Synergistic Effect of Cationic Surfactants in Adsorption

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Abstract. The corrosion behaviour of cationic surfactants, namely: cetyl trimethyl ammonium bromide (CTAB) and dodecyl trimethyl ammonium bromide (DTAB), have been used as corrosion inhibitors for carbon steel in well water. Protection efficiencies of the studied surfactants were depended on the hydrophobic chain length and concentration of the surfactants. The results shows that the order of protection efficiency is CTAB > DTAB. Tafel curves showed these surfactants are acting as an anodic inhibitors. Nyquist curves revealed that a protective film is formed on the metal surface. FTIR spectra suggest that the tested surfactants protective film consists of Fe²⁺-CTAB, Fe²⁺-DTAB and Zn(OH)₂. Protection efficiency values and synergism parameters obtained weight loss; potentiodynamic polarization and electrochemical impedance spectroscopy are consistent.

Introduction

Iron-based alloys are used in different applications and they are susceptible to corrosion due to its thermodynamic instability especially in aggressive media. A variety of attempts have been made to prevent/retard the destructive effect of corrosion on metals and alloys. Corrosion control can be achieved by various methods, corrosion inhibition being one of the most effective alternatives [1,2]. Surfactants are special type of organic compounds and exhibit unique properties due to their amphiphilic structure, consisting of hydrophilic and hydrophobic molecular segments. They form hydrophobic barrier film as a result of the interaction of hydrophilic side with the metal surface, which prevents direct contact between metal surface and corrosive environment. The surfactant inhibitors have many advantages, such as being environmentally friendly, high efficiency, low price and availability [3–5].

Adsorption of surfactants on metal surface can markedly increase the corrosion-resistance [6] and therefore the study of the relationship between the adsorption and corrosion inhibition is of great importance.

The adsorption of a surfactant markedly changes the corrosion resisting property of a metal, and for these reasons studies of the relation between adsorption and corrosion inhibition are of considerable importance [7–10]. In corrosion inhibition with surfactant inhibitors, the critical micelle concentration (CMC) is the most important parameter. When the concentration of surfactant adsorbed on the solid surface is high enough, organized structures (hemi-micelles such as bi-or multilayer) are formed, which decrease the corrosion reaction by blocking the metallic surface [11–13]. The objective of this work is to study the effect of investigated surfactants on the protection of corrosion of carbon steel in well water.

Materials and Methods

Materials. Carbon steel used for corrosion inhibition studies the compositions was (Wt%): 0.026% S, 0.06% P, 0.4% Mn, 0.1% C and balance being Fe. Specimens of size 1.0cm×4.0cm×0.2cm were press cut from the carbon steel sheet, were machined and abraded with a series of emery papers. This was followed by rinsing in acetone and double distilled water and

finally dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage. The inhibitors CTAB and DTAB, molecular structure formula of CTAB and DTAB are shown in Table 1. Zn^{2+} ions were used as received.

Table 1: Molecular and Structure formula of CTAB and DTAB

Structure formula	Molecular formula	Molecular weight
<p>cetyl trimethyl ammonium bromide</p>	$\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{-Br}$	364.45
<p>dodecyl trimethyl ammonium bromide</p>	$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{-Br}$	308.30

Stock solution of 1000ppm of CTAB was prepared in double distilled water and the desired concentration was obtained by appropriate dilution. The concentration of CTAB used for the study ranges from 10 to 150ppm. The study was carried out at room temperature in open atmosphere.

Weight - loss Measurements. Carbon steel specimens were suspended in 150mL beakers containing 100mL of test solution maintained at room temperature with the aid of glass rods and hooks. The weight loss taken was the difference between the weight at a given time and the original weight of the specimens. The measurements were carried out for the uninhibited solution and the solution containing CTAB, CTAB – Zn^{2+} , DTAB and DTAB – Zn^{2+} mixture. Weight loss experiments were performed for the seven days duration. The specimens were immersed in triplicate and the average corrosion rate was calculated.

