Indian Journal of Chemical Technology
Vol. 16, July 2009, pp. 328-333

Corrosion inhibition and biocidal activity of a cationic surfactant

P Shanthy[a], P Rengan[a], A Thamarai Chelvan[b], K Rathika[c] & S Rajendran[c*]

[a]Department of Chemistry, Yadava College, Madurai, India
[b]PG and Research Department of Chemistry, Thiagarajar College, Madurai, India
[c]Corrosion Research Centre, PG and Research Department of Chemistry, GTN Arts College, Dindigul, India
Email: srmjoany@sify.com

Received 10 December 2008; revised 8 May 2009

The inhibition efficiency (IE) of CTAB - Zn^{2+} system in controlling corrosion of carbon steel in well water has been evaluated by weight loss method. Enumeration of microorganisms from well water and biocidal efficiency of inhibitor system (CTAB-Zn^{2+}) were also determined by serial dilution technique and spread plate method. The formulation consisting of 200 ppm of CTAB and 5 ppm of Zn^{2+} shows an IE of 98%. Potentiodynamic polarization curves indicate that the CTAB – Zn^{2+} system functions as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra suggest that the protective film consists of Fe^{2+}- CTAB complex and $Zn(OH)_2$. The optimum concentration of CTAB for destroying the bacterias *viz. E.coli*, *Salmonella* and *Shigella* is ≥ 25 ppm. At ≥ 25 ppm of CTAB, it shows 100% biocidal efficiency in well water containing 5 ppm of Zn^{2+}.

Keywords: Corrosion inhibition, Carbon steel, Biocidal activity, *N*-Cetyl-*N,N,N*-trimethyl ammonium bromide (CTAB), CTAB-Zn^{2+} system

Surfactant molecules have one or more long alkyl chains (with atleast six methylene units) and a polar head group. They are called amphiphathic molecules[1]. Their unique structure confers in them both hydrophobic and hydrophilic properties. This gives them the fundamental property to form association structure of different types, such as monolayer, spherical micelle and rod-like micelle. Depending on the nature and length of the hydro carbon chain, the head group, concentration, temperature and other additives, the size (aggregation number) and shape of these aggregates may vary. Depending on the nature of the head group, these aggregates can be cationic, anionic or non ionic: Above a certain concentration range, the surfactant molecules aggregate in aqueous solution to form particles of colloidal dimensions, called micelles. The micelle formation takes place over a narrow range of surfactant concentration, around the critical micelle concentration (CMC) and is accompanied by distinct changes in various physical properties like surface tension. Below and upto the CMC, the monomeric surfactant exists as a strong electrolyte, fully dissociated and unaggregated. At the critical concentration, aggregation begins, at first with the formation of relatively small micelles which grow rapidly over a very limited concentration range to a size which for a given surfactant remains approximately constant with further increase in surfactant concentration. For a wide variety of ionic surfactants, ionic micelles have been found to be spherical at low concentration and rod shaped at high concentration[2]. Surfactants have been used alone as corrosion inhibitors[3] or in combination with other compounds, such as trans–cinnamaldehyde[4] or 1-phenyl-2-propyne-1-ol[5], to improve their performance as inhibitors. A comparative study of the effectiveness of different organic surfactants in inhibiting carbon steel corrosion in a natural geothermal environment has been reported[6]. Non-ionic surfactants are found to have a marked inhibiting efficiency on iron in acidic media by absorption onto its surface[7].

The inhibition effect of non-ionic surfactants such as Tween 20, Tween 40 on steel in acidic chloride solution has been investigated by studying their absorption behaviour with the use of gravimetric method in order to determine the inhibition efficiency[8]. Non-ionic surfactants prepared by direct esterification of fatty acids (stearic, oleic, recinolic and linoleic) with poly ethylene glycol have been used to prevent acid corrosion of admiralty[9]. Effects of metallic cations on corrosion inhibition by sodium dodecyl sulphonate, an anionic surfactant for mild steel in hydrochloric acid have been reported[10]. The influence of a cationic surfactant namely, *N*-cetyl-*N,N,N*-trimethyl ammonium bromide (CTAB) on the HEDP – Zn^{2+} system[11], the ATMP - Zn^{2+} system[12] and the calcium gluconate - Zn^{2+} system[13] in controlling corrosion of carbon steel in aqueous environment has been investigated. Corrosion inhibition of carbon steel by non-ionic poly oxy ethylene (80) monopalmitate, cationic CTAB and anionic SDS in sea water has been evaluated by weight loss method, correlated with absorption measurements and X-ray analysis[14]. CTAB has been used to inhibit the corrosion of carbon steel in sulphuric acid[15] over a temperature range 30 - 60°C. Water containing low chloride ion or ground water or well water can be used in cooling water systems. When well water is used in cooling water system, the corrosion caused by micro organisms present in well water should also be taken into consideration. Microbial induced corrosion can be controlled by using biocides such as *N*-cetyl-*N,N,N*-trimethyl ammonium bromide (CTAB).

