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Investigation of the inhibiting effect of nano film by sodium meta silicate- Zn^{2+} system on the corrosion of carbon steel in neutral chloride solution

The inhibition of corrosion of carbon steel in 120 ppm chloride solution by Sodium meta silicate (SMS) in the presence and absence of Zn^{2+} ions is studied. The tests performed to measure the efficiencies of these substances reveal that 150 ppm of SMS and 75 ppm of Zn^{2+} gives 82 % inhibition efficiency. Scanning probe microscopic analysis and AC impedance show the formation of thin film on the surface of the metal. FTIR spectroscopy suggests that the film is formed by iron –inhibitor complex and $Zn(OH)_2$. Potentiodynamic studies reveal that the inhibitor system is of mixed type controlling the cathodic processes predominantly. An attempt was made to explain the mechanism based on the above studies.

Key words: Corrosion of carbon steel, sodium meta silicate, zinc ions, chloride solution

INTRODUCTION

The principles and practice of corrosion inhibition in recent years have become conscious to health and safety considerations. Hence there is a search for the non-toxic, ecofriendly corrosion inhibitors. Owing to the low cost and non-poisonous nature, silicate is of special interest as corrosion inhibitor. Silicates form oxide layers of ferrous or ferric silicate that act as efficient diffusion barrier. Dissolved oxygen helps to create the required cathodic area, which can promote anodic passivation of the remaining surface at the prevailing rate of reduction of SiO_3^{2-} ions. The lower surface and interfacial tensions of silicates also enhance its ability to displace air from crevices and assist its penetration into the deposit. Current literature on these inhibitor systems is also found to be extensive. Suzuki et al [1] have determined the influence of silicate ion as corrosion inhibitor for carbon steel immersed in various alkyl iodide solutions. Armstrong and Zhou [2] have investigated the behavior of modified silicates ($CaO.x SiO_2.nH_2O$) as an inhibitor for the corrosion of iron. Katsanis et al [3] have discussed the role of soluble silicates as corrosion inhibitors for ferrous metals, Pb, Cu and alloys including brass in water systems. Saji and Shibli [4] have reported the existence of synergism between sodium silicate and sodium tungstate in controlling the corrosion of carbon steel in neutral

aqueous media. They have also evaluated the synergistic effect of sodium silicate and sodium phosphate with sodium tungstate at low concentrations for cooling water systems [5]. Abdel Salam Hamdy [6] has investigated the corrosion inhibition characteristics of AA6061 T6-10 % Al_2O_3 composite in NaCl in the presence of silicate/cerate coating. Sodium silicate has been reported to be a good synergistic co-inhibitor with sodium molybdates in cooling waters [7]. Silicates are effective against special forms of corrosion like stress corrosion cracking, [8] and are used with corrosion resistance lubricants, greases, gels, and in various water borne acyclic, epoxy, polyurethane and silicone paints [9,10]. Sodium meta silicate is primarily used in laundry and as a base for detergent.

The present study is undertaken i) to evaluate the inhibition efficiency of sodium meta silicate [SMS] in controlling the corrosion of carbon steel in 120 ppm chloride solution in the absence and presence of Zn^{2+} ii) to analyze the protective film on carbon steel by FTIR spectrophotometry and Atomic Force Microscopy iii) to study the mechanistic aspects by UV-visible, AC Impedance and Potentiodynamic polarization studies and iv) to propose suitable mechanism for corrosion inhibition.

EXPERIMENTAL

Preparation of the specimen

Carbon steel specimens were chosen from the same sheet of the following composition: 0.1% C, 0.026 % S, 0.06 % P, 0.4 % Mn and rest Fe. Carbon steel specimens of the dimensions $1.0 \times 4.0 \times 0.2$ cm were polished to mirror finish, degreased with trichlo-

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roethylene and used for mass-loss and surface examination studies.