These uncertainties or RSD for three replicate measurements were less than 5%. The corrosion rates (C_R) were measured using the equation:

$$\text{Corrosion Rate } \left(\frac{\text{mm}}{\text{y}} \right) = \frac{87.6 \times W}{A T D}$$

Where W = weight loss of carbon steel (mg)

A = area of the specimens (cm^2)

T = exposure time (h)

D = density of the specimen (g cm^{-3}).

The inhibition efficiency (IE) of CTAB and Zn^{2+} mixture was calculated by using the following equation:

$$\%IE = \frac{CR_o - CR_i}{CR_o}$$

Where CR_o = corrosion rate in the absence of inhibitor

CR_i = corrosion rate in the presence of inhibitor

Surface analysis by FTIR spectroscopy. The specimen immersed the one day duration in various environments, the specimens were taken out of the test solution and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout.

FTIR spectrum of the powder (KBr Pellets) was recorded using perkin-elmer-1600 FTIR spectrophotometer with resolving power of 4 cm^{-1} .

Electrochemical studies. Electrochemical studies were carried out using the electrochemical workstation model CHI- 760d and experimental data were analysed by using the electrochemical software (Version: 12.22.0.0). Measurements were conducted in a conventional three electrode cylindrical glass cell with platinum electrode as auxiliary electrode and saturated calomel electrode as reference electrode.

The working electrode was carbon steel embedded in epoxy resin of polytetrafluoroethylene so that the flat surface of 1 cm^2 was the only surface exposed to the electrolyte solutions.

The three electrodes set up was immersed in control solution of volume 100ml both in the absence and presence of the inhibitors formulations and allowed to attain a stable open circuit potential (OCP). The pH values of the solution were adjusted to 7.0 and the solutions were unstirred during the experiments.

Tafel curves were recorded in the potential range of -750 to -150 mV with a resolution of 2mV. The curves were recorded in the dynamic scan mode with a scan rate of 2 mV s^{-1} in the current range of -20mA to +20mA. The Ohmic drop compensation has been made during the studies. The corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) were obtained by extrapolation of anodic and cathodic regions of the Tafel plots. The inhibition efficiency (IE_p) values were calculated from the I_{corr} values using the equation.

$$IE_p(\%) = [1 - (I'_{\text{corr}}/I_{\text{corr}})] \times 100$$

Where I_{corr} and I'_{corr} are the corrosion current densities in case of control and inhibited solutions respectively.

Nyquist plots were recorded at OCP in the frequency range from 60 KHz to 10MHz with 4 to 10 steps per decade. A sine wave, with 10mV amplitude, was used to perturb the system. The impedance parameters viz., charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) were obtained from the Nyquist plots. The inhibition efficiencies (IE_i) were calculated using the equation,

$$IE_i(\%) = 100 [1 - R_{\text{ct}} / R'_{\text{ct}}]$$

Where R_{ct} and R'_{ct} are the charge transfer resistance values in the presence and absence of the inhibitor respectively.

Results and Discussion

Weight – loss measurements

Information of Table 2 shows that, protection efficiency dependence on the altering concentration of surfactants in the range from 10ppm to 150ppm. It is apparently that, at room temperature the protection efficiency increases with raising concentration of the each surfactant. The lowest corrosion rate is obtained by CTAB therefore I.E tends to decrease in the following order CTAB > DTAB. This action was attributed to effect of alkyl chain length. Co-adsorption (Zn^{2+}) acts as a good synergism attain in surfactants

Table 2: Weight – loss measurements for carbon steel in well water without and with an inhibitor of different concentration of surfactants at room temperature

