Inhibition effect of sodium benzoate, zinc benzoate and zinc bromide on low carbon steel corrosion in dilute H$_2$SO$_4$ and HCL solution

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Abstract : The corrosion inhibition performance of inorganic chemical compounds of sodium benzoate, zinc benzoate and zinc bromide on low carbon steel was studied in 0.5 M H$_2$SO$_4$ and HCl solution at volumetric concentrations of 10%, 30%, 50% and 70%. Results obtained from LCS inhibition in H$_2$SO$_4$ showed sodium benzoate performed poorly with highest and lowest inhibition efficiency value of 50.5% and 36.24% at concentrations of 70% and 10%. Zinc bromide performed most effectively in H$_2$SO$_4$ with highest and lowest results of 90.96% and 76.96% at concentrations of 50% and 10%. Zinc benzoate displayed good results with peak value of 88.32% at 70% concentration and lowest value of 46.79% at 10% concentration. The corresponding performance of the compounds in HCl solution showed zinc benzoate performed more effectively with highest and lowest value of 70.17% and 33.26% at concentrations of 50% and 10%. Sodium benzoate and zinc bromide displayed average performance in HCl solution with optimal values of 67.38% and 55.40% at 30% concentration. Statistical analysis through analysis of variance showed exposure time is the only relevant factor (independent variable) in both acids responsible for the inhibition performance of the compounds with significance factor above 100%. The second independent variable (inhibitor concentration) was determined to be statistically irrelevant with significance factor below zero.

1. INTRODUCTION

Carbon steel has extensive industrial and domestic applications, constituting about 85% of the global steel production in tonnage [1]. The steel is relatively cheap, recyclable, readily available and possesses adjustable mechanical and physical properties. The steel is the major material of construction for equipment’s, mechanical parts, component and structures in marine, petrochemical, refining, chemical processing, mining, construction, metal-processing and power plants applications. [2]. Most industrial operating conditions contains corrosive anions harmful to carbon steels. The anions are responsible for the accelerated deterioration and short lifespan of carbons steels due to their inability to passivate unlike stainless steels. HCl and H$_2$SO$_4$ as significantly applied as intermediate chemicals in the production of dyestuffs, pharmaceuticals, oil-well acidizing, pickling of steels, synthetic resins etc. [3-6]. HCl is responsible for the corrosion of metallic parts of crude distillation unit [7–10]. H$_2$SO$_4$ is present in acid rain and is responsible for the destruction of ancient artifacts and architectural monuments. Damages resulting from corrosion cause plant shut downs and its attendant economic effect. Process interruptions in chemical manufacturing and the collateral damage from unscheduled interruptions is also a major problem due to corrosion. Corrosion is responsible for material degradation, resulting from chemical and electrochemical interaction between the metallic surfaces the corrosive anions within their environment [11]. When carbon steels interact with its environments, oxides do form on their surfaces which are porous and allows for continuity of the corrosion reaction mechanism; hence limiting their operational lifespan [12–14]. Chemical compounds
known as corrosion inhibitors have been proven to be effective in controlling corrosion of metallic alloys [15-17]. Sodium benzoate occurs naturally, along with benzoic acid and its esters, in many foods. It is widely used as a food preservative [18]. Zinc benzoate is an organic metal salt with slight solubility in H₂O. The compound is used as a preservative in food and feed additives and as a source of zinc. Zinc bromide is used as an electrolyte in the zinc bromide battery. It is also used to displace drilling mud when transitioning from the drilling phase to the completion phase in oil and natural gas wells. This manuscript focuses on the corrosion inhibition performance of sodium benzoate, zinc benzoate and zinc bromide on low carbon steel in dilute H₂SO₄ and HCl solution.

2. MATERIAL AND METHODS

Low carbon steel (LCS) rod with nominal weight composition (wt. %) of 0.8% Mn, 0.04% P, 0.05% S, 0.16% C and 98.95% Fe was cut into 6 separate sets of 5 specimens each. The specimens were washed and cleansed with distilled H₂O and propanone. Inorganic compounds of sodium benzoate (SBZ), zinc benzoate (ZBZ) and zinc bromide (ZBR) were used as the corrosion inhibiting compound. The compounds were each prepared in volumetric concentrations of 0%, 10%, 30%, 50% and 70% per 200 mL of 0.5 M H₂SO₄ and HCl solution. The acids were prepared from analar grade reagents (98% H₂SO₄ and 37% HCl) purchased from Sigma Aldrich, USA. LCS specimens were individually immersed in 200 mL of 0.5 M H₂SO₄ and HCl solution, and weighed at 48 h interval for a total of 672 h of exposure. Corrosion rate, \( C_R \) (mm/y) was from the equation below;

\[
C_R = \frac{87.6 \omega}{DAt}
\]  

\( \omega \) indicates weight loss (g), \( D \) indicates density (g/cm³), \( A \) indicates total exposed surface area of MS specimen (cm²), 87.6 is a corrosion rate constant and \( t \) indicates is the time (h). Inhibition efficiency (\( \eta \)) of the inorganic compounds was determined from the equation below;

\[
\eta = \left( \frac{\omega_1 - \omega_2}{\omega_1} \right) \times 100
\]  

\( \omega_1 \) and \( \omega_2 \) indicates weight loss of LS at specific SBZ, ZBZ and ZBR concentrations.