Mass-loss method

Carbon steel specimens in duplicate were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} for one day. The weight of the specimens before and after immersion were determined, using a ACCULAB Electronic top loading balance, with readability/sensitivity of 0.1 mg in 210 g range. The corrosion IE was then calculated using the equation:

$$IE = 100 [1 - W_2 / W_1] \%$$

Where

W_1 = corrosion rate in the absence of inhibitor and

W_2 = corrosion rate in the presence of inhibitor.

Potentiodynamic polarization study

Potentiostatic polarization studies were carried out using CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm² area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. Polarization curves were recorded using iR compensation. The results such as Tafel slopes, I_{corr} and E_{corr} values were calculated. During the polarization study, the scan rate (v/s) was 0.01; Hold time at E_f (s) was zero and quiet time (s) was 2.

AC impedance spectra

A CHI electrochemical impedance analyzer (model 660A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open circuit potential. The real part Z' and imaginary part Z'' of the cell impedance were measured in ohms at various frequencies. The values of the charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

$$R_t = (R_s + R_t) - R_s$$

where R_s = solution resistance

$$C_{dl} = 1/2\pi R_t f_{max}$$

where f_{max} = maximum frequency

Ac Impedance spectra were recorded with initial $E(v) = 0$; High frequency (Hz) = 1×10^5 , Low frequency (Hz) = 1; Amplitude (v) = 0.05 and Quiet time (s) = 2.

The UV-Visible absorption spectra

The possibility of formation of Zn- Inhibitor complex and also Fe^{2+} -inhibitor complex in solution was examined by mixing the respective solutions and recording their UV-visible absorption spectra using Systronix UV-Visible Spectrophotometer 119 which is a PC controlled single beam scanning spectrophotometer. It covers wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1 nm.

Surface Analysis by FTIR spectroscopic study

FTIR spectra (KBr pellet) were recorded using Perkin –Elmer 1600 FTIR spectrophotometer. After immersion period of one day in various environments, the specimens were taken out of the test solutions and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout.

Atomic Force Microscopy

Samples were scanned at various scan areas using a Shimadzu SPM 9500-21 Scanning Probe Microscope. For high resolution, contact mode micro cantilever was used for all analyses. Digital images were stored in computer and processed.

RESULTS AND DISCUSSION

Analysis of the mass-loss method

The corrosion rates [CR] of carbon steel immersed in 120 ppm chloride solution in the presence of sodium meta silicate (SMS) and Zn^{2+} and the inhibition efficiencies [IE] of the inhibitor system are given in the Table 1. 75 ppm of Zn^{2+} and 150 ppm of SMS offers 82 % IE. This shows the existence of synergism between Zn^{2+} and SMS [11-16]. A silvery white coating that produces VIBGYOR with light was found on the surface of the steel.

Table 1 - Inhibition efficiencies (IE) of SMS + Zn^{2+} on carbon steel in chloride obtained by weight loss method

SMS (ppm)	Inhibition efficiency (IE)% , Zn^{2+} (ppm)					
	0	10	25	50	75	100
0	0	15	19	26	30	40
50	29	18	37	43	46	35
100	31	24	40	54	66	46
150	39	29	59	63	82	53
200	41	23	37	36	62	58
250	40	22	26	33	51	54
300	39	22	21	31	35	54

Analysis of the results of potentiodynamic polarization curves

The potentiodynamic polarization curves of carbon steel immersed in 120 ppm chloride ion solution in the presence and absence of Zn²⁺ and SMS are given in Fig 5. The corrosion parameters of carbon steel immersed in chloride ion solution in the presence and absence of 75 ppm of Zn²⁺ and 150 ppm of SMS are given in Table 2. When carbon steel is immersed in chloride ion solution, the corrosion potential (E_{corr}) is -505 mV vs SCE and the corrosion

current is 8.090 x 10⁻⁵ A/cm². When 75 ppm of Zn²⁺ and 150 ppm of SMS are added to the chloride ion solution the corrosion potential is found to be -515 mV vs SCE. The corrosion current is 6.924 x 10⁻⁵ A/cm². The cathodic slope is found to change from 464 to 422 mV/decade and the anodic slope does not change. The linear polarization resistance has increased from 8.113 x 10² to 9.191 x 10² Ωcm². This shows that the formulation functions as a mixed inhibitor but predominantly controls the cathodic process [17-20].

