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Adsorption behaviour of o-hydroxy acetophenone benzoyl hydrazone on mild steel/hydrochloric acid interface

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ABSTRACT

The effect of synthesised o-hydroxy acetophenone benzoyl hydrazone (HABH) on the corrosion of mild steel in 1 M HCl was investigated using potentiodynamic polarisation (PDP), electrochemical impedance spectroscopy (EIS), thermogravimetric analysis, contact angle measurement and weight loss methods. The inhibition efficiency of HABH increases with surface roughness of emery paper up to 800 grits and thereafter it decreases with additional increase in surface roughness. TGA results also indicated that the inhibitor film on the surface had a relatively good thermal stability. The adsorption behaviour of HABH is experimentally investigated by contact angle measurement of acid solution on metal surface.

1. Introduction

Various attempts have been made to prevent or retard the destructive effect of corrosion on metals and alloys. Inhibitor has been an important means of corrosion prevention by affecting the chemistry of corrosion medium. The corrosion protection by inhibitors is based mostly on the modification of metal surfaces by the adsorption of inhibitor molecules and the subsequent formation of a protective (blocking) layer.

Hence, many researchers are trying to introduce new organic compounds which are more efficient, cost effective with easy access [1–7].

A wide range of studies have investigated the corrosion inhibition of Schiff base compounds for mild steel, copper, zinc and aluminium [8–10]. Schiff bases are the condensation products of an amine and a ketone or aldehyde, and have the general formula RC=NR. Some works have revealed that the inhibition efficiency of these compounds is much higher than the corresponding effect obtained with amines and aldehydes. This phenomenon is attributed to the presence of the imine group (–C=N–) in the molecules [11–14].

In view of appreciable efficiency of Schiff bases, o-hydroxy acetophenone benzoyl hydrazone have been synthesised to investigate its inhibition activities on corrosion of mild steel in 1 M HCl solution under the impact of such factors, as inhibitor concentration, solution temperature and surface roughness using electrochemical impedance spectroscopy (EIS), potentiodynamic polarisation (PDP) and weight loss (WL) methods. The structure of HABH is given as Fig. 1.

Hydrochloric acid is an important mineral acid with many uses, including acid pickling of steel, acid treatment of oil wells, chemical cleaning and processing. So, hydrochloric acid has been chosen for working medium.

2. Experimental

2.1. Synthesis of o-hydroxy acetophenone benzoyl hydrazone

O-hydroxy acetophenone benzoyl hydrazone (HABH) was prepared by reacting *o*-hydroxy acetophenone (50 mM, 6.0 ml) with benzoyl hydrazine (50 mM, 6.8 g) dissolved in 50 ml ethanol. The reactants were taken in a R.B. flask and refluxed for 6 h. The solution was transferred into a beaker from which cream yellow coloured crystals of the product were obtained after cooling the solution to room temperature within 1 h. The cream yellow product was filtered, washed with ethanol and dried in a desiccator over anhydrous $CaCl_2$. Yield (75%). M.p. 435 K. *Anal.* Calc. for $C_{15}H_{14}N_2O_2$ (254): C, 70.87; H, 5.51; N, 11.02. Found: C, 70.60; H, 5.55; N, 11.14%. IR (ν cm^{-1}, KBr): ν(OH + NH) 3449b, 3276b; ν(C=O) 1653s; ν(C=N) 1633m; ν(N–N) 987w. ^{1}H NMR (DMSO-d6; δ ppm): 2.49 (s, 3H, CH_3);

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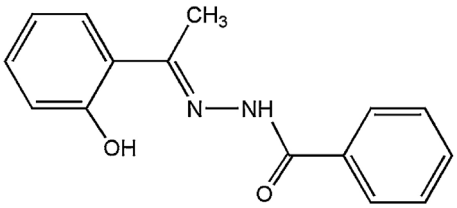

Fig. 1. Molecular structure of o-hydroxy acetophenone benzoyl hydrazone (HABH).

6.90–6.93 (d, 2H, J = 7.8 Hz, Ar-H); 7.28–7.33 (dd, 1H, J = 7.3 Hz, Ar-H); 7.54–7.65 (m, 4H, Ar-H); 7.93–7.95 (d, 2H, J = 7.2 Hz) 11.32 (s, 1H, NH); 13.35 (s, 1H, Ar-OH). ^{13}C NMR (DMSO-d6; δ ppm): 14.03 (CH_3); 117.27 (C13); 118.47 (C6); 119.37 (C7); 128.07 (C12, C14); 128.37 (C5, C8); 131.22 (C11, C15); 131.92 (C3); 132.94 (C10); 158.71 (C–OH); 158.12 (C=N); 164.34 (C=O).

