



POLARIZATION BEHAVIOUR AND PERFORMANCE OF INORGANIC CORROSION INHIBITORS IN AQUEOUS SOLUTION CONTAINING 60 PPM OF CL

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ABSTRACT

The inhibition efficiency of sodium metavanadate (SMV) – glutaric acid system is controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of Cl⁻ has been evaluated by weight loss method. 250 ppm of SMV has 56% of Inhibition Efficiency. Addition of glutaric acid to SMV improves the inhibition efficiency of the system. Formulation consisting of 250 ppm of SMV and 200 ppm of glutaric acid has 98% IE. Synergistic effects exist between SMV and glutaric acid, if the synergism parameters are greater than 1. Mechanistic aspects of corrosion inhibition have been studied by electrochemical studies like polarization and electrochemical impedance spectroscopy. Fourier Transfer Infrared Spectra reveal that the protective film consists of Fe²⁺ - SMV complex and Fe²⁺ -glutaric acid complex, the protective film has been analyzed by fluorescence spectra, Scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM).

KEYWORDS: Example (Carbon steel, corrosion inhibition, fluorescence, synergism effect, SEM.)

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1. INTRODUCTION

The corrosion inhibition properties of numerous compounds have been examined through the years with the hope of providing a chromate replacement. These compounds include molybdate Stern M.[1], vanadate-based compounds. Bienstock D [2] boron based compounds Whitehouse N.R et al [3-4] and rare earth salts Hinton B.R.W [5]. Recently many of these compounds have been examined for inhibitor efficacy on aerospace aluminium alloys Hinton B.R.W et al [5-7].

Vanadium compounds also have been used to enhance the corrosion protection provided by coatings. Small amounts of vanadate added to sulfuric acid (H₂SO₄) anodizing solutions have

been found to make the anodized coating much more protective after hydrothermal sealing. In other studies, vanadate compounds were used to seal thickened oxide layers on AA6061-T6 (UNS A96061)-alumina composites by direct application a vanadate solution Hamdy. A.S [8].

These vanadate-sealed surfaces promoted adhesion of subsequently applied fluoro polymer coatings and resulted in coating systems with very high levels of corrosion resistance in a range of environments. Vanadium compounds also have been used as primary ingredients in several film formation processes. Solutions comprising vanadate, one of several other transition metal ions, and an acid-resistant organic resin will form protective films on Zn and Zn-Al alloys provided that the coating solution pH is <3.12 Corrosion-resistant sol-gel coatings doped with vanadates have been demonstrated on steel and aluminum substrates Buxton.D et al [9,10] . In other studies, acidic vanadate-phosphate coating chemistries have been developed to form corrosion-resistant coatings on aluminum and aluminium alloy substrates Riley P.J. [11].

2. EXPERIMENTAL

2.1. PREPARATION OF SOLUTION

Sodium metavanadate was prepared by dissolving 1g of SMV in double distilled water and making up to 100 ml. This solution was used as a corrosion inhibitor in the present study.

2.2. 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 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.3. WEIGHT LOSS METHOD

Carbon steel specimens in triplicate were immersed in 100 ml of the solutions containing various concentrations of the inhibitor (sodium metavanadate and glutaric acid solution) for three day. 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 [12]. The inhibition efficiency (I.E.) was then calculated using the equation

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

Where W_1 = Corrosion rate in the absence of the inhibitor

W_2 = Corrosion rate in the presence of the inhibitor

2.4. SURFACE EXAMINATION

The carbon steel specimens were immersed in various test solutions for a period of one day, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed

2.4.1. FTIR SPECTRA

FTIR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was by various surface analysis techniques.carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

2.5. POTENTIODYNAMIC POLARIZATION

A three electrode cell consisting of mild steel as working electrode (WE), a platinum wire counter electrode (CE), and a saturated calomel electrode (SCE) reference electrode were used for measurements. All the potential values reported here was VS SCE. The working electrode was mechanically polished on various grades of emery sheet, rinsed with double distilled water,

decreased with trichloroethylene potentiodynamic polarization curves were recorded using an H & CH electrochemical work station impedance analyzer model CHI 660A

2.6 AC IMPEDANCE MEASUREMENTS

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

2.7 SYNERGISM PARAMETER (S_I)

Synergism parameter is indication of synergistic effect existing between the inhibitors [13]. S_I value is found to be greater than 1 suggesting that the synergistic effect between the inhibitors.

$$I - I_{1+2} \quad [2]$$

$$S_I = \frac{I - I_{1+2}}{I - I_1 - I_2}$$

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

$$I_1 = \text{Surface coverage of inhibitor SMV}$$

$$I_2 = \text{Surface coverage of inhibitor Glutaric acid}$$

$$I_{1+2} = \text{Combined surface coverage of inhibitor SMV and GA}$$

$$\text{Surface coverage } (\theta) = I.E/100$$

F- Test was carried out to investigate whether synergistic effect existing between inhibitor systems is statically significant [14]. If F-value is above 5.32 for 1, 8 degree of freedom, it was proved to be statistically significant. If the value is below 5.32 for 1, 8 degree of freedom, it was statistically insignificant at 0.05 level of significance confirmed.