3. RESULTS AND DISCUSSION

3.1 Weight loss analysis

The plots of LCS corrosion rate versus exposure time in 0.5 M H₂SO₄ and HCl solution at specific concentrations (10%, 30%, 50% and 70%) of SBZ, ZBZ and ZBR inhibitor compounds are shown from Figures. 1(a) to Figure. 3(b). Comparison of the performance of SBZ in H₂SO₄ and HCl solution shows SBZ performance is at best average in both solutions with lowest corrosion rate value of 7.284 mm/y in H₂SO₄ at 70% SBZ concentration while in HCl, the corresponding value is 1.381 mm/y at 30% SBZ concentration. The inhibition performance of SBZ in H₂SO₄ is proportional to it concentration whereas its performance in HCl solution is visibly independent of concentration. Observation of the plots of SBZ inhibition efficiency versus exposure time in both solutions [Figures. 4(a) and (b)] corroborate the corrosion rates results earlier discussed. The plot of SBZ inhibition efficiency versus exposure time in H₂SO₄ solution shows that inhibition efficiency increases with increase in concentration. It is also observed that dependence of inhibition efficiency to changes in exposure time decreases with increase in SBZ concentration signifying non-dependence on exposure time with respect to concentration. In H₂SO₄ solution, the highest and lowest inhibition efficiency results are 50.5 at 70% SBZ and 39.03% at 10% SBZ. The performance of SBZ in HCl solution from observation of inhibition efficiency results in Figure. 4(b) significantly contrasts its performance in H₂SO₄ solution. SBZ performed poorly at higher SBZ concentration (70% and 50% SBZ concentration) with inhibition efficiency values of 6.72% and 16.4% whereas at 10% and 30% SBZ
concentration the inhibition efficiency values obtained are 67.38% and 56.35%. Generally, the performance of SBZ is quite poor while in HCl its performance is average.

The corrosion rate results of ZBZ compound on LCS in H$_2$SO$_4$ and HCl solution are shown from Figure 2(a) to 2(b). Observation of Figure 2(a) shows the corrosion rate decreases significantly with respect to ZBZ concentration. The lowest corrosion rate value of 1.719 mm/y at 70% ZBZ concentration (672 h) compared to the highest corrosion rate of 7.828 mm/y obtained at 10% ZBZ concentration. The corresponding plot in HCl solution was quite different were the lowest corrosion rate of 1.251 mm/y was obtained at 50% ZBZ concentration while the highest value of 2.799 mm/y was obtained at 10% ZBZ concentration. It must be noted that the corrosion rate of the control LCS (14.7129 mm/y and 4.1935 mm/y) at 0% ZBZ in both acids (H$_2$SO$_4$ and HCl) significantly contrast the values obtained at specific ZBZ inhibitor concentration signifying effective ZBZ inhibition performance compared to SBZ. The corresponding plots of inhibition efficiency versus exposure time [Figure. 5(a) and (b)] shows the highest and lowest inhibition ZBZ efficiency values in H$_2$SO$_4$ are 46.79% and 88.32% at 10% and 70% ZBZ concentration. Whereas in HCl solution the highest and lowest ZBZ inhibition efficiency values are 33.26% at 10% ZBZ concentration and 70.17 at 50% ZBZ concentration. While the inhibition efficiency values of ZBZ in H$_2$SO$_4$ were generally constant after 10% ZBZ concentration, the inhibition efficiency values ZBZ in HCl decreased with exposure time from effective performance values above 85% to final values earlier stated at 672 h of exposure. Plots of LCS corrosion rate versus exposure time in the presence of specific concentrations of ZBR in H$_2$SO$_4$ and HCl solution are shown Figure. 3(a) and 3(b) while the corresponding plots of ZBR inhibition efficiency versus exposure time in both acids are shown in Figure. 6(a) and (b). The corrosion rates of LCS at specific ZBR concentrations in HCl solution decreased significantly from the onset of the exposure hours culminating at highest and lowest corrosion rate values of 2.170 mm/y and 1.870 mm/y at 10% and 30% ZBR concentration. These values slightly differ from the corrosion rate value (4.194 mm/y) of LCS at 0% ZBR signifying marginally effective inhibition performance. The corresponding plot of ZBR inhibition efficiency versus exposure time [Figure. 6(b)] in HCl solution shows the inhibition performance of ZBR increases with increase in ZBR concentration and exposure time. However, observation of the final inhibition efficiency values shows ZBR performed marginally effectively as earlier stated with highest inhibition efficiency value of 55.4% at 30% ZBR concentration and 48.26% at 10% ZBR concentration. The performance of ZBR on LCS in H$_2$SO$_4$ significantly differs from its performance in HCl solution [Figure. 6(a)]. The lowest inhibition efficiency value of 76.96% was obtained at 10% ZBR concentration while the highest value of 90.96% was obtained at 50% ZBR concentration. The inhibition efficiency plots show ZBR performance increased with exposure time before attaining relative stability at 88 h. The corresponding plot of corrosion rate [Figure. 3(b)] confirms the inhibition efficiency results with highest and lowest corrosion rate values of 3.391 mm/y and 1.330 mm/y at 10% and 50% ZBR concentration. These values significantly differ from LCS corrosion rate of 14.713 mm/y at 0% ZBR concentration signifying effective inhibition performance in H$_2$SO$_4$ solution.
Figure 1. Plot of LCS corrosion rate versus exposure time at specific SBZ concentrations in (a) H$_2$SO$_4$ solution and (b) HCl solution