The present work is undertaken (i) to study the corrosion inhibition efficiency of a biocide *viz*. CTAB in controlling corrosion of carbon steel in well water in the presence and absence of Zn^{2+} (ii) to analyse the protective film formed on the metal surface by FTIR spectroscopy (iii) to understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization studies and AC impedance spectra (iv) to propose a suitable mechanism for corrosion inhibition (v) to enumerate the micro organisms from well water (vi) to study the biocidal efficiency of the biocide CTAB in well water in the presence and absence of Zn^{2+}.

Experimental Procedure

Preparation of specimens

Carbon steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of dimensions 1.0 × 4.0 × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Weight loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for three days. The weight of the specimens before and after immersion were determined using Shimadzu balance, model AY 62. The corrosion products were cleansed with Clarke's solution[16]. The inhibition efficiency (I.E.) was then calculated using the equation

$$I.E = 100\,[1-(W_2/W_1)]\%$$

where W_1 = Corrosion rate in the absence of the inhibitor and W_2 = Corrosion rate in the presence of the inhibitor.

Surface examination

The carbon steel specimens were immersed in various test solutions for a period of three days, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by FTIR spectroscopic study.

FTIR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

Electrochemical studies

Carbon steel specimens of the above composition was emasculated in Teflon and used in electrochemical studies. The exposed area of the metal surface was 1 cm^2.

Potentiodynamic polarization

Polarization studies were carried out in an H & CH Electrochemical Work station Impedance Analyzer Model CHI 660A. A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The area of the counter electrode was much larger compared to the area of working electrode. This can exert a uniform potential field on the working electrode and minimize polarization effect on the counter electrode.

AC impedance measurements

The instrument used for polarization was used for AC impedance study also. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance (R_t), and the double layer capacitance (C_{dl}) were calculated.

Biocidal efficiency

The biocidal efficiency of the system was determined using nutrient agar medium and calculating the number of colony forming units per mL, using a bacterial colony counter.

Results and Discussion

Weight loss method

The physico-chemical parameters of well water used in the study are given in Table 1. The corrosion inhibition efficiencies of CTAB – Zn^{2+} system in controlling corrosion of carbon steel immersed in well water obtained by weight loss method are included in Table 2.

It is observed that CTAB itself (in the absence of Zn^{2+}) offers good corrosion protection to carbon steel. As a self assembling cationic surfactant, CTAB forms monolayers on the surface of the metal. Hence it offers good corrosion protection to carbon steel. At concentrations ≥ 250 ppm of CTAB, the protection efficiency decreases. It may be due to the fact that these molecules aggregate together and form micelles. They are not uniformly absorbed on the metal surface. Hence corrosion inhibition efficiency decreases.

Table 1 — Physico – chemical parameters of well water*

Parameter	Value
*p*H	8.5
Conductivity	1017
Chloride	135
Sulphate	65
Total dissolved solid	710
Calcium	28
Magnesium	43
Total hardness	250
Alkalinity	12
Sodium	108
Potassium	35

*All values except *p*H and conductivity are in mg/L

Table 2 — Corrosion inhibition efficiency offered by CTAB - Zn^{2+} system to carbon steel immersed in well water.

Immersion period : 3 days

CTAB (ppm)	IE (%) Zn^{2+}(ppm)						
	0	5	10	15	20	25	50
0	-	10	15	20	30	40	45
50	63	96	80	80	90	55	81
100	81	98	96	95	95	64	63
150	94	98	98	96	96	70	50
200	95	98	98	98	98	72	20
250	82	92	96	97	95	81	9

Influence of Zn^{2+} on the IE of CTAB

It is observed from Table 2 that, the IE of CTAB increases in the presence of Zn^{2+}. A synergistic effect exists between CTAB and Zn^{2+}. This is the case when the concentration of Zn^{2+} is 5, 10, 15 and 20 ppm. However, at higher concentration of Zn^{2+} namely 25 and 50 ppm, the inhibition efficiency of CTAB decreases. At concentration ≥ 250 ppm CTAB forms micelles. They are not uniformly absorbed on the metal surface. Protective film is not formed and hence IE decreases when the concentration of CTAB is ≥ 250 ppm.

