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Investigation of Lignosulphonate Mannich Bases as Corrosion Inhibitors

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Abstract: To seek for new acidic corrosion inhibitor, this work used aliphatic amine, formaldehyde and sodium lignosulphonate as the raw materials to prepare new Mannich bases as eco-friendly corrosion inhibitors. The inhibition of these Mannich bases for mild steel corrosion in 2M HCl solution was investigated by weight loss technique. Through the single factor experiments, the optimal mole ratio was determined. Meanwhile, the influences of temperature and inhibitor dosage on the corrosion inhibition performance of the products were studied. The adsorptions on the surface of mild steel and inhibition mechanism were also discussed. Potentiodynamic polarization studies indicate that extracts are mixed-type inhibitors.

Keywords: Sodium lignosulphonate, Mannich base, Acidification, Corrosion inhibitor.

1. INTRODUCTION

Acidification of the low permeable reservoirs is one of the efficient operations to enhance the permeability [1]. While it is also a great challenge for the metal instruments involved in the acidification, and there is a need to improve the resistance properties of the steel against such corrosion in acidic media. Therefore, the most common and effective way is using inhibitor in acid fluid during acidification treatment [2, 3]. Based on field practice, the process of this method is simple, low-cost, and has strong adaptability. Therefore, the development of corrosion inhibitor with good performance, low cost and environmental protection is particularly important.

Lignin is an organic substance binding the cells, fibers and vessels which constitute wood and the lignified elements of plants. Following cellulose, it is the most abundant renewable carbon source on the earth. Between 40 and 50 million tons per annum are produced worldwide as a mostly non-commercialized waste product. Lignosulphonate, a by-product of papermaking industry, is playing an important role in bio-based materials, environment protect, sustainable development and economic benefits [4, 5]. Mannich base is a kind of excellent acidic corrosion inhibitor in nearly several dozens years [6]. In this paper, by using sodium lignosulphonate (LSS) as the raw material, lignosulphonate Mannich bases (LM) were prepared through Mannich reactions and were evaluated for the corrosion inhibition of mild steel in 2M HCl solution.

2. EXPERIMENTAL

2.1. Materials

A commercially available grade of mild steel identified and obtained locally was employed in this study. A small hole of about 5 mm diameter near the upper edge of the coupons was made to help hold them with cotton cords and suspend them into the corrosive medium [7]. Before all measurements the exposed area was mechanically abraded with 100, 600 and 1000 grade emery paper to remove rust particles. Then, the specimens are rinsed by petroleum ether, degreased by ethanol and dried in air. Finally, the coupons were treated through a procedure that consisted of measuring the length, width, thickness and diameter and stored in moisture-free desiccators before use [8].

2.2. Inhibitors

The inhibitor used in this study was synthesized according to the following procedure. The reaction equation was shown as Scheme (**1**). To a certain amount of sodium lignosulphonate in flask containing distilled water, amine was added dropwise under stirring, and then formaldehyde solution was added in dropwise. The mixture was heated to reflux for 3-4 h. After the reaction, the mixture was cooled to room temperature to give the lignosulphonate Mannich bases solution. The reactants and the name of the products were listed in Table **1**. Appropriate concentrations of the corrosion inhibitors were prepared by dilution. The inhibitors' concentration ranges from 100 to 2000mg/L.

2.3. Medium

The corrosive medium for the study was solution of hydrochloric acid. It was prepared by appropriate dilution of

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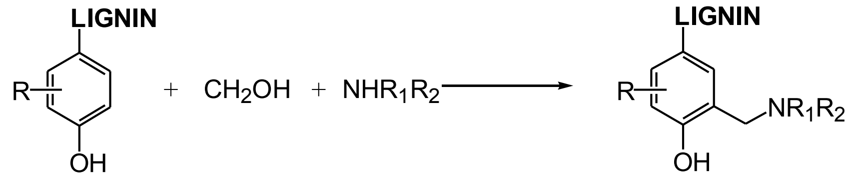

Scheme (1). The Mannich reaction of lignosulfonate.

