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Gravimetric study and statistical data on the symbiotic effect of organic intermixtures on corrosion inhibition of P4 mold steel

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Abstract. The corrosion protection properties of the intermixed of l-leucine and vanillin (LLVL) on P4 mold steel within 1.5 M H₂SO₄ and HCl media was studied by weight loss analysis. Calculated data revealed the inhibition effect of the intermixed compound performed poorly at low H₂SO₄ concentrations due to inability of the combined inhibitor molecules to aggregate and effectively hinder the dispersion of the destructive anions to the steel surface. The inhibition efficiency decreased significantly with time to values below effective inhibitor performance. However, from mid to optimum concentration, inhibition efficiency of the compound was generally stable with time with values generally above 85%. In HCl media, the inhibition efficiency of the intermixture was generally above 80% at all concentrations with respect to the inspection time. The inhibitor compound exhibited greater stability in HCl compared to H₂SO₄ solution. Calculated values of standard deviation in H₂SO₄ were broadly greater than the outputs received in HCl due to the degree of variation between LLVL inhibition efficiency values. The margin of error at 95% confidence shows 65% of LLVL inhibition efficiency values obtained in H₂SO₄ solution have values above 70% inhibition efficiency with margin of error at $\pm 12.07\%$ while in HCl solution, 100% of the LLVL inhibition efficiency data obtained is above 70% with margin of error of $\pm 1\%$. Analysis of variance showed the statistical relevance of inhibition efficiency in H₂SO₄ and HCl solution is significantly higher the corresponding relevance for inspection time with values of 70.45% and 71.18%.

Keywords: corrosion; steel; inhibitor; adsorption; organic

1. Introduction

Corrosion of metallic alloys occurs due to molecular interaction with their environment. This phenomenon is a major cause of concern for industries and national economies [1-3]. Petrochemical, energy generation, aerospace, consumer and defense industries etc. are prone to the debilitating effect of corrosion due to the enormous cost of maintenance required resulting from corrosion damage. [4-10]. Corrosion problem is often encountered in application where carbon and low grade steels are extensively utilized due to their low cost, ease of fabrication and replacement, availability, recyclability and absence of passivating elements within their microstructure. [11]. In addition to general surface deterioration mostly experienced by carbon steels, low grade alloys undergo extensive localized degradation due to



the disintegration of the pseudo protective layer on the alloy exterior, causing the rapid evolution of destructive microscopic holes [12, 13]. The economic cost of corrosion is enormous as earlier stated leading to accelerated decline in the service life of metallic components and in some cases avoidable accidents and industry down time. Most corrosion damage from low grade steels are insidious and undetectable until the damage is intensive. Fluid derivatives commonly identified as corrosion inhibitors have been successfully utilized to mitigate the adverse effect of corrosion. However, they are usually, inorganic in nature, toxic and unsustainable [15-24]. Organic fluids have been proven to be successful but their application in some industries such as fertilizer production, food processing and other consumer industries is limited due to their toxicity which is quite lower than inorganic fluids but yet harmful to humans and the environment. Literature on the application of corrosion inhibitors onto low grade alloy steels is scarce. Some biodegradable compounds do offer effective inhibitor protection but their performance is limited by short shelf life, poor adsorption and limited protection with respect to time. The combined effect of biodegradable sustainable inhibitors coupled with the pseudo passivating effect of limited passivating elements on low grade alloy steels will undoubtedly provide long term effective protection against corrosion. The data output laid out in this report discusses the evaluation of the corrosion inhibition output of intermixed l-leucine and vanillin compounds onto P4 mold steel (low grade alloy steel) in dilute H₂SO₄ and HCl solution for documentation purpose, thus aiding appropriate material and inhibitor selection.