Potentiodynamic polarization study

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors (CTAB - Zn^{2+}) are shown in Fig. 1. The corrosion parameters such as corrosion potential (E_{corr}), Tafel slopes (b_c, b_a), linear polarization resistance (LPR) and corrosion current (I_{corr}) are given in Table 3. It reveals that when inhibitors (200 ppm CTAB +5 ppm Zn^{2+}) are added to well water, the corrosion potential shifts to the more noble side. This suggests that a protective film is formed on the metal surface. This is supported by the fact that in the presence of inhibitors, the LPR value increases and corrosion current decreases. The

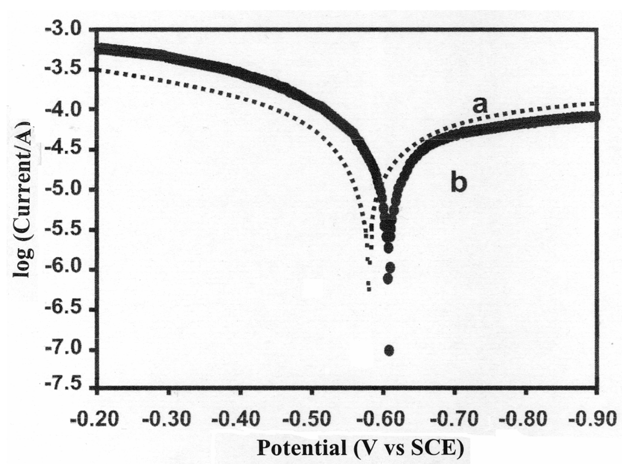

Fig. 1 — Polarization curves of carbon steel immersed in various test solutions (a) well water; (b) well water containing 200 ppm of CTAB and 5 ppm of Zn^{2+}

Table 3 — Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitor system obtained by potentiodynamic polarization technique

CTAB (ppm)	Zn^{2+} (ppm)	E_{corr} (mV vs SCE)	b_c (mV/decade)	b_a (mV/decade)	I_{corr} (A/cm^2)	LPR (ohm cm^2)
0	0	-608	528	200	5.234×10^{-5}	1.206×10^{3}
200	5	-577	321	236	3.834×10^{-5}	1.542×10^{3}

CTAB – Zn^{2+} system functions as anodic inhibitor, since the corrosion potential is shifted to the anodic side.

AC impedance spectra

The AC impedance spectra of carbon steel immersed in various test solutions are shown in Fig. 2. The equivalent electrical circuit for the model is shown in Fig. 3. The impedance parameters such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 4. It is observed that in the presence of inhibitors, R_t value increases and C_{dl} value decreases. This confirms the formation of protective film on the metal surface.

FTIR spectra

The FTIR spectrum of pure CTAB is shown in Fig. 4a. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing 200 ppm of CTAB and 5 ppm of Zn^{2+} is shown in Fig. 4b. It is observed that the C-N stretching frequency has shifted from 1141 to 1020 cm^{-1}. This suggests that nitrogen atom of CTAB has coordinated with Fe^{2+} resulting in the formation of Fe^{2+} - CTAB complex on the anodic sites of the metal surface. The band at 1380 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface[17]. Thus, FTIR spectral study leads to the conclusion that the protective film consists of Fe^{2+} - CTAB complex and $Zn(OH)_2$.

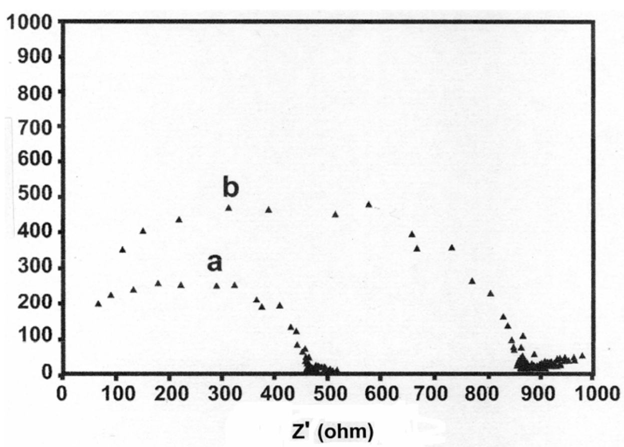

Fig. 2 — AC impedance spectra of carbon steel in various test solutions (a) well water; (b) well water containing 200 ppm of CTAB and 5 ppm of Zn^{2+}