Table 1. The reaction of lignin sulfonate and different reagents.

Amine	R_1	R_2	Product Name	Solubility
diethylamine	C_2H_5	C_2H_5	LM1	water
morpholine	$(CH_2CH_2)_2O$	$(CH_2CH_2)_2O$	LM2	water
piperazine	$(CH_2CH_2)_2N$	$(CH_2CH_2)_2N$	LM3	water
dimethylamine	CH_3	CH_3	LM4	water
diethanolamine	C_2H_4OH	C_2H_4OH	LM5	water

analytical grade of the acid reagent with double-distilled water without further purification [9]. All corrosion experiments were performed under normal atmospheric pressure.

2.4. Weight Loss Determination

In the weight loss experiment, inhibition efficiency (IE) was determined at 30-60 °C for 2h by hanging two pieces of the mild steel into acid solution (130 mL) containing the synthesized inhibitors with different concentrations (from 100mg/L to 2000mg/L). The weights of the specimens were noted before immersion. After every immersion time of 2h, the coupons were removed, scrubbed with bristle brush under running water in order to remove the corrosion product, washed with acetone, degreased by ethanol, dried and reweighed. From the initial and final weights of the specimens, the loss of weights was calculated, and the corrosion rate was calculated from the following equation 1.

$$V_i = \left(10^6 \Delta m\right) / \left(A_i \bullet \Delta t\right) \quad (1)$$

where V_i is the corrosion rate of a single specimen, Δt is reaction time, Δm is the mass loss during corrosion and A_i is specimen surface area.

The percentage inhibition efficiency (IE(%)) was calculated using the relationship below [15]:

$$IE(\%) = \left(\frac{W_{corr} - W_{corr(inh)}}{W_{corr}}\right) \times 100 \quad (2)$$

where W_{corr} and $W_{corr(inh)}$ are the corrosion rates of mild steel in the absence and presence of inhibitor, respectively.

2.5. Electrochemical Measurements

The electrodes were mechanically abraded with a series of emery papers (800 and 1,200 grades), then rinsed in acetone and double-distilled water before their immersion in the experimental solution. Electrochemical measurements were conducted in a conventional three-electrode thermostated cell. The electrode was inserted into a Teflon tube and isolated with polyester so that only its section (0.5 cm^2) was allowed to contact the aggressive solutions. A platinum disk as counter electrode and standard calomel electrode (SCE) as the reference electrode have been used in the electrochemical studies.

The potentiodynamic curves were recorded using a CS350 system connected to a personal computer. The working electrode was first immersed in the test solution for 60 min to establish a steady state open circuit potential. After measuring the open circuit, potential dynamic polarization curves were obtained with a scan rate of 0.5 mV/s. Corrosion rates (corrosion current densities) were obtained from the polarization curves by linear extrapolation of the anodic and cathodic branches of the Tafel plots at points 100 mV more positive and more negative than the Ecorr.

3. RESUTLS AND DISCUSSION

3.1. Gravimetric Measurements

3.1.1. Effects of Corrosion Inhibitor Dosage and the Types of Amine

The values of the inhibition efficiency, IE(%), obtained by use of weight loss method for different concentrations of LM after 2h immersion at 60 °C are summarized in Fig. (**1**). It is very clear that these compounds inhibit the corrosion of mild steel in 2M HCl solution at all the concentrations used in this study, and that the inhibition rate increases continuously with increasing additive concentration at 333K. The inhibition efficiencies, IE, of modified Mannich bases with various amine are much higher than that of sodium lignosulphonate, the maximum IE of 93.8% was achieved by LM4 at 1000mg/L.

