Research Article



ROSMARINUS OFFICINALIS L. HERB AS CORROSION INHIBITOR FOR MILD STEEL IN SULPHURIC ACID MEDIUM

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ABSTRACT

The effect of *Rosmarinus Officinalis L*. leaves extract on the corrosion inhibition of mild steel in 2.5 M H_2SO_4 solution was investigated using the Mylius thermometric technique. Results of the study revealed that *Rosmarinus Officinalis L*. leaves act as corrosion inhibitor for mild steel in the acidic medium. In general, with constant sulphuric acid concentration, the inhibition efficiency increases with increase in the inhibitor concentration. The addition of 0.05 M potassium chloride, potassium bromide and potassium iodide to the inhibitor enhanced the inhibition efficiency. The order of reactivity of halide ions is of the order KI > KBr > KCI. The inhibition efficiency increased 86 % to 94% at a concentration of 0.05 M KI and 1.0 % of inhibitor concentration. The values of adsorption of *Rosmarinus Officinalis L*. leaves extract onto the mild steel surface show that the process is spontaneous.

Keywords: Rosmarinus Officinalis L; Mild steel; Corrosion inhibition; Mylius thermometric Method.

INTRODUCTION

Natural products are nontoxic, biodegradable and readily available. They have been used widely as inhibitors. Rosmarinus Officinalis L. or more commonly knew as rosemary a well known medicinal and aromatic plant. It belongs to the Lamiaceae family and this herb is used for medicinal, culinary and cosmetic application in the ancient civilizations. The herb is useful in food and medicine fields activity of the extracts of rosemary particularly in food and medicine fields is due to its antioxidant oil and phenolic components. It prevents the degradation of oil and lipid containing foods. Rosemary is also useful to protect plants and various therapies. Rosemary has antibacterial and antioxidant properties. The essential oil enhances blood circulation of the limbs, induces anti-rheumatic effect and relives neuralgic pains. The main chemical components of rosemary include borneol, bornyl acetate, camphor, cineole, camphene and alpha-pinene. It is reported that oils of rosemary were found to be rich in 1,8-cineole, camphor, bornyl acetate and high amount of hydrocarbons. Since it is attractive and tolerates some degree of drought, it is also used in landscaping. It is considered easy to grow for beginner gardeners, and is pest-resistant. Rosemary grows on friable loam soil with good drainage in an open sunny position; it will not withstand water logging. It grows between pH 7–7.8 with average fertility.

The leaves extract of rosemary was investigated for corrosion inhibition of mild steel using thermometric method. The effect of halides addition on the inhibition efficiency of the inhibitor is also studied. Furthermore, the biomasses effectively adsorb on surface area and block the active sites and thereby reduce the corrosion rate¹⁻³.

MATERIALS AND METHODS

Rosmarinus Officinalis L. leaves dried was purchased and powdered. Plant materials was extensively washed with distilled water then dried in an oven at 80°C to a constant weight. The extract was prepared by refluxing 25 g of powdered dry leaves in 2.5 M sulphuric acid for one hour and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500 ml using the same acid and this was taken as stock solution.

Mild steel metal (the percentage elemental composition was found to be, C (0.048%), Mn (0.335%), Si (0.029%), P(0.041%) ,S (0.025%), Cr (0.050%), Mo (0.016%), Ni (0.019%) and Fe (99.437%) having a surface area of 5x1cm² were cut from a large sheet. The specimens were polished successively with emery sheets, degreased and dried. Sulphuric acid used for preparing solutions was AR grade. The concentrations of the inhibitor from 0.2 % to 1.0 % was prepared and used in the study. The specimens in triplicate were immersed in 2.5M acid solutions containing various concentrations of the inhibitor for two hours at 300K. The specimens were removed washed with water and dried. The mass of the specimens before and after immersion was determined using an electronic digital balance⁴. The concentrations of H_2SO_4 (blank) used were in the range 0.5 M – 2.5 M and Synergistic effects was studied in the presence of 0.05 M halide additives namely potassium chloride, potassium bromide and potassium iodide. The corrosion rate for room temperature with various concentrations of inhibitor was obtained from the following formula,

C.R (mpy) =
$$\frac{436.095 \text{ X } 1000 \text{ X W}}{\text{A X T}}$$

Where, W = Weight loss in grams, A = Area of specimen in cm² T = Exposure time in hours. The unit of the corrosion rate is in mills per year (mpy).



Mild steel specimens were completely immersed in blank and in combination with different concentrations of sulphuric acid, inhibitor and halides mixture. The volume of the test solution was kept at 100 ml. The initial temperature in all experiments was kept at 27° C. The temperature was measured to $\pm 0.05^{\circ}$ C on a calibrated thermometer (0-100°C). This method allowed for the evaluation of the reaction number (RN). The RN is defined as

$$\mathbf{RN} (\mathrm{Kmin}^{-1}) = \frac{[\mathbf{T}_{\mathrm{m}^{-}} \mathbf{T}_{\mathrm{i}}]}{t}$$

T_m =Maximum temperature attained by solution.

T_i=Initial temperature of solution.

t = time required to attain maximum temperature.

The inhibition efficiency (IE %) was evaluated from percentage reduction in the reaction number using equation $^{5,6.}\,$

$$IE \% = \frac{[RN_f - RN_i]}{RN_f} X 100$$

Where, RN_f is the reaction number in free solution, RN_i is the Reaction number in inhibited solution.