3. RESULTS AND DISCUSSION

3.1. EVALUATION OF IMPROVEMENT OF (I.E) OF SMV WITH GLUTARIC ACID

The inhibition efficiency (IE) of sodium metavanadate (SMV) in controlling the corrosion of carbon steel immersed in aqueous solution containing 60 ppm of Cl^- for a period of three days is given in Table 1. It is seen that from the data SMV alone shows some IE, where as glutaric acid shows some IE. When SMV is combined with glutaric acid ions, For example 250ppm of SMV has only 56% and 200 ppm of glutaric acid has 89% IE interestingly their combination shows 98% IE. This suggests a synergistic effect existing between the binary inhibitor Formulation SMV and glutaric acid ions

TABLE 1: CORROSION RATES (CR) AND INHIBITION EFFICIENCIES (IE) OF CARBON STEEL IN AQUEOUS SOLUTION CONTAINING 60 PPM OF Cl^- IN THE ABSENCE AND THE PRESENCE OF INHIBITORS AND INHIBITION EFFICIENCY (IE) OBTAINED BY WEIGHT LOSS METHOD.

| SMV ppm | Glutaric Acid ppm | IE (%) | CR (mdd) |
|---------|-------------------|--------|----------|
| 0 | 0 | - | 22.73 |
| 50 | 0 | 8 | 20.96 |
| 100 | 0 | 12 | 20 |
| 150 | 0 | 30 | 15.91 |

| | | | |
|-----|-----|----|--------|
| 200 | 0 | 45 | 12.5 |
| 250 | 0 | 56 | 10 |
| 0 | 50 | 79 | 4.773 |
| 0 | 100 | 82 | 4.0914 |
| 0 | 150 | 84 | 3.6368 |
| 0 | 200 | 86 | 3.1822 |
| 0 | 250 | 89 | 2.5003 |
| 50 | 50 | 82 | 4.914 |
| 100 | 100 | 84 | 3.636 |
| 150 | 150 | 89 | 2.5003 |
| 200 | 200 | 98 | 0.4546 |
| 250 | 250 | 98 | 0.4546 |

3 2. SYNERGISM PARAMETER

The value of synergism parameters are shown in Table 2. The value of S_I is greater than one, suggesting synergistic effect. S_I approaches 1 when no interaction exists between the inhibitor compounds. When $S_I > 1$, this indicating synergistic effect.

TABLE 2: SYNERGISM PARAMETERS OF CARBON STEEL IMMERSSED IN AQUEOUS SOLUTION CONTAINING 60 PPM OF Cl^- IN THE ABSENCE AND THE PRESENCE OF INHIBITOR

| GA ppm | IE% | θ_2 | SMV ppm | IE % | θ_1 | IE % I'_{1+2} | θ'_{1+2} | S_I |
|--------|-----|------------|---------|------|------------|-----------------|-----------------|-------|
| 50 | 79 | 0.79 | 250 | 8 | 0.8 | 82 | 0.8 | 1.07 |
| 100 | 82 | 0.82 | 250 | 12 | 0.12 | 84 | 0.8 | 1 |
| 150 | 84 | 0.84 | 250 | 30 | 0.3 | 89 | 0.9 | 1.01 |
| 200 | 86 | 0.86 | 250 | 45 | 0.45 | 98 | 1 | 3.85 |
| 250 | 89 | 0.89 | 250 | 56 | 0.56 | 98 | 1 | 2.42 |

3 3. ANALYSIS OF VARIANCE (ANOVA)

F-Test is used if the synergistic effect exist between inhibitors is statistically significant. The results are given in Table 3. Influence of various concentration of glutaric acid (50, 100, 150, 200 and 250ppm) on the Inhibition efficiency of SMV (250ppm) is shown in the Table 3. The calculated F-value is 8.24. It is statistically significant, since it is greater than the critical value (5.32) for 1, 8 degree of freedom of 0.05 level of significance. Hence it is concluded that the influence of 250ppm of SMV to the various concentration of glutaric acid shows statistically significant.