Figure 2. Plot of LCS corrosion rate versus exposure time at specific ZBZ concentrations in (a) H$_2$SO$_4$ solution and (b) HCl solution

Figure 3. Plot of LCS corrosion rate versus exposure time at specific ZBR concentrations in (a) H$_2$SO$_4$ solution and (b) HCl solution
Figure 4. Plot of SBZ inhibition efficiency versus exposure time at specific in (a) $H_2SO_4$ solution and (b) HCl solution

Figure 5. Plot of ZBZ inhibition efficiency versus exposure time at specific in (a) $H_2SO_4$ solution and (b) HCl solution

Figure 6. Plot of ZBR inhibition efficiency versus exposure time at specific in (a) $H_2SO_4$ solution and (b) HCl solution
3.2 Statistical Analysis (ANOVA)

Statistical analysis through ANOVA at 95% confidence level (significance level of $\alpha = 0.05$) was used to evaluate the relevance of SBZ, ZBZ and ZBR concentration, and exposure time on the inhibition efficiency results of SBZ, ZBZ and ZBR inhibitor compounds according to equations 3 to 5 below;

The Sum of squares among SBZ, ZBZ and ZBR concentration
\[
SS_c = \sum \frac{\tau_c^2}{nr} - \frac{\tau^2}{N}
\]  

(3)

Sum of Squares among exposure time
\[
SS_r = \sum \frac{\tau_r^2}{nc} - \frac{\tau^2}{N}
\]  

(4)

Total Sum of Squares
\[
SS_{Total} = \sum x^2 - \frac{\tau^2}{N}
\]  

(5)

Results from ANOVA analysis showing the influence of SBZ, ZBZ and ZBR concentrations, and exposure time on the inhibition performance of the inhibitor compounds on LCS are shown from Tables 1 to 6. Tables 1 and 2 show the statistical influence of SBZ inhibition performance on LCS in $\text{H}_2\text{SO}_4$ and $\text{HCl}$ solutions. Observation of the Tables show exposure time is the only statistically relevant variable for SBZ performance in both acids while influence of SBZ concentration is completely negligible. In $\text{H}_2\text{SO}_4$ and $\text{HCl}$, the mean square ratio for SBZ concentration -8.87 and -8.77. These values are significantly lower than the theoretical significance factor of 3.16; hence their irrelevance. The percentage significance factor for exposure time in both acids is 175.63% and 788.63%. Observation of Tables 3 and 4 shows also shows exposure time is the only statistically relevant variable compared to inhibitor concentration. Data shows the mean square ratio for the influence of exposure time on ZBZ inhibition in $\text{H}_2\text{SO}_4$ and $\text{HCl}$ solution are 3.55 and 3.84 which are greater than the theoretical significance factor of 3.16 and 2.77. The values earlier mentioned (3.55 and 3.84) gave percentage significant factor of 173.39% and 167.70%. Tables 5 and 6 show the statistical relevance of exposure time and ZBR inhibitor concentration on ZBR inhibition performance. Data shows similar trend to the results already obtained for SBZ and ZBZ. Exposure time was the only statistically relevant variable while data obtained for ZBR inhibitor concentration shows it is statistically irrelevant. The results obtained from the tables (Tables 1-6) shows the inhibition performance of SBZ, ZBZ and ZBR compound is significantly influenced by exposure time i.e. the performance of the inhibitors generally improves with time.