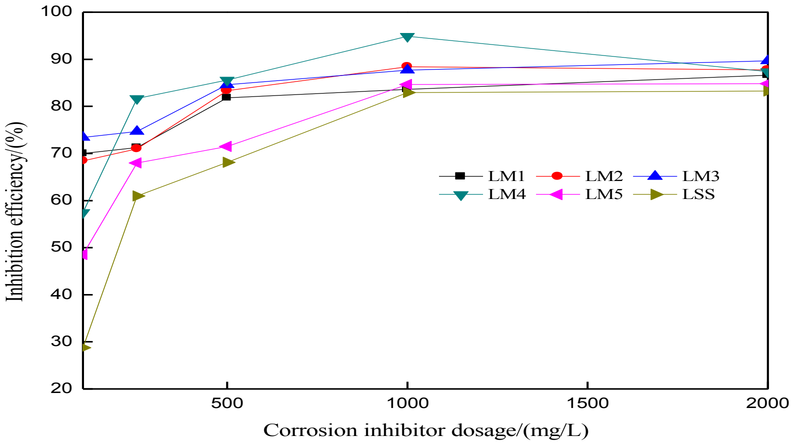

Fig. (1). The inhibition efficiency curves obtained from weight loss measurements of mild steel in 2M HCl in the presence of different concentrations of Mannich base 1-5 at 333K.

Table 2. The inhibition efficiency (IE) obtained from weight loss measurements of mild steel in 2M HCl containing 1000mg/L Mannich bases at different temperatures.

T/°C	Inhibition Efficiency (%)					
	LM1	LM2	LM3	LM4	LM5	LSS
30	75.1	79.9	77.7	81.1	73.1	71.1
45	76.4	88.2	91.0	92.4	81.5	82.2
60	83.5	88.5	87.7	93.8	84.4	82.3

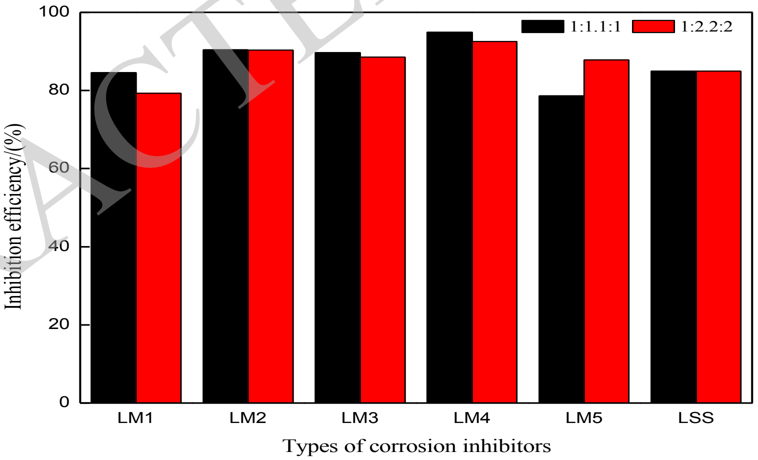

Fig. (2). The inhibition efficiency of different molar ratio at 333 K.

3.1.2. Effect of Temperature

Temperature is an important fact in the studies on metal corrosion inhibition. The effect of temperature on the inhibition rates of mild steel was studied in 2M HCl and in the presence of 1000mg/L Mannich bases. The corrosion inhibition efficiency offered by the Mannich bases in the temperature range of 30 to 60°C after 2h immersion is given in Table **2**. As shown in Table **2**, in the presence of the Mannich bases, the values of the inhibition efficiency increases with increasing temperature, the maximum IE about 94.9% was achieved at 60°C.

3.1.3. Effect of Molar Ratio

Two kinds of corrosion inhibitors which have different molar ratio (sodium lignosulphonate: formaldehyde : amine) of 1:1.1:1 and 1:2.2:2 were used for the present study. The result of inhibition for mild steel in 2M HCl containing 1000mg/L Mannich base is summarized in Fig. (**2**). The results reveal that increasing the molar ratio does not effect the IE effectively. Therefore, from the viewpoint of efficiency and economy, it is not necessary to increase the ratio any more.