Name of surfactant	Conc. of Zn ²⁺ (ppm)	Conc. of surfactant (ppm)	C _R (mm ⁻¹)	%IE	Surface coverage (θ)	Synergism (S _I)
CTAB	Blank	-	194.4	-	-	-
	25	-	155.5	20	0.20	-
	-	10	188.6	3	0.03	-
	-	25	178.9	8	0.08	-
	-	50	171.1	12	0.12	-
	-	75	163.3	16	0.16	-
	-	100	155.5	20	0.20	-
	-	125	149.7	23	0.23	-
	-	150	141.1	27	0.27	-
	25	10	143.9	26	0.26	1.0486
	25	25	130.3	33	0.33	1.0985
	25	50	114.7	41	0.41	1.1932
	25	75	93.3	52	0.52	1.4000
	25	100	62.2	68	0.68	2.0000
	25	125	44.7	77	0.77	2.6782
	25	150	17.5	91	0.91	6.4889
DTAB	-	10	196.4	-1	0.01	-
	-	25	182.0	6	0.06	-
	-	50	175.0	10	0.10	-
	-	75	149.7	23	0.23	-
	-	100	163.3	16	0.16	-
	-	125	171.1	12	0.12	-
	-	150	178.9	8	0.08	-
	25	10	151.6	22	0.22	1.03
	25	25	134.1	31	0.31	1.08
	25	50	101.1	48	0.48	1.38
	25	75	42.7	78	0.78	2.80
	25	100	70.0	64	0.64	1.86
	25	125	83.6	53	0.53	1.49
	25	150	108.9	44	0.44	1.31

FTIR spectroscopy

FTIR spectra powerful technique for find out the functional group were recorded to understand the interaction of inhibitor molecule with the metal. Figs. 2 and 3 shows the IR spectra of pure and scraped samples of surfactants obtained from after corrosion experiments in well water respectively.

Pure CTAB, the IR peak observed at 621 cm⁻¹ has been assigned to C-Br of CTAB. Scraped sample, the IR peaks that appeared at 572 cm⁻¹ and 1382 cm⁻¹ have been assigned to C-Br and Zn – O. All the peaks displayed substantial shift with fairly low or high intensity indicating coordination through carbon and bromine of CTAB moiety. It is therefore inferred that CTAB and Zn²⁺ are involved in complex formation with Fe²⁺ as well as Zn²⁺ and the presence of [Fe²⁺- Zn²⁺- CTAB] and Zn(OH)₂

Similarly, pure DTAB the IR peak observed at 530.42 cm⁻¹ has been assigned to C-Br of DTAB. Scraped sample, the IR peaks that appeared at 470.63 cm⁻¹ and 1381 cm⁻¹ have been assigned to C-Br and Zn – O [14-16]. All the peaks displayed substantial shift with fairly low or high intensity indicating coordination through carbon and bromine of DTAB moiety, it is therefore inferred that

DTAB and Zn^{2+} are involved in complex formation with Fe^{2+} as well as Zn^{2+} and the presence of $[\text{Fe}^{2+} - \text{Zn}^{2+} - \text{DTAB}]$ and $\text{Zn}(\text{OH})_2$.

Figure 1: FTIR spectrum of CTAB a) Pure sample b) Scraped sample

Figure 2: FTIR spectrum of DTAB a) Pure sample b) Scraped sample

Tafel curves

Datas of corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic slope (β_a) and cathodic slope (β_c) can be evaluated from anodic and cathodic region of the Tafel curves. The linear Tafel segments of anodic and cathodic plots were extrapolated to obtain corrosion current (I_{corr}).

Figs. 3 and 4 represent the Tafel curves of carbon steel in well water, without and with an inhibitor formulation of the CTAB and DTAB. It can see from Figs. 3 and 4 that, with inhibitors, the curves are shifted to lower current regions, showing the inhibition tendency of the surfactants. There was definite trend observed in the E_{corr} values in the presence of both the surfactants. In the present study, shift in E_{corr} values in more positive zones suggesting that they all acts as anodic inhibitors.