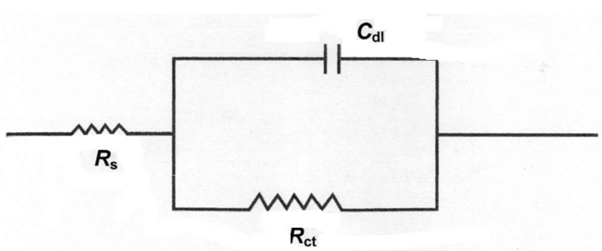

Fig. 3—Equivalent electrical circuit

Biocidal study

Enumeration of micro organisms from well water

Table 5 shows the number of colonies of bacteria enumerated from well water in nutrient agar medium for different dilutions. It is observed from Table 5 that as dilution increases, number of colonies formed decreases. At lower dilution (10^{-2}), the number of colonies formed is 122, it decreased to 14 for 10^{-7} dilution.

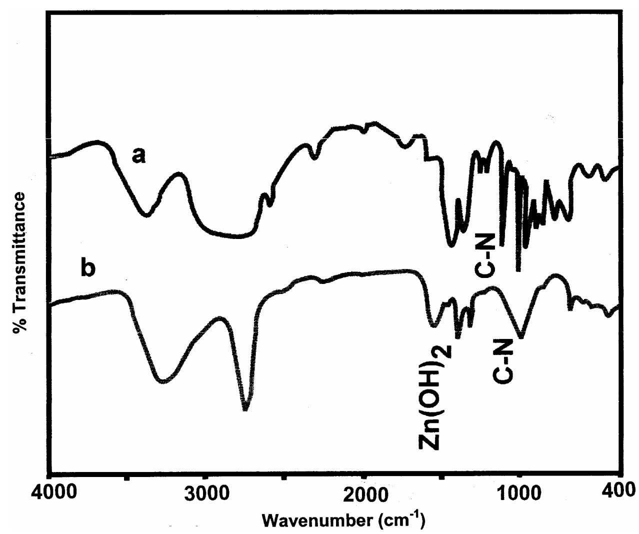

Fig. 4 — FTIR spectra of (a) pure CTAB and (b) film formed on the metal surface after immersion in well water containing 200 ppm of CTAB and 5 ppm of Zn^{2+}

Table 4 — Impedance parameters of carbon steel immersed in well water in the presence and absence of inhibitor system

CTAB (ppm)	Zn^{2+} (ppm)	R_t (Ω cm^2)	C_{dl} (F/cm^2)
0	0	399.98	3.6365×10^{-8}
200	5	755.6	1.925×10^{-8}

Table 5 — Enumeration of micro organisms from the well water

Dilution factor	Number of colonies	Number of colonies		
		E.coli	*Salmonella*	*Shigella*
10^{-2}	122	54	46	43
10^{-3}	100	50	40	38
10^{-4}	78	35	30	30
10^{-5}	60	20	15	25
10^{-6}	38	8	5	15
10^{-7}	14	5	2	2

Table 6 — Biocidal efficiency of CTAB-Zn^{2+} system for *E.coli*, *Salmonella* and *Shigella*

Sl. No.	CTAB (ppm)	Zn^{2+} (ppm)	*E.coli*			*Salmonella*			*Shigella*		
			Number of colonies	Bulk bacterial count (CFU/mL)	BE (%)	Number of colonies	Bulk bacterial count (CFU/mL)	BE (%)	Number of colonies	Bulk bacterial count (CFU/mL)	BE (%)
1	0	0	35	$35x10^5$	--	30	$30x10^5$	--	30	$30x10^5$	--
2	0	5	9	$90x10^4$	74	8	$80x10^4$	73	9	$90x10^4$	70
3	25	0	Nil	Nil	100	Nil	Nil	100	Nil	Nil	100
4	10	5	1	$10x10^4$	89	1	$10x10^4$	88	1	$10x10^3$	89
5	25	5	Nil	Nil	100	Nil	Nil	100	Nil	Nil	100
6	50	5	Nil	Nil	100	Nil	Nil	100	Nil	Nil	100

The number of colonies formed for *E.coli*, *Salmonella* and *Shigella* for different dilutions are also given in Table 5. As the dilution increases, the number of colonies formed decreases. At higher dilution very small number of colonies was seen on the petridishes.

Biocidal efficiency of the CTAB - Zn^{2+} inhibitor system

The biocidal nature of CTAB[18] has also been studied. The inhibitor system CTAB - Zn^{2+} which offered the best corrosion inhibition efficiency was selected. Biocidal efficiency of CTAB at various concentration in the presence and absence of Zn^{2+} in well water was determined. The number of colony forming units of *E.coli*, *Salmonella* and *Shigella* at various concentrations of CTAB in the presence and absence of Zn^{2+} in well water are given in Table 6. From Table, it is seen that 5 ppm of Zn^{2+} alone has 74% biocidal efficiency in well water. When 10 ppm of CTAB is added to the above environment, the biocidal efficiency increases to 89%. The 100% biocidal efficiency is achieved when the concentration of CTAB is ≥ 25 ppm i.e when the concentration of CTAB is ≥ 25 ppm, no colonies of *E.coli* are formed.