Table 2- Corrosion parameters of carbon steel immersed in various test solutions, obtained by polarization curves

Sample	E _{corr} mV vs SCE	b _c mV/decade	b _a mV/decade	R _p Ωcm ² .	I _{corr} A/cm ²
Chloride ion Solution(120 ppm)	-505	464	224	8.113×10 ²	8.090×10 ⁻⁵
SMS(150 ppm) + Zn ²⁺ (75 ppm) in Cl ⁻ solution	-515	422	224	9.191×10 ²	6.924×10 ⁻⁵

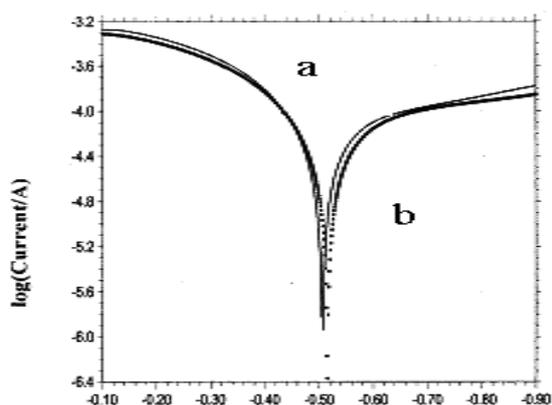


Fig. 1- Polarization curves of carbon steel immersed in various test solutions, a) Cl⁻ (120 ppm) in DD water b) Cl⁻ (120 ppm + Zn²⁺ (75 ppm) + SMS (150 ppm)

Analysis of AC impedance spectra

The AC impedance spectra of carbon steel immersed in 120 ppm of chloride ion solution containing the inhibitor formulation are shown in Fig 2. The AC impedance parameters namely charge transfer resistance and the double layer capacitance are given in Table 3. When carbon steel is immersed in chloride ion solution the R_t value is found to be 352.02 Ω cm². The C_{dl} value is 1.4475 x 10⁻⁸ μF/cm². When 75 ppm of Zn²⁺ and 150 ppm of SMS are added the R_t value has increased from 352.02 Ω cm² to 494.16 Ωcm² and the C_{dl} value decreased from 1.4475 x 10⁻⁸ μF/cm² to 1.0312 x 10⁻⁸ μF/cm². The increased R_t values and decreased double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in

chloride ion solution [21]. This behavior means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film [22,23].

Table 3- AC impedance parameters of carbon steel immersed in various test solutions obtained from AC impedance spectra

Sample	R _t Ohm cm ²	C _{dl} F/cm ²
Chloride ion Solution(120 ppm)	352.02	1.4475x10 ⁻⁸
SMS(150 ppm) + Zn ²⁺ (75 ppm) in Cl ⁻ solution	494.16	1.0312x10 ⁻⁸

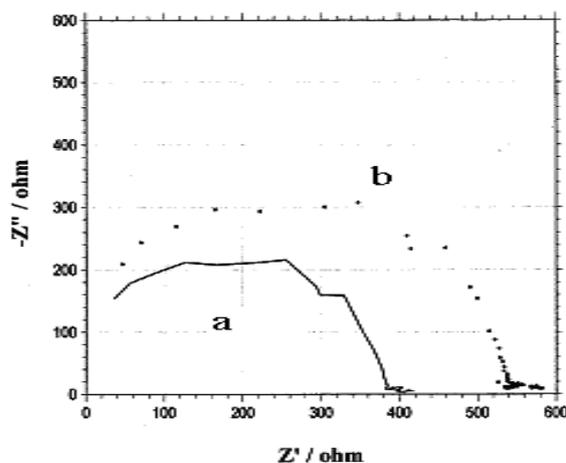


Fig. 2 -AC impedance spectra of carbon steel immersed in various test solutions, a) Cl⁻(120 ppm) in DD water b) Cl⁻ (120 ppm + Zn²⁺ (75 ppm) + SMS (150 ppm)

