Materials Chemistry and Physics 120 (2010) 643–648

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Artemisia pallens as corrosion inhibitor for mild steel in HCl medium

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ARTICLE INFO

Article history:
Received 21 April 2009
Received in revised form
26 November 2009
Accepted 13 December 2009

Keywords:
Artemisia pallens
Mild steel
Polarization
Corrosion inhibition

ABSTRACT

Methanolic extract of *Artemisia pallens* was tested as corrosion inhibitor for mild steel in 4N HCl and conc. HCl. Weight loss and polarization techniques were used for evaluating corrosion inhibition in 4N HCl, whilst weight loss, SEM and FT-IR studies were carried out in conc. HCl. The inhibition efficiency was found to increase with increase of the inhibitor concentrations due to the adsorption of the inhibitor molecules on the metal surface and the adsorption follows Langmuir's adsorption isotherm. The inhibition efficiency was found to be 93% at 1.5 g l^{-1} in 4N HCl and 96.5% at 40 g l^{-1} in conc. HCl.

1. Introduction

Mild steel has been extensively used in industries for different purposes under different conditions like handling acids, alkalis and salt solution. Corrosion problems arise in the pipe lines due to the aggressiveness of the liquids carried by them, and also due to its thermodynamic instability. Hence the study of mild steel corrosion and its inhibition in acid medium is of recent interest and gaining greater importance in the field of engineering and industries involving electrochemical process. The addition of inhibitors is one of the practical methods to overcome the corrosion of mild steel and its alloys. Most of the chemicals used as corrosion inhibitors are very toxic to all living organisms even in very small concentration.

In modern life with the scientific and technological advancement much attention is paid to safety, sanitation and health of the environment. The general realization of health hazards associated with chemicals has led to increased search for natural inhibitors. Normally for acidization, 15–28% of HCl is used in petroleum oil and gas well [1], whilst conc. HCl is used in pickling solution for mild steel [2]. Several studies have been carried out using natural products as corrosion inhibitors for metals such as mild steel [3–13], copper [14,15], steel [16–25], aluminum and zinc [26–29]. However, study on the inhibition efficiency of natural products for mild steel in conc. HCl medium is still lacking. Aiming to find cheap, environmentally benign, non-toxic natural compound that could be used for acidization and acid pickling of mild steel in acid medium, *Artemisia pallens* (Wall., Family Asteraceae) an aromatic, evergreen, small fragrant herb popularly known as Davana was selected for the present study. The plant is easily biodegradable; readily available from the renewable sources. The chemical constituents present in *A. pallens* are tetrahydrofuran, davanone, linalool, ethylcinnamate, sesquiterpenoids, terpenoids, artemone, etc. [30–32]. The plant is used in the manufacture of essential oils, oleoresins, terpenes and the oil has both antibacterial and anti fungal properties [33–35]. Apart from that, no literature for their corrosion inhibitory activities could be traced out. Hence, an attempt has been made to explore the inhibition efficiency of *A. pallens* for mild steel corrosion in 4N HCl solution and conc. HCl.

2. Experimental

2.1. Material

Commercial mild steel strips of the following composition 0.07% C, 0.034% Mn, 0.08% P and the remainder iron were used in this study. Specimens of size 10 mm × 50 mm × 2 mm were used for weight loss measurements and for surface analysis. For potentiodynamic polarization measurements, the mild steel working electrode was sealed with Araldite, having an exposed surface area of 1 cm^2. The specimens were polished with different grades of emery papers, degreased with acetone and washed thoroughly with double distilled water. The test solution of 4N HCl was prepared by the dilution of analytical grade 37% HCl with double distilled water and the same analytical grade HCl (37%) was used as such for conc. HCl test medium.

2.2. Inhibitor

Freshly collected aerial parts of *A. pallens* were thoroughly washed with distilled water to remove soil, dust, etc. and allowed to dry in the shadow for 4 days. The dried materials were ground to fine powder prior to solvent extraction. 100 g of *A. pallens* powder was extracted in methanol using soxhlet apparatus. To know the mass of the extract, it was vacuum dried, weighed and used for further experiments.

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doi:10.1016/j.matchemphys.2009.12.015

Table 1
Inhibition efficiency of the inhibitor for mild steel corrosion in 4N HCl by weight loss method.

Inhibitor concentration ($g\,l^{-1}$)	(%) Inhibition efficiency				
	1 h	2 h.	3 h	4 h	24 h
0.1	43	58	52	30	35
0.3	60	68	76	51	52
0.5	65	73	77	83	69
0.7	73	78	81	83	88
1.0	82	82	83	87	89
1.5	89	87	84	85	93

2.3. Weight loss measurements

Mild steel specimens were immersed in triplicate in 100 ml of the test solutions (4N and conc. HCl) with and without addition of plant extract of different concentrations. After the desirable interval periods, the test specimens were removed and their weight losses were determined using the Afcoset electronic balance (precision ± 0.0001 g).

The corrosion rate in mpy was obtained from the following equation:

$$\text{corrosion rate (mpy)} = \frac{KW}{DAT}$$

where K – 3.45×10^6, T – the exposure time (h), A – the surface area of the test specimen (cm^2), W – the weight loss (g) and D – density of the test specimen ($g\,cm^{-3}$).

The percentage inhibition efficiency (IE) and the degree of surface coverage (θ) were calculated by the following equations:

$$\%\,IE = \frac{W - W_1}{W} \times 100 \quad (1)$$

$$\theta = \frac{W - W_1}{W} \quad (2)$$

where W and W_1 are the weight loss of metal without and with inhibitors, respectively.