### Table 1
Analysis of variance for SBZ inhibition performance on LCS in 0.5M $\text{H}_2\text{SO}_4$ solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Mean Square Ratio (F) | Significance F | F (%) |
|---------------------|----------------|-------------------|-------------|----------------------|---------------|-------|
| SBZ Conc.           | 32734.56       | 2                 | 16367.28    | -8.87                | 3.16          | -173.41|
| Exposure Time       | -33153.73      | 5                 | -6630.75    | 3.59                 | 2.77          | 788.63 |
| Residual            | -18458.10      | 10                | -1845.81    |                      |               |       |
| Total               | -18877.27      | 17                |             |                      |               |       |

### Table 2
Analysis of variance for SBZ inhibition performance on LCS in 0.5M $\text{HCl}$ solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Mean Square Ratio (F) | Significance F | F (%) |
|---------------------|----------------|-------------------|-------------|----------------------|---------------|-------|
| SBZ Conc.           | 66982.36       | 2                 | 33491.18    | -8.77                | 3.16          | -1602.90|
| Exposure Time       | -32955.47      | 5                 | -6591.09    | 1.73                 | 2.77          | 788.63 |
| Residual            | -38205.71      | 10                | -3820.57    |                      |               |       |
| Total               | -4178.83       | 17                |             |                      |               |       |
Table 3 Analysis of variance for ZBZ inhibition performance on LCS in 0.5M $H_2SO_4$ solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Mean Square Ratio (F) | Significance F | F (%) |
|---------------------|----------------|------------------|-------------|----------------------|----------------|-------|
| ZBZ Conc.           | 123152.86      | 2                | 61576.43    | -8.75                | 3.16           | 171.20|
| Exposure Time       | -124728.32     | 5                | -24945.66   | 3.55                 | 2.77           | 173.39|
| Residual            | -70360.63      | 10               | -7036.06    |                      |                |       |
| Total               | -71936.09      | 17               |             |                      |                |       |

Table 4 Analysis of variance for ZBZ inhibition performance on LCS in 0.5M $HCl$ solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Mean Square Ratio (F) | Significance F | F (%) |
|---------------------|----------------|------------------|-------------|----------------------|----------------|-------|
| ZBZ Conc.           | 87349.34       | 2                | 43674.67    | -8.88                | 3.16           | 155.01|
| Exposure Time       | -94501.56      | 5                | -18900.31   | 3.84                 | 2.77           | 167.70|
| Residual            | -49200.21      | 10               | -4920.02    |                      |                |       |
| Total               | -56352.43      | 17               |             |                      |                |       |

Table 5 Analysis of variance for ZBR inhibition performance on LCS in 0.5M $H_2SO_4$ solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Mean Square Ratio (F) | Significance F | F (%) |
|---------------------|----------------|------------------|-------------|----------------------|----------------|-------|
| ZBR Conc.           | 160186.38      | 2                | 80093.19    | -8.75                | 3.16           | 143.42|
| Exposure Time       | -180832.18     | 5                | -36166.44   | 3.95                 | 2.77           | 161.59|
| Residual            | -91530.75      | 10               | -9153.07    |                      |                |       |
| Total               | -112176.54     | 17               |             |                      |                |       |

Table 6 Analysis of variance for ZBR inhibition performance on LCS in 0.5M $HCl$ solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Mean Square Ratio (F) | Significance F | F (%) |
|---------------------|----------------|------------------|-------------|----------------------|----------------|-------|
| ZBR Conc.           | 53895.48       | 2                | 26947.74    | -8.76                | 3.16           | 143.42|
| Exposure Time       | -60722.95      | 5                | -12144.59   | 3.95                 | 2.77           | 161.59|
| Residual            | -30750.79      | 10               | -3075.08    |                      |                |       |
| Total               | -37578.26      | 17               |             |                      |                |       |

4. CONCLUSION

Sodium benzoate, zinc benzoate and zinc bromide were studied for their corrosion inhibition performance on low carbon steel in dilute $H_2SO_4$ and $HCl$ solution. Results obtained showed zinc benzoate and zinc bromide performed effectively in $H_2SO_4$ solution with peak inhibition values of 88.32% and 90.96%. The performance of sodium benzoate was average at peak value of 50.5% in $H_2SO_4$ solution. In $HCl$ solution, the inhibition performance of sodium benzoate and zinc benzoate were generally above average with peak values of 67.38% and 70.17%. Zinc bromide performed poorly in $HCl$ solution with peak value of 55.40%. Data from analysis of variance shows exposure time is the only statistically relevant independent variable compare to inhibitor concentration whose relevance was determined to be statistically negligible.

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