Scanning probe microscopic analysis

The three dimensional surface morphology of the carbon steel suspended in 120 ppm chloride ion solution as revealed by scanning probe microscope is given in Fig 3.

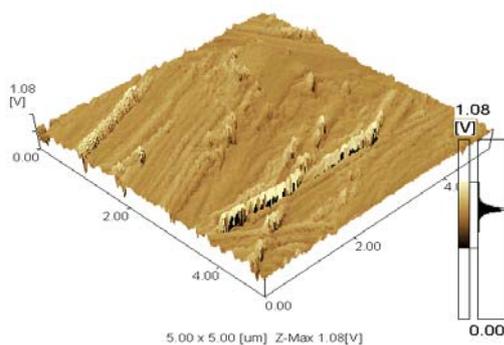
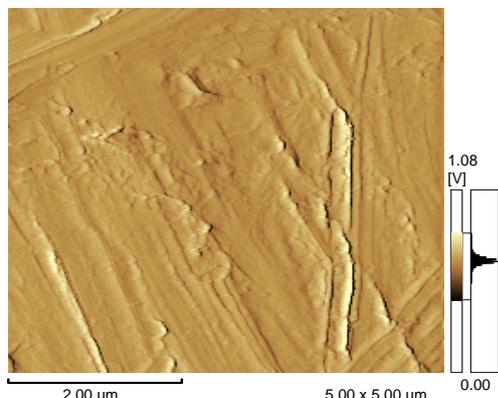


Fig. 3- Three dimensional surface morphology of carbon steel immersed in 120 ppm of chloride solution

The appearance of the surface of the specimen immersed in sodium chloride solution reveals that the surface is uneven and not compact. The two dimensional surface morphology and section analysis of the film formed on the surface of the carbon steel immersed in 120 ppm chloride ion solution is shown in Fig 4. The characteristics of the thin film formed on the surface of the carbon steel immersed in 120 ppm chloride solution in the presence and absence of the inhibitor formulation are given in the Table 4. The thickness of the film is found to be 380.71 nm. The roughness of the section A-B is found to 39.73 nm and that of the section C-D is 75.66 nm. The potential produced is found to be 1.08 volts. The three dimensional surface morphology of the carbon steel immersed in the chloride solution containing 75 ppm of Zn²⁺ and 150 ppm of SMS as revealed by scanning probe microscope is given in Fig 3A. Viewing the

visuals of the surface of the specimen immersed in the inhibitor formulation reveals that the surface is smooth and compact. The two dimensional morphology and section analysis of the film formed on the surface of the carbon steel immersed in chloride ion solution containing inhibitor formulation is shown in Fig 4A. The thickness of the film is found to be 379.54 nm. The roughness of the section A-B is 44.19 nm and that of section C-D is 82.94 nm. The potential produced is found to be 1.64 volts. The increase in the potential when the specimen is immersed in the inhibitor system obviously reveals that the film formed by the inhibitor system shows greater resistance and greater firmness than that is formed during the immersion of the test specimen in chloride ion solution.