2.4. Electrochemical measurements

Electrochemical measurements were carried out using (Eco Chemie B.V., Netherlands) Autolab with PGSTAT30 computer controlled electrochemical measurement system. Three compartment cell with Ag/AgCl as reference electrode, platinum as auxiliary electrode and mild steel as working electrode was used in 4N HCl without and with inhibitor concentration of 0.5, 1.0 and 1.5 $g\,l^{-1}$. The working electrode was allowed for 10 min in the test solution for stabilization of corrosion potential before recording the polarization curves. All the experiments were performed at 30 ± 1 °C and each value is the mean of triplicate experiments.

2.5. Solution analysis

CHNS analysis of the plant extract was carried out using CHNS-elemental analyzer model Vario EL III. After the weight loss experiments in conc. HCl medium, the test solutions were analysed by Atomic Absorption Spectrometer GBC-932 plus model to measure the amount of iron leached out from the specimens.

2.6. Surface analysis

The test specimens were immersed in 100 ml of conc. HCl with the extract concentration of 10 and 40 $g\,l^{-1}$, for 20 min. After termination of the experiment the specimens were washed with distilled water, dried and examined for their surface morphology and adsorbed molecules using Scanning Electron Microscope (SEM) Hitachi model-3000H, resolution 3.5 nm and Fourier Transform Infrared (FT-IR) spectra (Nexus 670-ThermoElectron corporation make). The vacuum dried plant extract was also characterized using FT-IR.

3. Results and discussion

3.1. A. pallens extract in 4N HCl

3.1.1. Weight loss measurements

From Fig. 1 it is evident that there is a tremendous decrease in the corrosion rate with addition of inhibitor. A gradual decrease in the corrosion rate is noticed with increase in the concentration of the inhibitor and hence the rate is concentration dependent.

Table 1 shows the inhibition efficiencies of the inhibitor at different concentrations in 4N HCl for mild steel. The results reveal that the inhibition efficiency increases with increase in the concentration of the inhibitor. At lower inhibitor concentrations 0.1, 0.3 and 0.5 $g\,l^{-1}$; the maximum inhibition efficiency was obtained in 2, 3 and 4 h, respectively and after which it tended to decrease with exposure time. It could be attributed to the weak inhibitor metal ion complex film formed due to the inadequacy of the inhibitor as opined by Oguzie et al. [36]. In the case of higher concentration (0.5–1.0 $g\,l^{-1}$), the inhibition efficiency experienced an exponential increase over the period of time. Comparing the literature available [3–13], it is implicit that the inhibitor shows the highest inhibition efficiency (93.48%) at 1.5 $g\,l^{-1}$ in 4N HCl and hence this inhibitor can be used for acidization process.

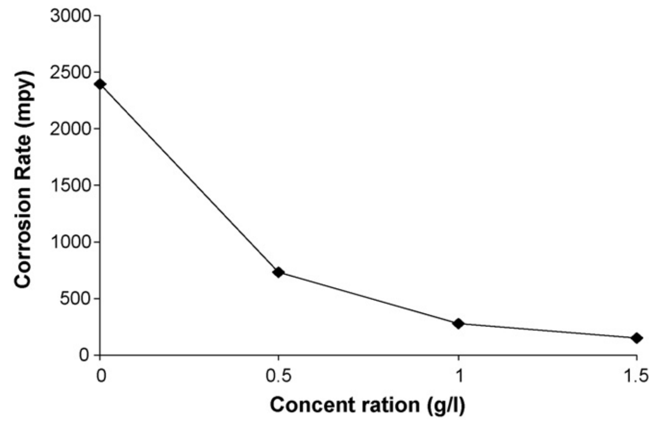

Fig. 1. Corrosion rate of mild steel exposed for 24 h in 4N HCl with different concentrations of the inhibitor.

3.1.2. Adsorption isotherm

The adsorption of inhibitors from the aqueous solution can be regarded as a quasi substitution process between the inhibitor in the solution and the water molecule at the metal surface [37].

$$Inh_{(sol)} + x(H_2O)_{(ads)} \rightleftharpoons Inh_{(ads)} + x(H_2O)_{(sol)}$$

where x is the number of water molecule displaced by one molecule of the inhibitor. In the mean time, partial anodic reaction takes place at the mild steel surface [38].

$$Fe \rightarrow Fe^{2+} + 2e^-$$

The inhibitor ($Inh_{(ads)}$) combines with the Fe^{2+} ions and forms the metal inhibitor complex $(Fe–Inh)^{2+}$. This complex may reduce or accelerate the corrosion. Fig. 2 shows the relation between con-

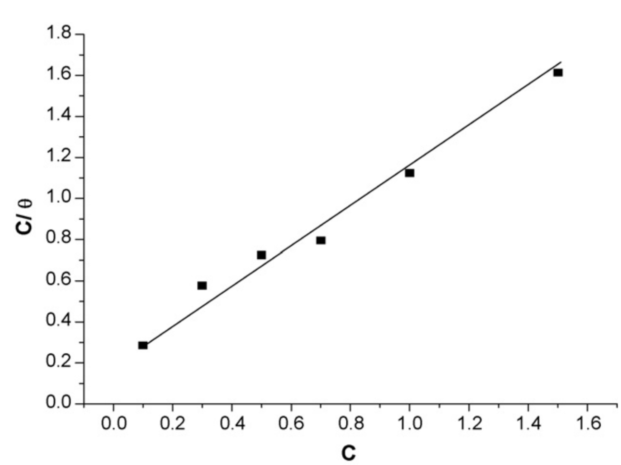

Fig. 2. Langmuir adsorption isotherm plot for mild steel in 4N HCl with different concentrations of the inhibitor exposed for 24 h.