2 Experimental methods

2.1 Coupon measurement

L-leucine and vanillin abbreviated as LLVL were intermixed in equal ratios and concocted in cubic concentrates of 0%, 0.25%, 0.5%, 0.75%, 1%, 1.25% and 1.5% LLVL per 200ml of 1.5M H₂SO₄ and HCl solution. The acid solutions were concocted from standardized reagents with distilled water. P4 mold steel (P4ST) rods were manually cut into 7 test pieces for coupon analysis. The test pieces have an average dimension is 1.6 cm diameter and 0.7 cm thickness. The exterior ends of the steel were smoothed with SiC papers of 80, 120 and 220 grits. Weighed pieces of the P4ST were individually immersed in H₂SO₄ and HCl solution at specific LLVL concentrations for 240 h at 30° ambient temperature. P weighed at 24 h P4ST was weighed at 24 h interval with Ohaus measuring device. Tabulated results of P4ST corrosion at specific LLVL concentrations in the acid media are shown from Table 1 to 2. Corrosion rate was computed from below;

$$R = \left[\frac{87.6W}{DAT} \right] \quad (1)$$

W represents weight loss (g), D represents density (g/cm²), A represents area (cm²), and T represents time of inspection (h). W is computed from the numerical contrast between the first weight of the steel (the same for 240 h) and the final weight every 24 h. Tables 3 and 4 presents the outputs of inhibition efficiency (IE) computed from below;

$$IE = \left[\frac{W_1 - W_2}{W_1} \right] * 100 \quad (2)$$

W_1 and W_2 represents weight-loss of the control and protected P4ST in the electrolyte in relation to inspection time.

2.2 Statistical computation

Binary-factor mono level experimental ANOVA test (F - test) was employed to evaluate the statistical influence of the inhibitor concentrations and inspection time on the inhibition performance of the LLVL compound on P4ST in 3 M H_2SO_4 and HCl, solutions. The evaluation was done at confidence level of 95% (i.e. a significance level of $\alpha = 0.05$) analogous to the following equations. The addition of squares between columns (inspection time) was gotten from equation 4.34

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \quad (3)$$

Addition of squares between rows (inhibitor concentration)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \quad (4)$$

Total addition of squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \quad (5)$$

3 Results and discussion

3.1 Coupon analysis

Observation of Tables 1 and 2 displays the corrosion rate outputs of control P4ST in 1.5 M H_2SO_4 is substantially greater than the outputs obtained HCl. This is by reason of the greater ionization potential of H_2SO_4 in comparison to HCl. Secondly, the corrosion rate of control P4ST in HCl increases progressively throughout the inspection hours compared to its behavior in H_2SO_4 were the corrosion rate appreciated progressively till 168 h after with it decreases till 240 h. Thirdly, the contrast in corrosion rate output between the inhibited and control P4ST in HCl is significantly high at all LLVL concentrations due to the electrochemical action of LLVL in suppressing the deteriorating action of Cl^- anions on the steel surface. The difference in corrosion rate between the inhibited and control P4ST in H_2SO_4 is generally small throughout the inspection hours from 0.25% - 0.75% LLVL. Beyond 0.75% LLVL, the difference in corrosion rate significantly increases signifying effective corrosion inhibition as shown in Table 3. Data on inhibition efficiency in Table 3 indicates LLVL performed poorly at low LLVL concentration due to inability of the protonated inhibitors to aggregate on the steel exterior in the presence of SO_4^{2-} anions. This phenomenon is the product of weak intermolecular forces between the inhibitor molecules at low concentration in H_2SO_4 solution. At higher concentration of LLVL the inhibitor molecules aggregate at close proximity preventing anodic-cathodic corrosion reaction processes. The inhibitor molecules adsorb to the steel surface in agreement with Freundlich and Frumkin adsorption isotherms. Previous research shows the adsorption mode is anodic signifying surface coverage of the inhibitor species hinder the evolution of corrosion pits on the steel [21]. The inhibition efficiency of LLVL was generally above 90% signifying effective inhibition. The inhibition efficiency values for LLVL in HCl as shown in Table 4 were above 90% from minimum to optimal concentration. This observation covers the whole inspection

period (24-240 h) showing the electrochemical performance of LLVL to be independent of time and concentration. LLVL displayed cathodic inhibition mechanism on the steel exterior in HCl solution. The small size of Cl⁻ anions enables their diffusion across the barrier of inhibitor molecules on steel surfaces. Hence the cathodic inhibition mechanism of LLVL is through discretionary distillation on the reactive sites on the steel surface.