Table 4- Results of Atomic Force Microscopy

sample	Z-Max volt	Thickness of the film, nm	roughness, nm A-B C-D
Chloride ion Solution(120 ppm)	1.08	380.71	39.73 75.66
SMS(150 ppm) + Zn ²⁺ (75 ppm) in Cl ⁻ solution	1.64	379.54	44.19 82.94

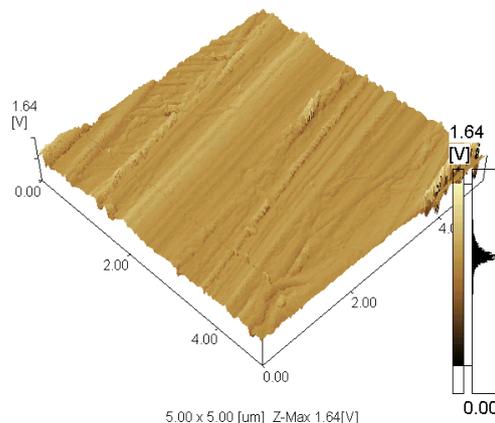
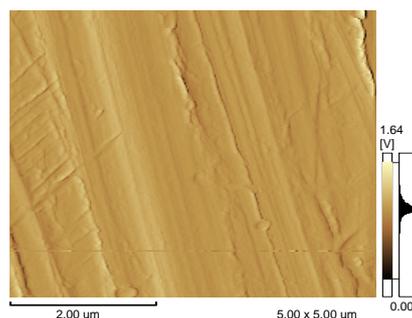


Fig. 3a- Three dimensional surface morphology of carbon steel immersed in 120 ppm of chloride solution containing Zn²⁺ and SMS.

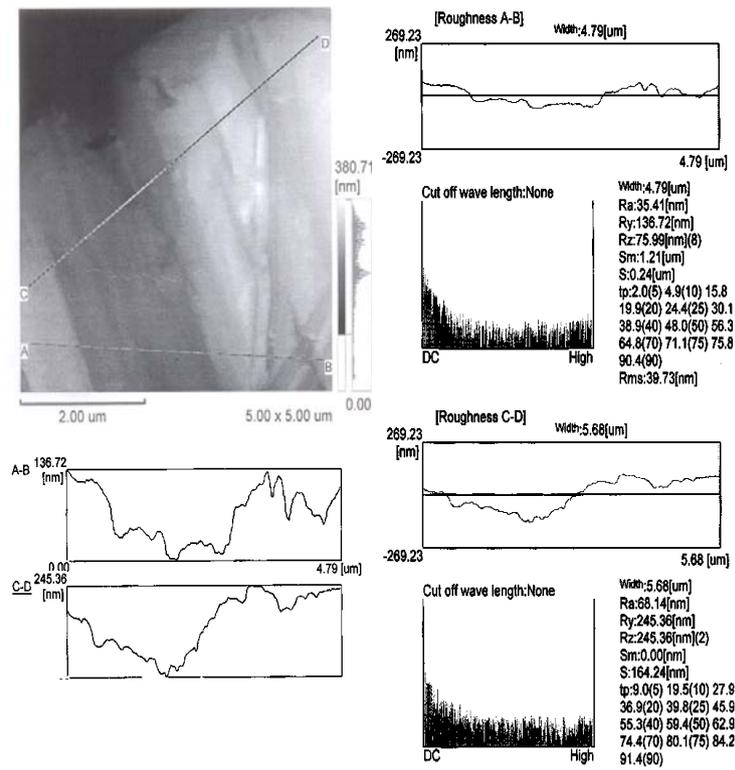


Fig. 4 - Section analysis of micrographs of the carbon steel immersed in 120 ppm chloride solution

