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Effects of alcohol-based inhibitors on corrosion of mild steel in hydrochloric acid

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ABSTRACT

The inhibition efficiencies of Octyl alcohol (OCAL) and propargyl alcohol (PRAL) on the corrosion of mild steel in 15% commercial hydrochloric acid have been evaluated by mass loss method, electrochemical techniques and surface analysis techniques with 0–1% inhibitor concentration at 30 °C and 105 °C. Both OCAL and PRAL are excellent inhibitors for the above-mentioned system. OCAL gives 87% and 82% inhibition efficiencies at 30 °C and 105 °C, respectively, for 1% inhibitor concentration whereas PRAL gives 100% and 99% efficiencies at 30 °C and 105 °C, respectively, for 0.6% inhibitor concentration. Polarization studies confirm that OCAL and PRAL are mixed type inhibitors. OCAL and PRAL obey Temkin's adsorption isotherm at both the temperatures. UV-reflectance, FT-IR and SEM studies confirm that the surface of mild steel is not affected at the maximum concentration of OCAL and PRAL.

1. Introduction

In oil and gas well acidization process, the commercial hydrochloric acid is used since it is more economical, efficient and trouble free when compared to other mineral acids. The great advantage of hydrochloric acid over the other mineral acids in acidization operation lies in its ability to form metal chlorides, which are extremely soluble in aqueous phase when compared to sulphate, nitrate, and phosphate. This higher rate of solubility of chloride salts causes the least polarizing effect and does not hamper the rate of reaction. The salts like $FeCl_3$ may be produced as a result of the reaction scales and acid have a depolarizing effect towards the base metal. To control this depolarizing effect of metal salts and the attack of the acid on the base metal surface, the use of efficient inhibitors in hydrochloric acid solutions during the above operations is essential.

The mechanism of corrosion of iron by HCl has been studied by Rajagopalan and Venkatachari [1]. Harrison and Lorenz [2] have reviewed the effect of anions on the metallic dissolution. Corrosion of steel in acidic solution has practical importance as it is rapidly corroded without formation of passive layer of corrosion products, and that the cathodic reaction consists of mainly hydrogen gas evolution by Horng et al. [3]. Singh et al. [4] found that in acid solutions, the iron surface acquired a positive charge (the zero charge potential of iron in aqueous acid solutions varies from −0.4 V to −0.7 V).

Acetylenic alcohols and similar compounds are reported as effective inhibitors for ferrous metals in acid media [5–7]. The corrosion of iron in acid medium and its inhibition constitute a very important problem in chemistry both from fundamental and industrial point of view [8–10]. Several authors have investigated the role of acetylenic alcohol compounds in acid solutions [11–20]. The high temperature performance is generally improved by using acetylenic compounds into the inhibitor package. The compound mostly used is propargyl alcohol.

In this present study, the inhibitive performance of Octyl alcohol and propargyl alcohol on the corrosion of mild steel in 15% commercial hydrochloric acid has been evaluated at various concentrations of inhibitors and at two different temperatures by mass loss method, potentiodynamic polarization and electrochemical impedance spectroscopic techniques. The surface of the mild steel was examined by UV–vis reflectance and FT-IR spectroscopic methods.

2. Experimental methods

2.1. Material used

Mild steel was used throughout the experiments. The chemical composition of mild steel has been given in Table 1. The rectangular metal coupons of size 2 cm × 4 cm × 0.03 cm were used for the mass loss studies. 1 cm^2 area of specimens with stem was used for potentiodynamic polarization and electrochemical impedance spectroscopic studies.

2.2. Acid and inhibitors used

30% commercial hydrochloric acid was purchased from Ranbaxy Fine Chemicals Ltd., and 15% acid was prepared by diluting with solar water. This 15% acid was used throughout the studies. The commercial alcohol compounds like Octyl alcohol

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Table 1
Chemical composition of mild steel.

Element	C	S	P	Si	Mn	Fe
% composition (w/w)	0.270	0.006	0.008	0.080	0.340	99.296

Table 2
Chemical structures of inhibitors.

Inhibitor's name	Structure
Octyl alcohol (OCAL)	$CH_3–(CH_2)_7–OH$
Propargyl alcohol (PRAL)	$CH{\equiv}C–CH_2–OH$

(OCAL) and propargyl alcohol (PRAL) were used as inhibitors. The structure of OCAL and PRAL is given in Table 2.

2.3. Techniques and instruments used

2.3.1. Weight loss measurements

Specially designed glass cells were used for weight loss measurements. The rectangular mild steels of size 2 cm × 4 cm × 0.03 cm were pickled, polished, degreased and weighed before immersion in the test solution as per usual procedures [21]. The specimens were immersed in the test solution in triplicate by means of glass hooks. The mass loss measurements were carried out for 6 h at 0–1% concentrations of inhibitors and at two different temperatures such as 30 °C and 105 ± 5 °C. At the end of 6th hour, the specimens were taken out, washed with water, dried and weighed again. The weight losses were measured. From the weight losses, the corrosion rate (CR), surface coverage (θ) and the inhibitor efficiency (IE, %) were calculated by the following expressions [22–24]:

$$\text{CR (mmpy)} = \frac{87.6 \times w}{ATD} \quad (1)$$

where w is corrosion weight loss of mild steel (mg), A the area of the coupon (cm^2), T the exposure time (h) and D the density of mild steel ($g\,cm^{-3}$).

$$\text{IE (\%)} = \frac{w_0 - w_i}{w_0} \times 100 \quad (2)$$

$$\theta = \frac{w_0 - w_i}{w_0} \quad (3)$$

where w_0 and w_i are the values of corrosion weight loss of mild steel in uninhibited and inhibited solutions, respectively.