Table 1: Data output on corrosion rate of P4S from 1.5M H₂SO₄/LLVL (0% - 1.5%) solution (n=1)

LLVL Conc. (%)								
Exp. Time (h)	0%	0.25%	0.5%	0.75%	1%	1.25%	1.5%	
24	10.958	1.640	2.781	2.306	2.948	2.837	2.467	
48	15.888	6.546	2.642	2.498	2.596	2.562	1.471	
72	19.006	9.289	3.579	3.655	1.772	1.770	1.131	
96	21.058	10.385	4.773	4.812	1.432	1.395	0.968	
120	22.978	14.102	6.941	7.168	1.269	1.223	0.800	
144	23.206	15.081	8.325	7.627	1.152	1.145	0.846	
168	23.114	16.152	8.914	8.307	1.046	1.056	0.899	
192	21.193	15.586	10.016	9.075	1.018	1.067	0.911	
216	19.995	16.450	10.990	10.339	0.972	0.988	1.006	
240	18.704	15.068	11.958	10.663	0.985	0.977	0.821	

Table 2: Data output on corrosion rate of P4S from 1.5M HCl/LLVL (0% - 1.5%) solution (n=1)

LLVL Conc. (%)								
Exp. Time (h)	0%	0.25%	0.5%	0.75%	1%	1.25%	1.5%	
24	5.007	0.308	0.259	0.321	0.456	0.043	0.204	
48	5.621	0.459	0.287	0.342	0.330	0.204	0.111	
72	6.496	0.323	0.204	0.495	0.325	0.160	0.080	
96	6.680	0.381	0.160	0.456	0.430	0.125	0.230	
120	7.241	0.316	0.285	0.398	0.358	0.113	0.205	
144	8.140	0.226	0.205	0.376	0.433	0.098	0.183	
168	7.943	0.508	0.237	0.476	0.464	0.097	0.198	
192	7.382	0.432	0.203	0.385	0.502	0.120	0.202	
216	7.522	0.406	0.242	0.356	0.472	0.127	0.294	
240	7.893	0.284	0.226	0.353	0.485	0.123	0.255	

Table 3: Data output on inhibition efficiency of LLVL (0%-1.5%) in 1.5M H₂SO₄ (n=1)

LLVL Conc. (%)							
Exp. Time (h)	0.25%	0.5%	0.75%	1%	1.25%	1.5%	
24	85.03	74.62	78.95	73.10	74.11	77.49	
48	58.80	83.37	84.28	83.66	83.87	90.74	
72	51.12	81.17	80.77	90.68	90.69	94.05	
96	50.68	77.33	77.15	93.20	93.37	95.40	
120	38.63	69.79	68.80	94.48	94.68	96.52	
144	35.01	64.13	67.13	95.04	95.07	96.36	
168	30.12	61.44	64.06	95.48	95.43	96.11	
192	26.45	52.74	57.18	95.20	94.97	95.70	
216	17.73	45.03	48.29	95.14	95.06	94.97	
240	19.44	36.07	42.99	94.73	94.77	95.61	

Table 4: Data output on inhibition efficiency of LLVL (0%-1.5%) in 1.5M HCl (n=1)

Exp. Time (h)	LLVL Conc. (%)					
	0.25%	0.5%	0.75%	1%	1.25%	1.5%
24	93.84	94.83	93.60	90.89	99.14	95.94
48	91.83	94.90	93.91	94.13	96.38	98.03
72	95.03	96.87	92.37	95.00	97.53	98.77
96	94.30	97.60	93.17	93.56	98.13	96.56
120	95.64	96.07	94.50	95.06	98.43	97.17
144	97.22	97.49	95.38	94.68	98.80	97.75
168	93.60	97.02	94.01	94.15	98.78	97.50
192	94.14	97.25	94.78	93.20	98.37	97.26
216	94.60	96.78	95.27	93.72	98.31	96.09
240	96.41	97.14	95.53	93.86	98.44	96.77