RESULTS AND DISCUSSION

Effect of sulphuric acid concentration: In this part the weight loss-time curves of mild steel are constructed, under weight loss method. Figure-1 represents the variation of weight loss with time of mild steel immersed in H_2SO_4 of different concentrations range (0.5 to 2.5 M). Analysis of the of these curves show that the weight loss (g/cm³), increases with time along a period of 60 minute (immersion time), and also upon increasing the concentration of all solutions under test. This may be attributed to the presence of water, air and H⁺ which accelerate the corrosion process^{5,6}. This indicates that the corrosion rate of mild steel in test solutions is a function of the concentration of acid solution. This observation agrees with the fact that the rate of a chemical reaction increases with increasing concentrations.



Figure 1: Weight loss-time curves for mild steel in solutions of different concentrations of sulphuric acid

The values of C.R, IE% and θ at different inhibitor concentrations are listed in Table-1. The data in table

reveals that as the inhibitor concentration is increased, the corrosion rate decreases while the efficiency percent and surface coverage increases⁷. This behaviour may be attributed to be the increased surface coverage (θ) due to the increase in the number of adsorbed molecules on mild steel surface. A good efficiency is observed at constant concentration of inhibitor (1.0 %).

The effect of sulphuric acid concentration on the corrosion of mild steel is illustrated in the plot of temperature ($^{\circ}$ C) against time (min) at different concentrations of H₂SO₄ as shown. It is observed that the dissolution of mild steel begins after a time lag from the immersion of the coupons in the test solution. Also the temperature rises gradually with time and then decreases after reaching a maximum temperature (Tm). It is also observed that as the concentration of the sulphuric acid increases, temperature (Tm) increases and the time required to reach the maximum temperature decreases. This may due to the fact that increase in H₂SO₄ concentrations of active species as well as increase in the rate of chemical reaction.



Figure 2: Variation of temperature with time for the dissolution of mild steel in given concentrations of H_2SO_4 (Blank).

Temperature change of the system involving mild steel in 2.5 M H_2SO_4 is a function of time in the absence and presence of given concentrations of Rosmarinus Officinalis L. leaves extract (table-2). The maximum temperature (Tm) measured in the free acid solution is 70°C and was attained after time (t) of 20 min. This corresponds to a reaction number (RN). Addition of inhibitor caused a decreased in the maximum temperature and an increase in the time required reaching it. This indicates that the inhibitor retards the dissolution rate of mild steel in the acidic solution, may be due to adsorption on the metal surface. The extent of inhibition depends on the degree of coverage of the metal by the adsorbed molecules. Adsorption is noted for inhibitor, since a simultaneous increase in time and decrease in T_m takes place, and both the factors cause a large decrease in the reaction number RN of the system (Table-2). Increasing the inhibitor concentration in the acid solution decreases the RN of mild steel and consequently the inhibition efficiency is increased.



Table 1: Effect of inhibitor concentration on corrosion rate (CR), inhibition efficiency (IE %) and surface coverage (θ) of mild steel in 2.5 M H₂SO₄ at 27^oC.

SI. No.	Concentration (%)	Weight loss (g)	Inhibition efficiency (%)	Degree of surface coverage (θ)	Corrosion rate (mpy)
1	Blank (2.5 M H ₂ SO ₄)	0.069		-	6018.11
2	0.2	0.049	28.99	0.12	5320.36
3	0.4	0.041	40.58	0.54	2791.01
4	0.6	0.027	60.87	0.72	1657.16
5	0.8	0.021	69.57	0.83	1046.63
6	1.0	0.018	73.91	0.87	784.97

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Concentration of inhibitor	Initial temp. (°C)	Max temp. (ºC)	Time (minutes)	Reaction Number RN _i	Reaction Number RN _f	Inhibition efficiency (%)
Blank (2.5 MH ₂ SO ₄)	27.8	70.5	20	2.14	-	-
0.2 %	27	62.5	23	1.44	0.21	20.51
0.4 %	27	50.4	25	1.14	0.33	32.75
0.6 %	27	46.3	33	0.58	0.73	72.67
0.8 %	27.1	44.1	37	0.46	0.79	78.53
1.0 %	27	39.1	42	0.29	0.87	86.54

Table 3: Synergistic effect of halides and Rosmarinus Officinalis L. concentration on the parameters of temperature for mild steel in 2.5 M sulphuric acid.

System concentration	Initial temp. (ºC)	Max temp. (°C)	Time (minutes)	Reaction Number RNi	Reaction Number RNf	Inhibition efficiency (%)
Blank (2.5 MH ₂ SO ₄)	27.8	70.5	20	2.14		-
1.0% inhibitor	27.0	37.2	48	0.29	0.87	86.51
1.0% Inhibitor+0.05 KCI	27.0	36.1	48	0.28	0.87	86.68
1.0% Inhibitor+0.05 M KBr	27.0	34.6	48	0.21	0.90	90.38
1.0% Inhibitor+0.05 % KI	27.1	31.6	48	0.11	0.95	94.98

The synergetic effects caused by halide ions are given in Table 2, shows the temperature vs time for the dissolution of mild steel in different concentrations of *Rosmarinus Officinalis L*. and halides mixture. This shows that *Rosmarinus Officinalis L*. in combination with iodide ions further retards the dissolution rate of mild steel n acidic medium when compared to *Rosmarinus Officinalis L*. alone. The order of reactivity of halide ions is of the order KI > KBr > KCI. The inhibition efficiency increased 86 % to 94% at a concentration of 0.05 M KI and 1.0 % of inhibitor concentration.

CONCLUSION

Rosmarinus Officinalis L. is found to be an inhibitor for mild steel corrosion in sulphuric acid medium. Inhibition efficiency increased with increasing inhibitor concentration. The addition of halides to *Rosmarinus Officinalis L.* enhances the inhibition efficiency. The inhibition efficiency increased 86% to 94% at a concentration of 0.05 M potassium iodide 1.0% of inhibitor concentration.

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