TABLE 3: DISTRIBUTION OF F VALUE BETWEEN THE INHIBITION EFFICIENCIES OF SMV -GA SYSTEM

| Source of variance | Sum of square | Degree of freedom | Mean square | F | Level of significance |
|--------------------|---------------|-------------------|-------------|------|-----------------------|
| Between the sample | 1708 | 1 | 1708 | | |
| Within the sample | 1620 | 8 | 202.5 | 8.24 | p>0.05 |

3.4. EFFECT OF SODIUM DODECYLSULPHATE (SDS) ON THE INHIBITION EFFICIENCY OF SMV-GA SYSTEM

The influence of various concentration of SDS on the IE of the SMV-GA system is shown in Table 4. It is observed that the IE of SMV-GA with 150ppm of SDS system was 98%. It is interesting to note that the Sodium metavanadate - GA system has some biocidal efficiency (BE) in Table 5. The BE increases from 84 to 97. When 150ppm of SDS is added 250ppm, 100% BE is noted. The formulation consisting of 250ppm of SMV, 250ppm of GA and 150 ppm of SDS has 100% BE and 98% of corrosion inhibition efficiency. This formulation may find application, if the investigation is carried out at high temperature and under flow condition [14].

TABLE 5. CORROSION RATE CARBON STEEL IN AQUEOUS SOLUTION CONTAINING 60 PPM OF CL⁻ IN PRESENCE AND ABSENCE OF INHIBITORS AND THE CORROSION INHIBITION EFFICIENCIES BY THE WEIGHT LOSS METHOD

| SMV ppm | GA ppm | SDS ppm | CR (mdd) | IE % | Colony forming units ml | Biocidal efficiency |
|---------|--------|---------|----------|------|-------------------------|---------------------|
| 0 | 0 | 0 | - | - | 1x10 ⁵ | - |
| 0 | 0 | 1.5 | 10 | 56 | 2.5x10 ⁴ | 84 |
| 250 | 250 | 50 | 6.36 | 72 | 1.9x10 ³ | 88 |
| 250 | 250 | 100 | 3.18 | 86 | 1.4x10 ³ | 91 |
| 250 | 250 | 150 | 2.27 | 90 | 8x10 ³ | 95 |
| 250 | 250 | 200 | 2.5 | 89 | 4x10 ³ | 96 |
| 250 | 250 | 250 | 4.54 | 80 | nil | 100 |

3.5. FTIR SPECTRA

The FTIR spectrum of pure SMV is shown in Fig 1a. VO₃⁻ stretching frequency appears at 1385 cm⁻¹. The FTIR spectrum of pure glutaric acid is shown in Fig 1b. The -C=O stretching frequency appeared at 1674 cm⁻¹. -OH stretching frequency appeared at 3350 cm⁻¹. The aliphatic -CH stretching frequency appeared at 2811 cm⁻¹. The FTIR spectrum (KBr pellet) of the film formed on the carbon steel surface after immersion in the solution containing 250ppm of SMV, 200ppm of glutaric acid as shown in Fig 1c. The VO₃⁻ stretching frequency of SMV shifted from 1385 cm⁻¹ to 1389 cm⁻¹ resulting in the formation of Fe²⁺ - SMV complex. The -C=O stretching frequency shifted from 1674cm⁻¹ to 1639 cm⁻¹ and -OH stretching frequency shifted from

3350 cm^{-1} to 3425 cm^{-1} . This suggests that oxygen atom of glutaric acid co-coordinated with Fe^{2+} on the anodic sides of the metal surface, resulting in the formation of Fe^{2+} - GA complex [15-16].