3.2 Statistical evaluation

The mean, standard deviation (SD) and margin of error for the calculated values of LLVL inhibition efficiency from H₂SO₄ and HCl media are laid out in Table 5. The SD values depict the amount of variation of between LLVL inhibition efficiency values. Observation shows that the SD values obtained for LLVL in H₂SO₄ are substantially greater than the outputs received from HCl. Secondly, the SD values generally decreases with LLVL concentration. The high SD values in H₂SO₄ compared to HCl shows the inhibition efficiency values obtained differs greatly from the mean value while the low standard deviation among the inhibition efficiency data obtained in HCl are most likely close to the mean value of the results. Another interesting observation is the lower the SD value, the higher the mean LLVL inhibition efficiency data i.e. the inhibition efficiency values are generally stable at higher inhibitor concentration. This explanation holds for the SD values in H₂SO₄ while in HCl solution, concentration dependence is minimal as the SD values are generally closer to unity. Comparing the data, the obtained for margin of error at 95% confidence, 65% of LLVL inhibition efficiency values obtained in H₂SO₄ solution have values above 70% inhibition efficiency with margin of error of $\pm 12.07\%$. In HCl solution, 100% of the LLVL inhibition efficiency data obtained is above 70% with margin of error of $\pm 1\%$.

Table 5: Statistical output for mean, standard deviation (SD) and margin of error for inhibition efficiency values of LLVL in H₂SO₄ and HCl solution

H ₂ SO ₄ Solution						
LLVL Conc. (%)	0.25	0.5	0.75	1	1.25	1.5
SD	20.63	15.86	14.02	7.28	6.97	5.80
Mean	41.30	64.57	66.96	91.07	91.20	93.30
Margin of Error	$\pm 12.07\%$					
HCl Solution						
LLVL Conc. (%)	0.25	0.5	0.75	1	1.25	1.5
SD	1.52	1.01	1.03	1.20	0.78	0.88
Mean	94.66	96.60	94.25	93.83	98.23	97.18
Margin of Error	$\pm 0\%$					

Statistical analysis was also performed with ANOVA to evaluate the numerical importance of inspection time and LLVL concentration (independent variables) on the inhibition output of LLVL compound in H₂SO₄ and HCl solution. The statistical importance of the independent variables is shown in Table 6 where statistical relevance (%) shows the percentage statistical

significance of the independent variables while the theoretical significance factor is the threshold minimum significant factor for which the mean square ratio must be greater than to be statistically relevant. Inspection of the values in Table 6 shows the statistical relevance of inhibition efficiency in H_2SO_4 and HCl solution far outweighs the related relevance for inspection time with values of 70.45% and 71.18%. The related data obtained for inspection time is 6.79% and 10.02%. The mean square ratio for inspection time in HCl is greater than the theoretical significance factor proving that it is statistically relevant to a minimal degree. However, the mean square ratio for inspection time in H_2SO_4 solution is lower than the theoretical significance factor showing that it is numerically important. The output from ANOVA analysis confirm the earlier assertion that inhibitor concentration dominates the inhibition output of LLVL compound.

Table 6: Statistical analysis (ANOVA) for LLVL inhibition performance on P4ST at 95% confidence level

H_2SO_4 Solution						
Origin of Variation	Addition of Squares	Extent of Freedom	Average Square	Average Square Ratio (F)	Theoretical Significance Factor	Statistical Relevance (%)
LLVL Conc.	21641.31	5	4328.26	27.85	2.53	70.45
Exp. Time	2085.78	9	231.75	1.49	2.42	6.79
Residual	6992.75	45	155.39			
Total	30719.84	59				
HCl Solution						
Origin of Variation	Addition of Squares	Extent of Freedom	Average Square	Average Square Ratio (F)	Theoretical Significance Factor	Statistical Relevance (%)
LLVL Conc.	160.51	5	32.10	34.07	2.53	71.18
Exp. Time	22.58	9	2.51	2.66	2.42	10.02
Residual	42.40	45	0.94			
Total	225.49	59				

4. Conclusion

Intermixture of l-leucine and vanillin poorly hindered the corrosion of P4 mold steel in H_2SO_4 and HCl solutions at low concentration. Effective inhibition performance was obtained at higher inhibitor concentration signifying strong concentration dependent action of the compound. Statistical calculations with analysis of variance presented the statistical influence of inspection time and inhibitor concentration on the inhibition efficiency output of the compound with inhibitor concentration being overwhelmingly statistically relevant. The mean, standard deviation and margin of error for the calculated values of inhibition efficiency in both acids gave further insight on the variation of inhibition with inspection time.

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