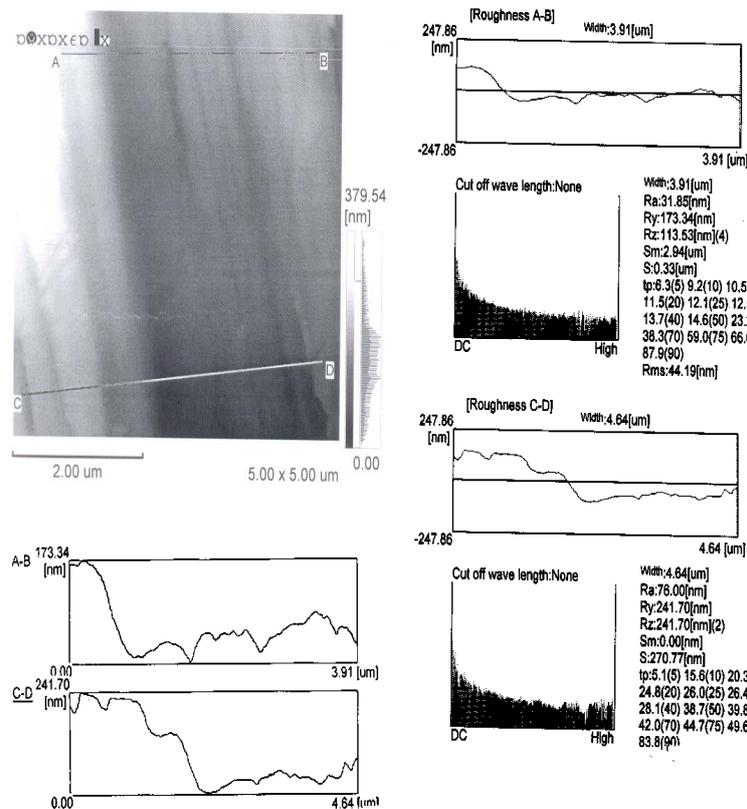
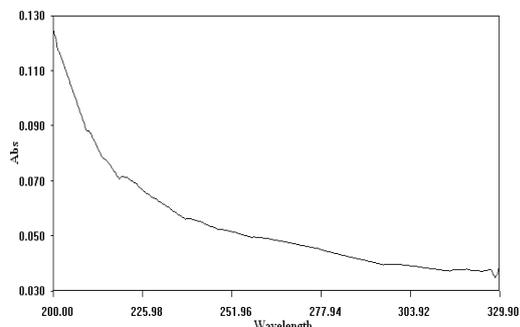


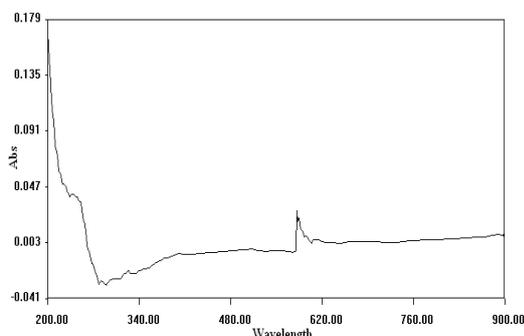
Fig. 4A - Section analysis of micrographs of the carbon steel immersed in 120 ppm chloride solution containing Zn²⁺ and SMS

UV-visible spectral study

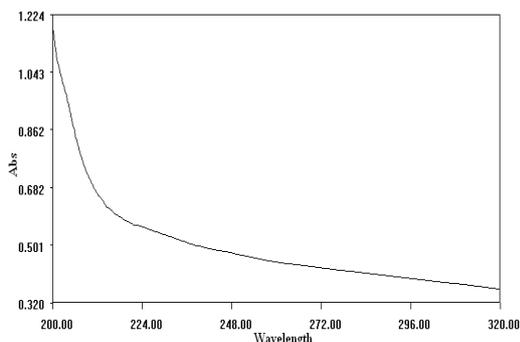
The UV-visible spectra of pure Zn^{2+} , Fe^{2+} , SMS, SMS + Zn^{2+} and SMS + Fe^{2+} are shown in the Fig. 5A-E. Fig. 5C shows that the absorbance of SMS alone in DD water is 1.183 at 200 nm. It decreases sharply up to 215 nm (0.614) and then gradually with increase in λ and reaches 0.363 at 319 nm.



