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Synthesis and Evluation of Lignosulphonate Mannich Base as Eco-Friendly Corrosion Inhibitors

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According to the corrosion of oilfield acidification, this paper mainly used aliphatic amine, methanal and sodium lignosulphonate as the main raw materials to produce a new Mannich base as an eco-friendly corrosion inhibitor. The inhibition of mild steel corrosion in 5 % hydrochloric acid solution by Mannich bases was studied by weight loss technique. Through single factor experiments, determined the optimal mole ratio and the types of raw material are selected. Meanwhile, the influences of temperature and corrosion inhibitor dosage on the corrosion inhibiting performance of the products were studied. Their adsorptions on the surface of mild steel and inhibition mechanism were also discussed.

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

INTRODUCTION

Acidizing is an important EOR technical measure during oilfield exploitation. However, acidizing can cause metal corrosion and lead to serious economic losses and security risks[1,2]. If the acidizing fluid flows into the formation, the geological will be damaged and environmental will be polluted. Therefore, for the oil industry, the most common and effective way is to add inhibitor into acid fluid during acidizing treatment[2,3]. Based on field practice, using inhibitor is an effective method of metal corrosion protection, the process of the 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.

Mannich base is a kind of excellent acidizing corrosion inhibitor in nearly several dozens years[4]. Lignosulphonate, a by-product of paper making industry, is playing an important role in biobased materails, environment protect, sustainable development and economic benefits[5,6]. In this paper, by using sodium lignosulphonate (LSS) as raw materials, sodium lignosulphonate Mannich bases (LM) were prepared through Mannich reactions and was evaluated for the corrosion inhibition of mild steel in 5 % HCl solution.

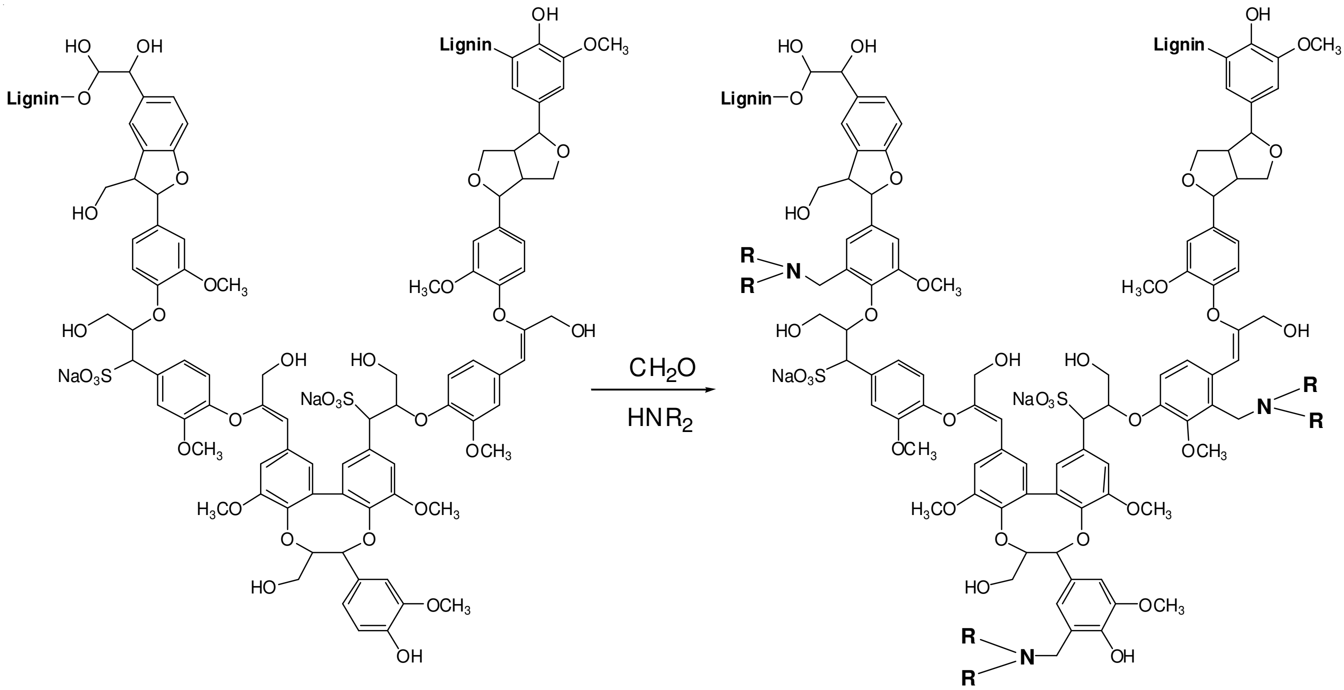
EXPERIMENTAL

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[7-12]. 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[13].