2.2. Corrosion measurements

Prior to all measurements, the mild steel specimens, having composition (wt%) C = 0.17, Mn = 0.46, Si = 0.26, S = 0.017, P = 0.019 and balance Fe, were abraded successively with emery papers from 600 to 1200 grits. The specimen were washed thoroughly with double distilled water, degreased with acetone and finally dried in hot air blower. After drying, the specimen were placed in desiccator and then used for experiment. The aggressive solution 1 M HCl was prepared by dilution of analytical grade HCl (37%) with double distilled water. All the concentrations of inhibitor for electrochemical and weight loss studies were taken in mol l^{-1}.

2.3. Electrochemical measurements

All electrochemical experiments potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) were performed in Gamry electrochemical cell with three electrodes connected to Gamry Instrument Potentiostat/Galvanostat with a Gamry framework system based on ESA400. Gamry applications include software DC105 for corrosion and EIS300 for EIS measurements, and Echem Analyst version 5.50 software packages for data fitting. The mild steel of 1 cm^2 was the working electrode, platinum electrode was used as auxiliary electrode, and saturated calomel electrode (SCE) was used as reference electrode. All potentials were measured versus SCE.

Tafel curves were obtained by changing the electrode potential automatically from −250 to +250 mV versus corrosion potential (E_{corr}) at a scan rate of 1 mV s^{-1}. EIS measurements were carried out in a frequency range from 100 kHz to 10 mHz under potentiostatic conditions, with amplitude of 10 mV peak-to peak using AC signal at E_{corr}. All experiments were measured after immersion for 30 min in 1 M HCl with and without addition of inhibitor which was proved to be sufficient to attain a stable value of E_{corr}; the OCP plot of mild steel in absence and presence of different concentration of studied inhibitor is given as Fig. 2. After each EIS run, the instrument turns on automatically to record the PDP curves. All experiments were conducted in stagnant HCl solutions at 308 K unless otherwise stated.

2.4. Weight loss studies

Weight loss experiments were done according to the method described previously [15,16]. Weight loss measurements were performed at 308 K (except for temperature effect) for 3 h (except for thermal stability of film experiment) by immersing the mild steel coupons into acid solution (100 mL) without and with various amounts of inhibitor. During metal dissolution, intermediate species $(M–In)_{ads}$ may formed and thereby resulting in to irregular slopes thus resulting in to simple blocking of metal surface. After the elapsed time, the specimen were taken out, washed, dried and weighed accurately.

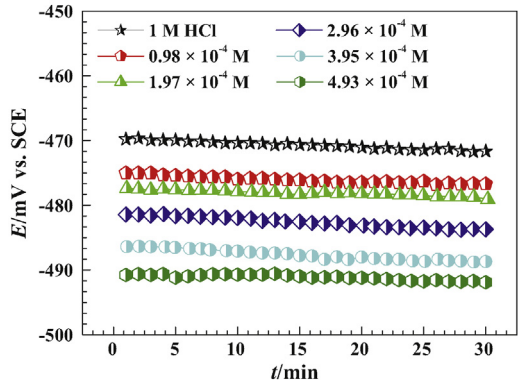

Fig. 2. OCP plots for mild steel in 1 M HCl in the absence and presence of different concentrations of HABH.

The surface coverage (θ) and inhibition efficiency (E_{WL}, %) were determined by using following equations:

$$\theta = \frac{w_0 - w_i}{w_0} \quad (1)$$

$$E_{WL}\,(\%) = \frac{w_0 - w_i}{w_0} \times 100 \quad (2)$$

where w_i and w_0 are the weight loss values in presence and absence of inhibitor, respectively. The corrosion rate of mild steel was calculated by an equation [17]

$$C_R = \frac{87.6 \times w}{AtD} \quad (3)$$

where w is the weight loss of mild steel in mg cm^{-2}, A the area of coupon (cm^2), t is the exposure time and D is the density of mild steel in g cm^{-3}. The values of inhibition efficiency have been plotted against concentration of inhibitor and given as Fig. 7.

2.5. Thermal stability of surface film

A mild steel coupon was immersed in 1 M HCl solution containing 4.93 × 10^{-4} M HABH for a period of 24 h. After this time interval, mild steel coupon was taken out, washed with double distilled water and dried. The HABH thin film was mechanically removed from the mild steel surface and its thermal stability was tested. The thermal analysis experiments were performed under the nitrogen atmosphere using Pyriss Diamond TG/DTA Perkin-Elmer thermal analysis and Pyriss 7.0 data-processing system at a heating rate of 10 °C min^{-1} over a temperature range of 30–600 °C.

2.6. Contact angle measurements (static sessile drop method)

For the measurements of the contact angle, the mild steel samples above described were used. Prior to any contact angle measurements, the mild steel coupons were carefully cleaned in order to remove surface contamination like grease, dust or organic traces that could influence contact angle measurements through surface pinning of the liquid drop and or contamination of the liquid when the latter is put into contact with the sample surface. Aqueous acid solutions with different concentrations of the HABH were prepared and the samples were then immersed into these solutions for 3 h. Upon removal from the solutions, the samples were dried by means of gently nitrogen flow. Contact angle