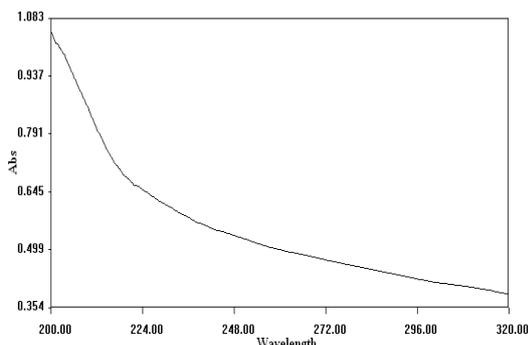
A) Zn^{2+} ions



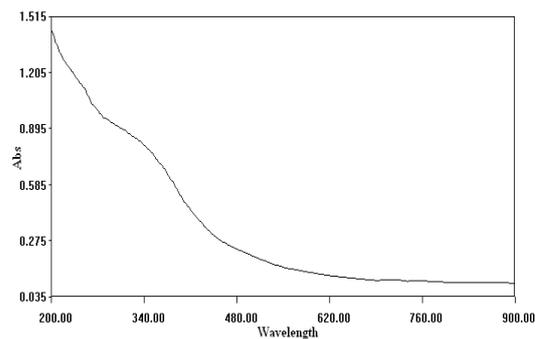
B) Fe^{2+} ions



C) SMS



D) SMS and Zn^{2+} ions



E) SMS and Fe^{2+} ions

Fig. 5 - UV-Visible absorption spectra of the test solutions in DD water

The absorbance of the solution containing 75 ppm of Zn^{2+} ions is 0.126 at 200 nm (Fig. 5A) and decrease with increase in λ value and reaches 0.038 at 319 nm. From the Figure-5_d it is obvious that the addition of Zn^{2+} ions to silicate suppresses the absorbance and it is found to be 1.050 at 200 nm. However, the fall in the absorbance with increase in λ is not as sharp as that of silicate ions alone. At 215 nm, the absorbance value is found to be 0.730 whereas, for silicate ions, the value is found to be 0.514. Then the absorbance decreases gradually and reaches 0.388 at 319 nm. This clearly indicates the influence of Zn^{2+} ion on silicate. The UV-visible spectrum of Fe^{2+} is shown in Fig. 5B. At 200 nm, the solution shows an absorbance of 0.169. The absorbance decreases sharply with increase in λ value and reaches 0.046 at 240 nm. A small peak is observed at 580 nm. When Fe^{2+} ions are added to silicate ions, the resulting solution shows an absorbance of 1.444 at 200 nm, (Fig. 5E) which is different from that of Fe^{2+} and silicate ions. The absorbance decreases gradually with increase in λ and reaches 0.151 at 530 nm after which a marginal decrease is noted with increase in wavelength and it reaches 0.041 at 897 nm. A comparison of curve SMS + Fe^{2+} and SMS + Zn^{2+} curve with the curves of the respective constituent ions clearly reveals the formation of iron-silicate complex and zinc silicate complex.

Analysis of FTIR spectra

FTIR spectrum (KBr) of pure SMS is shown in Fig 6A. The band at 3432.67 cm^{-1} represents the characteristic group frequency of -OH group. The peaks observed at 1241.93 cm^{-1} and at 1054.87 cm^{-1} are due to -Si-O stretching vibrations. The water of crystallization produces bands at 3432.67 cm^{-1} , 1764.55 cm^{-1} and at 1378.85 cm^{-1} [24-27]. The FTIR spectrum (KBr) of the film formed on the surface of the carbon steel after immersion in the solution containing 120 ppm of Cl^{-} ion, 75 ppm of Zn^{2+} and 150 ppm of SMS is shown in Fig 6B. The two - Si -

O stretching frequencies observed in the pure SMS have merged into one and appear at 1116.58 cm^{-1} in the spectrum of the thin film. This clearly shows the involvement of silicate ions in the complex formation. The bands at 3756.65 cm^{-1} , 1388.50 cm^{-1} and 952.66 cm^{-1} may be due to the -O-H stretching, in-plane

bending and out-of-plane bending respectively of the hydroxyl ions present in $\text{Zn}(\text{OH})_2$ [24,27,28]. The band at 769.46 cm^{-1} may be due to Zn-O stretching frequency [29]. The band at 495.62 cm^{-1} may be due to Fe-O stretching frequency [30].