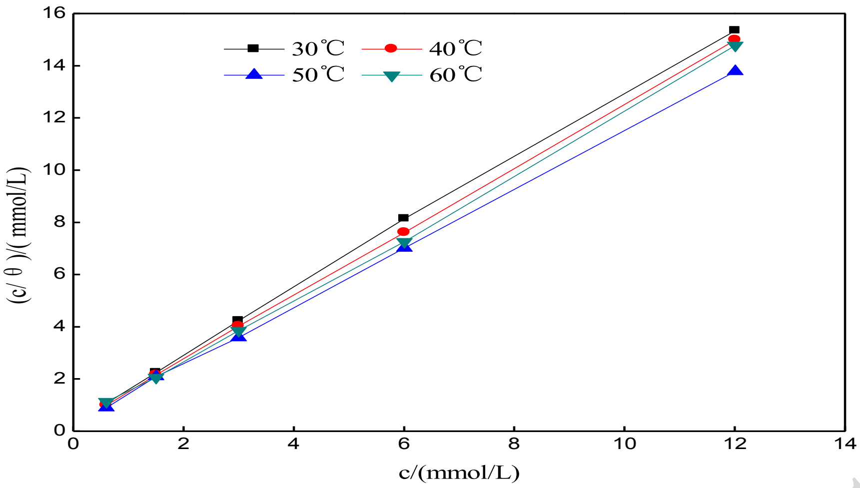

Fig. (3). Langmuir adsorption isotherm of Mannich base LM4 on mild steel in 5 % HCl at different temperatures.

Table 3. (c/θ)- c linear regression parameters of LM4.

T/°C	Correlation Index	Slope	The Adsorption Equilibrium Constant K（L/mol）
30	0.9995	1.2513	2379.25
40	0.9999	1.2223	3330.00
50	0.9998	1.1231	3536.07
60	0.9994	1.1992	3705.06

3.2. Adsorption Isotherm and Thermodynamics Calculations

Since the action of corrosion inhibitors are in most cases believed to be by adsorption on the metal surface by the inhibitor molecules using their adsorption centers, it is a good practice to find out the possible adsorption mode by testing the experimental data. In order to confirm the adsorption of the Mannich bases on mild steel surface, adsorption isotherms were studied. Adsorption isotherms can provide basic information on the interaction of inhibitor and metal surface. Thus, the degree of surface coverage values (θ), at different inhibitor concentrations in 2M HCl was evaluated from weight loss measurements (θ = IE (%)/100) in the temperature range 30°C to 60°C and tested graphically for fitting to a suitable adsorption isotherm using LM4 as the inhibitor [10].

On consideration of the Langmuir adsorption isotherm [11, 12], which is well described by equation 3, it was found that the experimental data gives a straight line graph on a plot of C/θ versus C and fits the adsorption isotherm as shown in Fig. (**3**).

$$\frac{C}{\theta}=\frac{1}{K_{ads}}+C \qquad (3)$$

where K_{ads} is the equilibrium constant of the adsorption process.

Integration of the above data as shown in Table **3**. From Table **3**, the plot of C/θ versus C gives a straight line (Fig. **3**) with a slope of around unity thereby confirming that the adsorption of Mannich bases on mild steel surface in the acids obeys the Langmuir adsorption isotherm [13]. Besides, the adsorption equilibrium constant increases continuously with increasing temperature, therefore, adsorption force also increases.