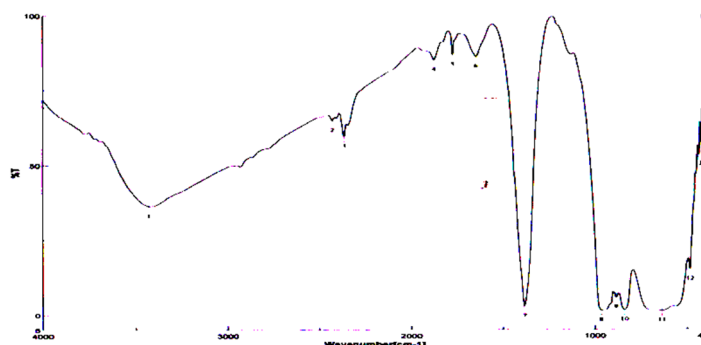


Figure1. (a) FTIR Spectrum of Pure SMV

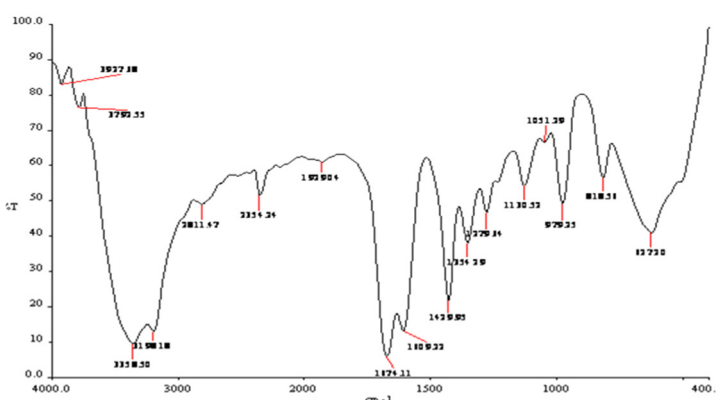


Figure1 (b) FTIR Spectrum of Pure glutaric acid

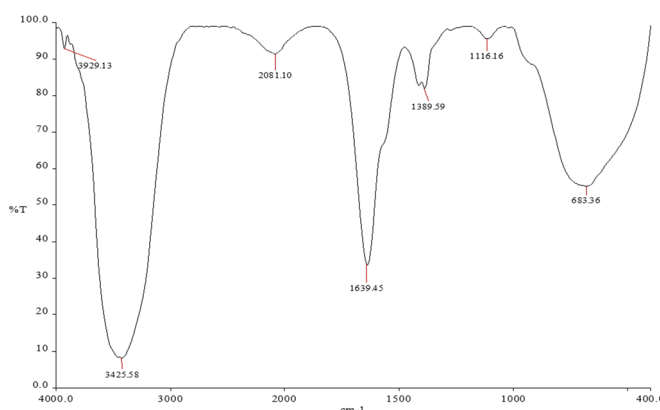


Figure1 (c) FTIR Spectrum of Film formed on surface of metal after immersion in aqueous solution containing 60 ppm of Cl^-

3.6. ANALYSIS OF POLARIZATION

The potentiodynamic polarization curves of metal immersed in aqueous solution containing 60 ppm of Cl^- are shown in Fig 2. The corrosion potential (E_{corr}), Tafel slope (b_c = cathodic; b_a = anodic, linear polarization resistance LPR and corrosion current I_{corr} are given in Table 6. When carbon steel is immersed in aqueous solution containing 60 ppm of Cl^- the corrosion potential E_{corr} -542mV vs SCE. When 250ppm of SMV and 200ppm of glutaric acid are added to the above system, the corrosion potential E_{corr} -578 mV vs SCE shifted to the cathodic side [17-18].

The LPR values is $2.0157 \times 10^4 \Omega\text{cm}^2$ and the corrosion current is $2.025 \times 10^{-6} \text{ A/cm}^2$, when carbon steel is immersed in aqueous solution containing 60 ppm of Cl^- (Fig 2). The corrosion potential is shifted to cathodic side -578 mV vs SCE . This suggests that a protective film is formed on the metal. The cathodic Tafel slope (b_c) is 193 mV/decade and anodic Tafel slope (b_a) is 198 mV/decade . The cathodic and anodic Tafel slopes were shows difference 52 mV/decade this shows change of current with change in potential is less during anodic polarization than during cathodic polarization.

The LPR value increase from 2.0157×10^4 to $3.373 \times 10^4 \Omega\text{cm}^2$. The corrosion current decrease from 2.025×10^{-6} to 1.278×10^{-6} . An increase in LPR value and decrease in corrosion current are indicate ions of formation of protective film on the metal surface¹⁹.

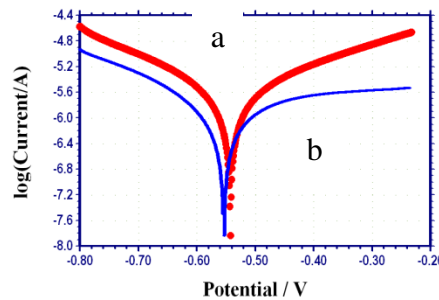


Figure 2: polarization curves of carbon steel immersed in various test solutions

(a)aqueous solution containing 60ppm of Cl^- (b)aqueous solution containing 60ppm of Cl^- +250 ppm SMV+ 200 ppm GA