2.3.2. Potentiodynamic polarization measurements

Specially designed three-electrode glass cell and SOLARTRON ELECTROCHEMICAL MEASUREMENT UNIT – 1280 B Model with software package of Z Plot 2 and CORRWARE 2 were used for the potentiodynamic polarization and electrochemical impedance measurements.

The potentiodynamic measurements were carried out over a potential range of −200 mV to +200 mV with respect to open circuit potential at a scan rate of 1 mV s^{-1} using specially designed three-electrode glass cell. In the experiments, mild steel, platinum foil and saturated calomel electrodes were used as working electrode, counter electrode and reference electrode, respectively. 15% commercial hydrochloric acid with various concentrations of inhibitor was used as test solution. From this technique, various corrosion kinetic parameters like I_{corr}, b_a, b_c and E_{corr} were predicted at different temperatures such as 30 °C and 105 ± 5 °C. From the I_{corr} values, the corrosion rate and inhibitor efficiency were calculated by the usual expressions [25].

2.3.3. Electrochemical impedance measurements

The same instruments mentioned above were used for the EI measurements. The impedance measurements were carried out using the same three-electrode glass cell and procedures as described in Section 2.3.2. A.C. amplitude of 10 mV was applied and the frequency was varied from 10 kHz to 10 mHz. The real and imaginary parts of the impedance were plotted as Nyquist plots. From the Nyquist plots, the charge transfer resistance R_{ct} and double layer capacitance C_{dl} values were calculated. Inhibitor efficiencies were calculated using the R_{ct} values only at 30 °C using different concentrations of inhibitor by the usual expression [25].

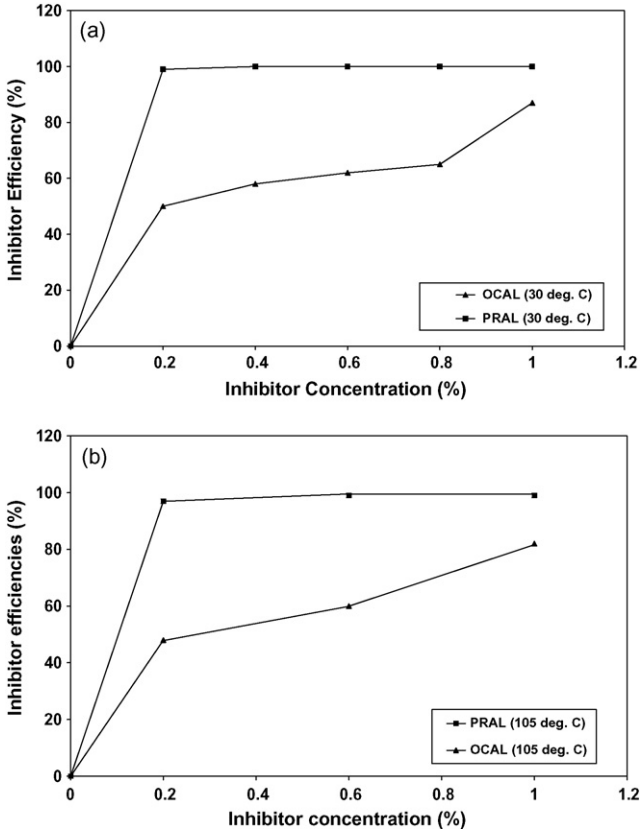

Fig. 1. Variation of inhibitor efficiencies as a function of OCAL and PRAL concentrations at (a) 30 °C and (b) 105 °C.

2.3.4. Surface examination studies

UV-reflectance spectroscopy (HITACHI Model U 3400) was used to draw UV-reflectance curves. FT-IR spectroscopy (PERKIN ELMER Model – PARAGON 500) was used to collect the transmittance spectra of mild steel. Scanning Electron Microscopy (HITACHI Model S 3000H) was used to study the topography of the mild steel surface.

3. Results and discussion

3.1. Weight loss measurements

The weight loss parameters of mild steel in 15% commercial HCl containing various concentrations of OCAL and PRAL at 30 °C and 105 °C are given in Table 3. From Table 3, it can be observed that the corrosion rate values decrease and the inhibitor efficiency values increase with the increase of the OCAL and PRAL concentrations for both the temperatures. But at a particular concentration of the

Table 3
Weight loss parameters of mild steel in 15% commercial HCl with and without various concentrations of OCAL and PRAL at 30 °C and 105 °C.

S. no.	Inhibitor concentration (%)	Weight loss (mg)				Corrosion rate (mmpy)				Inhibitor efficiency (%)			
		OCAL		PRAL		OCAL		PRAL		OCAL		PRAL	
		30 °C	105 °C	30 °C	105 °C	30 °C	105 °C	30 °C	105 °C	30 °C	105 °C	30 °C	105 °C
1	0.0	1424	3670	1424	3670	167	429	167	429	–	–	–	–
2	0.2	708	910	8	92	83	106	0.9	11	50	48	99	97
3	0.4	597	–	6	–	70	–	0.7	–	58	–	100	–
4	0.6	537	739	5	39	63	86	0.9	5	62	60	100	99
5	0.8	495	–	5	–	–	–	0.6	–	65	–	100	–
6	1.0	179	657	3	23	21	77	0.4	3	87	82	100	99