From Table 6, it is seen that for well water the number of colonies of *Salmonella* formed was 30 (30×10^5 CFU/mL). A 5 mL solution of Zn^{2+}alone shows 73% biocidal efficiency (BE). When 10 ppm of CTAB is added to the above solution, the BE increases to 88%. As the concentration of CTAB increases, BE also increases. This is due to the fact that at higher concentration of CTAB, the microbes are effectively killed. The activities of the microbes are totally prevented. 100% BE is observed when the concentration of CTAB is ≥ 25 ppm. This is the optimum concentration of CTAB. It is also clear that when the concentration of CTAB increases, biocidal efficiency against *Shigella* also increases. When the concentration of CTAB is ≥ 25 ppm 100% biocidal efficiency is obtained for *Shigella*.

Thus, analysis of data in Tables 2 and 6 reveal that the formulation consisting of 5 ppm of Zn^{2+} and 100 ppm of CTAB shows 98% corrosion inhibition efficiency and 100% biocidal efficiency.

Conclusion

The *N*-cetyl-*N,N,N*- trimethyl ammonium bromide (CTAB)-Zn^{2+} system exhibits the potential in controlling corrosion of carbon steel in well water. A synergistic effect exists between CTAB and Zn^{2+}. The formulation consisting of 200 ppm of CTAB and 5 ppm of Zn^{2+} has 98% IE. The CTAB - Zn^{2+} system functions as anodic inhibitor. A protective film is formed on the metal surface. The protective film consists of Fe^{2+} - CTAB complex and $Zn(OH)_2$. The optimum concentration of CTAB for destroying the bacteria *viz*., *E.coli*, *Salmonella* and *Shigella* is ≥ 25 ppm. The formulation consisting of 5 ppm of Zn^{2+} and 100 ppm of CTAB exhibits 98% corrosion inhibition efficiency and 100% biocidal efficiency.

Acknowledgement

The authors are thankful to University Grant Commission, India for help and encouragement.

References

1 Rajendran S, Mari Joany R & Palaniswamy N, *Corros Rev*, 20 (2002) 231.
2 Kalyanasundaram K, *Photochemistry in Micro Hetero Geneous Systems* (Academic Press, Inc. London), 1987, 25.
3 Abdel Fattah A A, Atia K M, Ahmed F S & Roushady M I, *Corros Prev Control,* 33 (1986) 67.
4 Growcock F B & Frenier W W, *J Electrochem Soc,* 135 (1988) 817
5 Growcock F B, Lopp V P & Josinski R J, *J Electrochem Soc*, 135 (1988) 823.
6 Amalhay M & Ignatiadis I, *Proc 8th Europ Symp on Corros Inhibitors, Ferrara, Italy* (1995) 1355.
7 Jian C J & Shou CJ, *Proc 6th Europ Symp on Corros Inhibitors, Ferrara, Italy* (1985) 257.

8 Osman M M & Shalaby M N, *Anti-Corros Methods Mater,* 44 (1997) 318.
9 Abdel Fattah A A & Sayed N A, *Proc 7th Europ Symp on Corros Inhibitors, Ferrara, Italy,* 2 (1990) 1099.
10 Mu G N, Zhao T P, Liu M & Gu T, *Corrosion,* 52 (1996) 853.
11 Rajendran S, Apparao B V & Palaniswamy N, *Bull Electrochem,* 13 (1997) 441.
12 Rajendran S, Apparao B V & Palaniswamy N, *J Electrochem Soc India*, 48 (1999) 89.
13 Rajendran S, Apparao B V & Palaniswamy N, *Anti-Corros Methods Mater,* 47 (2000) 11.
14 Shalaby M N, Osman M M & El Feky A A, *Anti-Corros Methods Mater,* 46 (1999) 254.
15 Osman M M, *Anti-Corros Methods Mater,* 45 (1998) 176.
16 Wranglen G, *Introduction to Corrosion and Protection of Metals* (Chapman and Hall, London, UK), 1985, 236.
17 Sekine I & Hirakwa Y, *Corrosion,* 42 (1986) 276.
18 Denyer S P, Mechanisms of Action of Biocides, International Biodeterioration, 26 (1990) 89.