3.3. Tafel Polarisation Measurements

The anodic and cathodic polarization curves for a mild steel electrode in 2M HCl in absence and presence of different concentrations of LM4 at 298 K are shown in Fig. (**4**). Table **4** shows the electrochemical corrosion kinetic parameters, i.e., corrosion potential (Ecorr), cathodic and anodic Tafel slopes (βa, βc) and corrosion current density Icorr obtained by extrapolation of the Tafel lines. The IE (%) is also calculated from the following equation:

$$E(\%)=\frac{I_{corr}-I_{corr(i)}}{I_{corr}}\times 100 \qquad (4)$$

where Icorr and Icorr(i) are corrosion current densities obtained in the absence and presence of inhibitors, respectively. As it was expected both anodic and cathodic reactions of mild steel electrode corrosion were inhibited by the increase of the LM4. This result suggests that the addition of the LM4

Table 4. Potentiodynamic polarization parameters for the corrosion of the steel in the HCl solution containing LM4.

Concentration (ppm)	Eo (V)	Io (A/cm^2)	Ba (mV)	Bc (mV)	Corrosion rate (mm/a)	IE (%)
0	-0.4544	2.9238×10^{-4}	203.05	130.75	3.4390	
100	-0.4479	1.9190×10^{-4}	179.72	109.45	2.4689	28.0
200	-0.4928	1.8551×10^{-4}	254.15	130.67	1.9121	44.4
500	-0.4822	1.6712×10^{-4}	257.02	132.33	0.6362	81.5
1000	-0.4789	1.0415×10^{-4}	236.26	109.47	0.4789	88.2

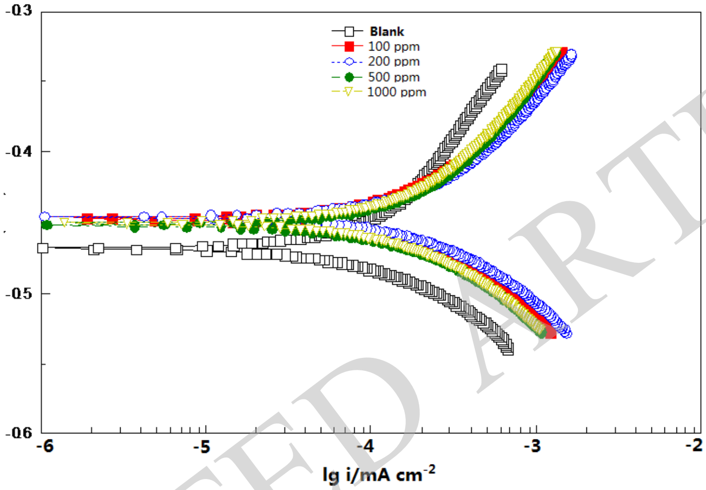

Fig. (4). The polarization curve of steel in 2M HCl solution containing LM4.

reduces anodic dissolution and also retards the hydrogen evolution reaction [14]. It can be seen that the corrosion rate is decreased and inhibition efficiency IE is increased by increasing inhibitor concentration [14]. With a concentration of 1000 ppm, LM4 exhibits maximum IE of 88.2%. Increasing IE with increasing concentration of the LM4 shows that the inhibition actions are due to its adsorption on the steel surface [15]. The IEs obtained from potentiodynamic polarization are quite different from those calculated from weight-loss measurements, which is attributable to the fact that the weight-loss method gives average corrosion rate, whereas electrochemical method gives instantaneous corrosion rates. These differences may arise frequently because of the difference in the time required to form an adsorbed layer of inhibitors on metal surface [15].

CONCLUSION

In this study, the inhibitory effect of eco-friendly inhibitors, lignosulphonate Mannich bases, on the corrosion of mild steel in 2M HCl was investigated. It was found that the inhibition efficiency of the mannnich bases are much higher than that of sodium lignosulphonate, and the results determined that the optimal raw material effect of mole ratio, lignin sulfonate: formaldehyde: amine = 1: 1.1: 1. With the optimum reaction conditons, the maximum IE (%) of 93.8 % was achieved by LM4 at 1000 mg/L at 60°C. The adsorption of these compounds on the steel surface was consistent with the Langmuir adsorption isotherm. Potentiodynamic polarization studies indicate that extracts are mixed-type inhibitors.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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