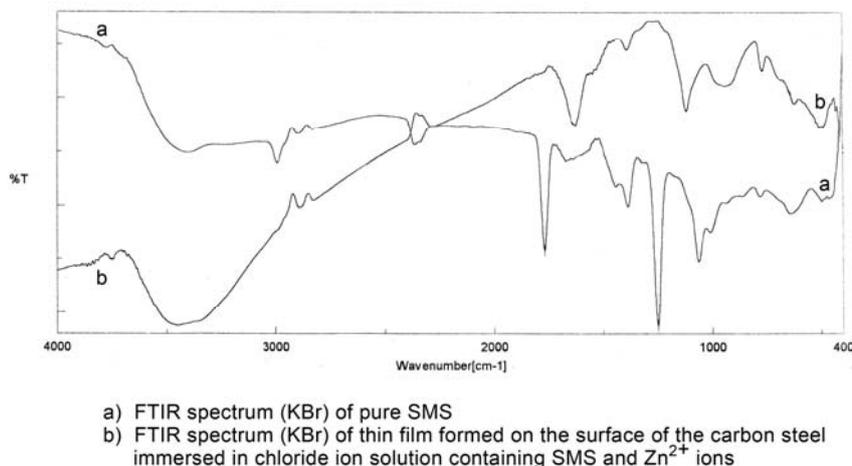


Fig6 - FTIR spectra

MECHANISM OF CORROSION INHIBITION

- The analysis of the results of the mass-loss method shows that the formulations consisting of 150 ppm of SMS and 75 ppm of Zn^{2+} offers IE of 82 %.
- The two-dimensional and three-dimensional surface morphology studies reveal the formation of a thin film on the surface of the carbon steel immersed in inhibitor formulation that has characteristics different from that of the film formed in chloride ion solution.
- The AC impedance spectral studies reveal the formation of a film with higher resistance on the surface of the carbon steel immersed in the synergistic combination than that of the film formed on the specimen immersed in chloride ion solution alone.
- The results of polarization studies show that this formulation functions as a mixed inhibitor, but more predominantly controls the cathodic reactions.
- The UV – visible absorption spectra, indicates the possibility of formation of iron - SMS complex and Zn^{2+} - SMS complex in the presence of the inhibitor formulation.
- The FTIR spectrum confirms the formation of iron - SMS complex and the presence of $\text{Zn}(\text{OH})_2$.

- Based on the above facts the following mechanism is proposed :
 - In chloride ion solution containing 75 ppm of Zn^{2+} and 150 ppm of SMS, a sort of complex is formed between Zn^{2+} and SMS [31, 32].
 - When the metal is immersed in this environment containing the inhibitor formulation, this complex diffuses from the bulk of the solution to the surface of the metal.
 - On the surface of the metal, Zn complex is converted into the iron complex at the local anodic sites, as the latter is more stable than the former.
- $$\text{Zn-Complex} + \text{Iron} \rightarrow \text{Iron - Complex} + \text{Zn}^{2+}$$
- The released Zn^{2+} ions form $\text{Zn}(\text{OH})_2$ in the local cathodic regions.
 - The protective film consists of iron-complex and $\text{Zn}(\text{OH})_2$.
 - The IE of the inhibitor formulation depends on the ability of the inhibitor to form complex with Zn^{2+} and the ability of Fe^{2+} to react with Zn^{2+} complex to form iron complex.

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