Figure 3: Tafel curves a) Blank b) 25ppm Zn^{2+} c) 150ppm CTAB d) 25ppm Zn^{2+} + 150ppm CTAB

Figure 4: Tafel curves a) Blank b) 25ppm Zn^{2+} c) 75ppm DTAB d) 25ppm Zn^{2+} + 75ppm DTAB

The values of various electrochemical parameters derived by Tafel plots of the inhibitors are given in Table 3. Investigation Table 3 revealed that the values of β_c change slightly in the presence of both the inhibitor formulations, whereas a more change occurs in the values of β_a , indicating that anodic reactions are affected. Thus, both the CTAB and DTAB acted as anodic corrosion inhibitors. The data obtained from fitted spectra are listed in Tables 3 and 4. The inhibition efficiency, surface coverage (θ) and synergism parameters are calculated from the Tafel plots by using following equation:

$$S_I = (1 - I_{1+2}) / (1 - I'_{1+2})$$

Where

$$I_{1+2} = (I_1 + I_2) - (I_1 \times I_2)$$

I_1 = surface coverage of inhibitors (surfactants)

I_2 = surface coverage of inhibitors (Zn^{2+})

I'_{1+2} = combined surface coverage of inhibitors (surfactants) and (Zn^{2+})

Table 3: Electrochemical parameters, inhibition efficiency (IE) and synergism parameter (S_I) from the polarization study for carbon steel in well water

Conc. of Zn^{2+} (ppm)	Conc. of CTAB (ppm)	$-E_{corr}$ mV vs SCE	β_a mV dec^{-1}	β_c mV dec^{-1}	I_{corr} , $A.Cm^{-2}$, $\times 10^{-5}$	IE_{pol} , %	Surface coverage (θ)	Synergism (S_I)
Blank	-	- 712	2.676	170.3	198.4	-	-	-
-	25	- 612	2.158	154.7	180.5	19.35	0.1935	-
150	-	- 655	1.988	149.7	156.9	25.71	0.2571	-
150	25	- 480	0.254	236.9	106.0	90.50	0.9050	6.3063

Table 4: Electrochemical parameters, inhibition efficiency (IE) and synergism parameter (S_I) from the polarization study for carbon steel in well water

Conc. of Zn^{2+} (ppm)	Conc. of DTAB (ppm)	$-E_{corr}$ mV vs SCE	β_a mV dec^{-1}	β_c mV dec^{-1}	I_{corr} , $A.Cm^{-2}$, $\times 10^{-5}$	IE_{pol} , %	Surface coverage (θ)	Synergism (S_I)
Blank	-	- 712	2.676	170.3	198.4	-	-	-
-	25	- 612	2.158	154.7	180.5	19.35	0.1935	-
75	-	- 625	2.081	136.0	233.1	22.23	0.2223	-
75	25	- 478	0.591	158.2	193.7	77.91	0.7791	2.8392

Nyquist plots

The inhibition effect, electrochemical impedance spectroscopy was well suited for monitoring in situ any perturbation by an inhibitor according to the electrochemical processes in the interface of metal/corrosion. The influence of Zn^{2+} on the adsorption of carbon steel, high corrosion inhibition effect of surfactant and the synergistic effect of the two have been studied. Figs. 5 and 6 shows Nyquist curves of without and with an inhibitor formulation (CTAB + Zn^{2+} & DTAB + Zn^{2+}), it is well known that the semi – circle diameter of the Nyquist plot is proportional to the anticorrosion behaviour. Large diameter reveals better anticorrosion performance.

The main fitting parameters for Nyquist curves data obtained for the substrate and samples immersed in well water are listed in Tables 5 and 6, a great improvement on the corrosion resistance of the substrate was obtained for (CTAB + Zn^{2+} & DTAB + Zn^{2+}) samples with a high total resistance R_{ct} . Namely, the (CTAB + Zn^{2+} & DTAB + Zn^{2+}) films acts as good barrier facing against the penetration of well water, subsequently enhancing the anticorrosion behaviour of carbon steel. The inhibition efficiency (I.E.) calculated from R_{ct} reaches a considerable percentage. For studying the synergism parameters of (CTAB + Zn^{2+}) and (DTAB + Zn^{2+}), surfactants with co-adsorption of Zn^{2+} , the synergism parameter S_I is defined as follows [17].