TABLE 6: CORROSION PARAMETER OF CARBON STEEL IMMERSSED IN AQUEOUS SOLUTION CONTAINING 60 PPM OF Cl^- OBTAINED BY POLARIZATION STUDY ARE GIVEN INHIBITOR: SODIUM METAVANADATE AND GLUTARIC ACID

| System | E_{corr} | b_c | b_a | LPR | I_{corr} |
|--|-------------------|--------------|---------------|--------------------|-----------------------|
| | (mV vs SCE) | (mv /decade) | (mv / decade) | ohm cm^2 | (A/ cm^2) |
| Aqueous solution containing 60 ppm of Cl^- | -542 | 193 | 198 | 2.02×10^4 | 2.03×10^{-6} |
| Aqueous solution containing 60 ppm of Cl^- + 250 ppm SMV+200 ppm GA | -578 | 160 | 250 | 3.37×10^4 | 1.28×10^{-6} |

3.7. AC IMPEDANCE SPECTRA

AC impedance spectra of metals immersed in aqueous solution containing 60 ppm of Cl^- are shown in Fig 2 .Nyquist plot and bode plots are shown in (Fig 3 & 4) .the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values (derived from Nyquist plots) and impedance , $\log(Z/\Omega)$ value (derived from Bode plots) are given in Table 7

When mild steel is immersed in aqueous solution containing 60 ppm of Cl^- the charge transfer resistance is $2363 \Omega \text{ cm}^2$ and the double layer capacitance is $2.1919 \times 10^{-9} \text{ F/cm}^2$ (Fig 4). The impedance $\log(Z/ \Omega)$, value 3.257

When carbon steel immersed in aqueous solution containing 60ppm of Cl^- the charge transfer resistances increases from 2363 to $3679 \Omega \text{ cm}^2$ and the double layer capacitance value decreases from 2.1919×10^{-9} to $1.3862 \times 10^{-9} \text{ F/cm}^2$. The impedance value increases from 3.257 to 3.69. This indicates the film formed on the metal surface [20-21].

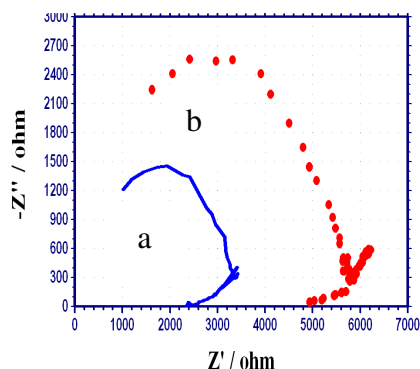


Figure 3: AC Impedance spectra of carbon steel immersed in various test solution

(a) Cl⁻ 60ppm (Nyquist) (b) Cl⁻ 60ppm + 250ppm SMV+200ppm GA (Nyquist)

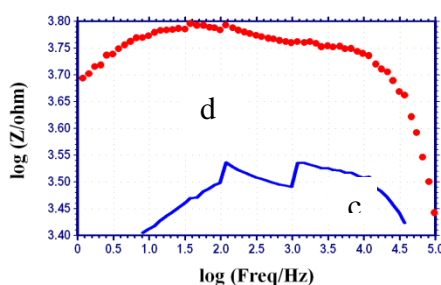


Figure 4: AC Impedance spectra of carbon steel immersed in various test solution

(a) Cl⁻ 60ppm (impedance-bode) (b) Cl⁻ 60ppm + 250ppm SMV+200ppm GA (impedance-bode)

TABLE 7 IMPENDENCE PARAMETER OF CARBON STEEL IMMERSIED IN AQUEOUS SOLUTION CONTAINING 60 PPM OF CL⁻ IN THE PRESENCE AND ABSENCE OF INHIBITOR SYSTEM OBTAINED FROM AC IMPEDANCE CURVES

| System | Nyquist plot | | Bode plot |
|--|----------------------|-------------------------|--------------------|
| | Rct Ωcm ² | Cdl F/cm ² | Impedance log(Z/Ω) |
| Aqueous solution containing 60 ppm of Cl ⁻ | 2363 | 2.19x10 ⁻⁹ | 3.257 |
| Aqueous solution containing 60 ppm of Cl ⁻ + 250 ppm SMV+200 ppm GA | 3679 | 1.39 x 10 ⁻⁹ | 3.69 |

4. CONCLUSIONS

The present study leads to the following conclusion

- The formulation consisting of 200 ppm of GA and 250 ppm of SMV offers 98% inhibition efficiency to carbon steel immersed in aqueous solution containing 60 ppm Cl⁻.
- Polarization study reveals that this formulation controls anodic reaction predominantly.
- AC impedance spectra reveal that a protective film formed on the metal surface.
- FTIR spectra reveal that the protective film consists of Fe²⁺-SMV complex and Fe²⁺-GA complex.

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