 X10^4	0.9937	1.966
	SDS	1.42 X10^4	0.996	2.144

Table 7.4 Effect of immersion time on inhibition efficiencies of 100 ppm of benzodiazepines and 20 ppm of CTAB for mild steel corrosion in 1M H_2SO_4

Name of the inhibitor	Surfactant	(%) Inhibition efficiency for various time interval					
		1 hr	2 hrs	3 hrs	4 hrs	5 hrs	6 hrs
BLANK	-	17.19	22.95	33.05	32.05	27.99	20.50
DPBD	CTAB	60.42	76.00	89.00	72.00	48.18	36.84
TMBD		52.30	68.50	78.40	64.10	46.50	32.25

Table 7.5 Effect of immersion time on inhibition efficiencies of 100 ppm of benzodiazepines and 20 ppm of SDS for mild steel corrosion in 1M H_2SO_4

Name of the inhibitor	Surfactant	(%) Inhibition efficiency for various time interval					
		1 hr	2 hrs	3 hrs	4 hrs	5 hrs	6 hrs
BLANK	-	13.75	21.35	29.51	27.56	22.71	18.65
PBD	SDS	58.13	72.55	86.30	70.24	42.21	34.25
TMBD		52.20	67.50	72.10	62.50	39.50	30.20

Table 7.6 Effect of temperature on inhibition efficiencies of 100 ppm of benzodiazepines on mild steel corrosion at optimum concentration in presence of 20 ppm of surfactants after 1 hour of immersion in 1M H_2SO_4

Inhibitor	Surfactants	(%) Inhibition Efficiency			
		303K	313K	323K	333K
DPBD	CTAB	74.5	64	51	46
	SDS	86.2	76	64.9	58.1
TMBD	CTAB	65.2	52.5	41	32
	SDS	72.0	58.4	49.5	45.3

Table 7.7 Effect of acid strength on inhibition efficiencies of 100 ppm of benzodiazepines on mild steel corrosion at optimum concentration in presence of 20 ppm of surfactants after 3 hours of immersion in 1M H_2SO_4 at 303 ± 1K

Inhibitor	Surfactants	(%) Inhibition Efficiency			
		1M H_2SO_4	**2M H_2SO_4**	**3M H_2SO_4**	**4M H_2SO_4**
DPBD	CTAB	89.00	50.16	32.15	14.50
	SDS	86.30	43.58	20.11	12.52
TMBD	CTAB	78.40	38.20	22.50	6.65
	SDS	72.10	26.35	18.50	2.05

Figures

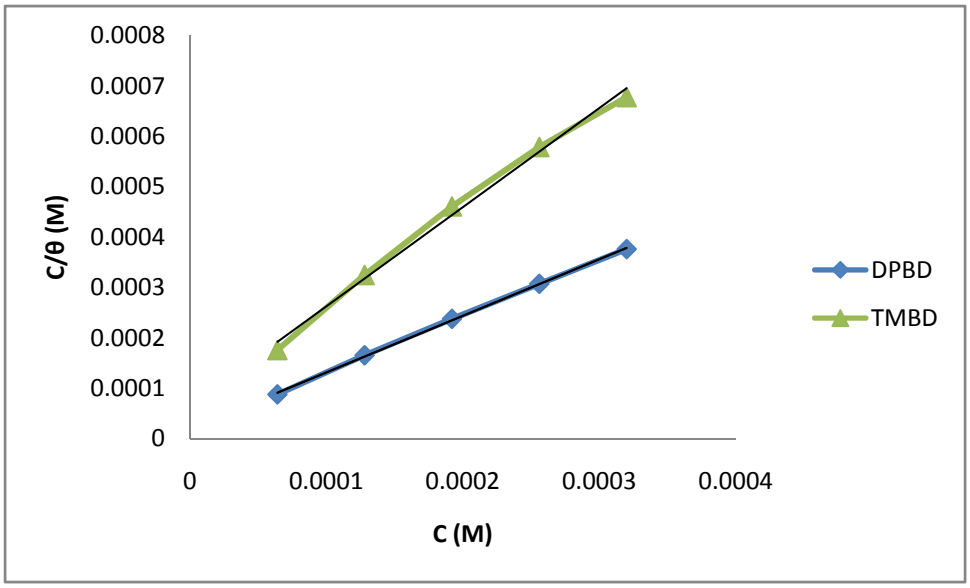


Figure 7.1 Langmuir adsorption plots for benzodiazepines with 20 ppm CTAB in 1M H_2SO_4

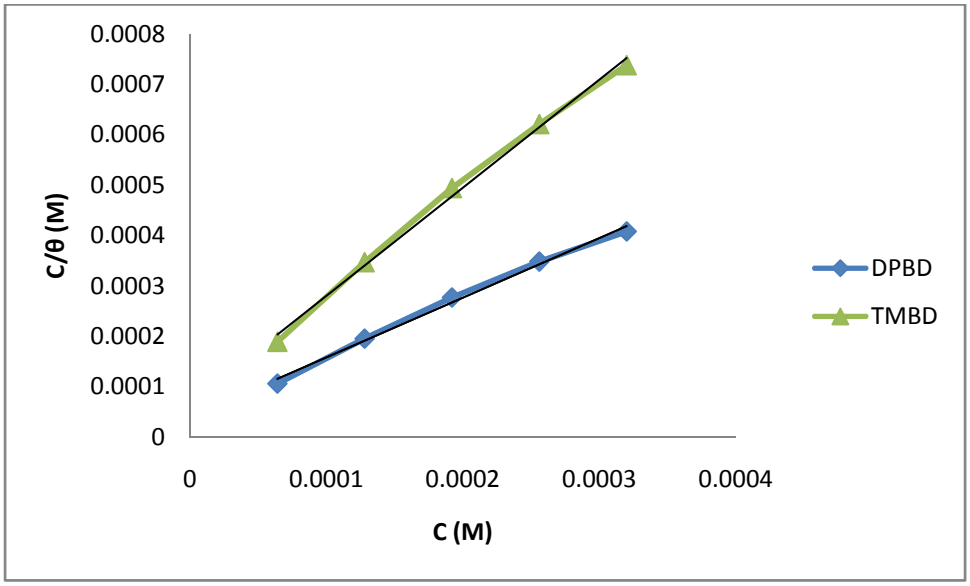


Figure 7.2 Langmuir adsorption plots for benzodiazepines with 20 ppm SDS in 1M H_2SO_4