Figure 5: Nyquist plots a) Blank b) 25ppm Zn^{2+} c) 150ppm CTAB d) 25ppm Zn^{2+} + 150ppm CTAB

Figure 6: Nyquist plots a) Blank b) 25ppm Zn^{2+} c) 75ppm DTAB d) 25ppm Zn^{2+} + 75ppm DTAB

Table 5: Electrochemical parameters, inhibition efficiency (IE) and synergism parameter (S_i) from the impedance study for carbon steel in well water

Conc. of Zn^{2+} (ppm)	Conc. of CTAB (ppm)	R_{ct} ohm.cm ²	C_{dl} F.cm ⁻² ×10 ⁻⁵	%IE _{imp}	Surface coverage (θ)	Synergism (S_i)
Blank	-	135.10	17.290	-	-	-
-	25	168.13	10.580	19.64	0.1964	-
150	-	180.69	9.371	25.23	0.2523	-
150	25	1330.0	0.174	89.84	0.8984	5.9133

Table 6: Electrochemical parameters, inhibition efficiency (IE) and synergism parameter (S_i) from the impedance study for carbon steel in well water

Conc. of Zn^{2+} (ppm)	Conc. of DTAB (ppm)	R_{ct} ohm.cm ²	C_{dl} F.cm ⁻² ×10 ⁻⁵	%IE _{imp}	Surface coverage (θ)	Synergism (S_i)
Blank	-	135.10	17.290	-	-	-
-	25	168.13	10.580	19.64	0.1964	-
75	-	174.81	10.415	22.71	0.2271	-
75	25	584.64	0.914	76.89	0.7689	2.6875

$$S_i = (1 - I_{1+2}) / (1 - I'_{1+2})$$

Where

$$I_{1+2} = (I_1 + I_2) - (I_1 \times I_2)$$

I_1 = surface coverage of inhibitors (surfactants)

I_2 = surface coverage of inhibitors (Zn^{2+})

I'_{1+2} = combined surface coverage of inhibitors (surfactants) and (Zn^{2+})

Mechanism of corrosion inhibitor

Character of the counter ions on the adsorption of cationic surfactants is important factor. The possible adsorption of organic cations in the presence of the bromine ion is due to the formation of intermediate bridge, the negative ends of the bromine metal dipoles being oriented towards the interface of solution, whereby setting up an additional potential difference between the metal surface/ interface. This will shift the zero charge potential positively.

Figure 7: The schematic diagram of adsorption of surfactants on carbon steel surface

This shift will make the charge on the metal surface more negative and facilitates the adsorption of positively charged quaternary ammonium compound by formation of covalent bonds. Hard acid and hard base interaction and soft acid (Fe^{2+}) and soft base (Br^-) interaction gives much more stable according to Pearson's rule. High hardness of Br^- ion (counter ion effect) and cationic part of CTAB and DTAB to occur (cooperative effect with Zn^{2+}) leads to high inhibition efficiency. Br^- ion acts as an adsorption mediator for bonding the two positive partners, the metal surface and the positively charged ammonium compound. This gives rise to the formation of an adsorption composite film in which the anions are sandwiched between the metal surface and positively charged part of the inhibitor [18]. This film acts as a barrier facing the corrosion process as shown in Fig. 7. From above, it is mentioned that a hydrophilic head group of chosen surfactants. Inhibition efficiency of CTAB is larger than DTAB may be due to;

- i. Br^- (soft base) is a borderline base attached with a borderline acid (Fe^{2+} surface) and soft acid (bulk iron metal surface) according to Pearson classification of acid and base.
- ii. Br^- ion is more hydrophobic, with large ionic radius and low electro negativity. N-Br bond loosely bonded. Thus it adsorbed more tightly on carbon steel surface.
- iii. The alkyl chain of CTAB is longer than DTAB. The greater will be the forces of attraction between the alkyl chains of adjacently adsorbed head group ions [19].

Conclusion

1. The investigated surfactants protect the corrosion of carbon steel in well water
2. The protection is due to adsorption of the surfactant molecules on the carbon steel surface and blocking its active regions.
3. Results shows from weight loss, Tafel curves and Nyquist plots are in reasonably good agreement and inhibition efficiency order of CTAB > DTAB.
4. Tafel curves shows that the investigated surfactants acts as an anodic inhibitor in well water
5. The FT – IR and AC impedance spectra confirm the formation of protective film on the carbon steel surface.

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