Inhibitors: The inhibitor used in this study was an organic compound with common name *i.e.*, Mannich base, which was synthesized according to the following procedure. The reaction equation was shown as **Scheme-I**.

To a certain amount of sodium lignosulphonate in flask containing distilled water, amine was added dropwise with stirring, then installed the thermometer, condenser pipe and blender, poured into booking volume of methanal solution. The reaction mixture heated to reflux allowed standing for 3-4 h, in which the substance ratio of sodium lignin sulfonate, methanal and amine is 1: 1.1: 1 and 1: 2.2: 2, respectively[14]. 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 range from 100 to 2000 mg/L.

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



Scheme-I: Mannich reaction of lignosulphonate

TABLE-1
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

dilution of analytical grade of the hydrochloric acid reagent with double-distilled water without further purification[13-14]. All corrosion experiments were performed under normal atmospheric pressure.

Weight loss determination: In the weight loss experiment, inhibitor efficiency was determined at 30-60 °C for 2 h by hanging 2 pieces of the mild steel into acid solution (130 mL) containing the synthesized inhibitors at different concentrations (from 100 to 2000 mg/L). The weights of the specimens were noted before immersion. After every immersion time of 2 h, 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 computed from the following eqn. 1.

$$V_i = (10^6\, \Delta m) / (A_i \cdot \Delta_t) \quad (1)$$

where V_i is the corrosion rate of a single specimen, Δt is reaction time, Δm is the mass loss of specimens 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 inhibition, respectively.

RESULTS AND DISCUSSION

Effects of corrosion inhibitor dosage and the types of amine: The values of the inhibition efficiency (%), obtained by use of weight loss method for different concentrations of sodium lignosulphonate Mannich bases (LM) after 2 h immersion at 60 °C are summarized in Fig. 1. It is clear that these compounds inhibit the corrosion of mild steel in 5 % HCl solution, at all the concentrations used in this study and that the inhibition rate increases continuously with increasing additive concentration at 333 K. The inhibition efficiencies, inhibition efficiency (%), of modified Mannich bases with various amine are greater than that of sodium lignosulphonate, the maximum inhibition efficiency (%) of 94.9 % was achieved by LM4 at 1000 mg/L.

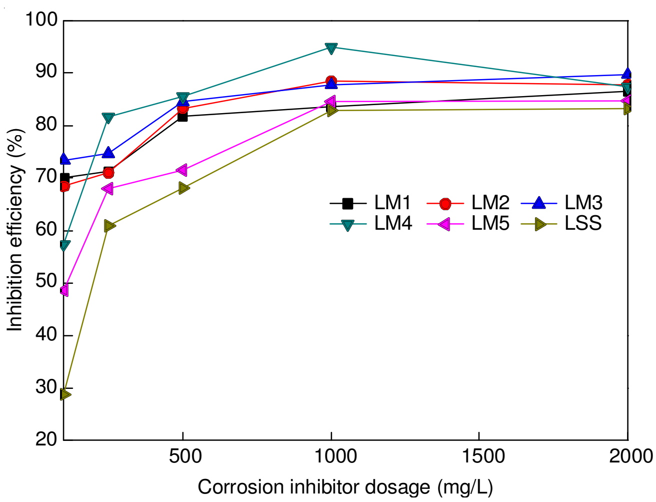


Fig. 1. Inhibition efficiency curves obtained from weight loss measurements of mild steel in 5 % HCl in the presence of different concentrations of compounds **1-5** at 333 K

Effect of temperature: Temperature is an important condition in the studies on metal corrosion inhibition. The effect of temperature on the inhibition rates of mild steel was studied in 5 % HCl alone and in the presence of 1000 mg/L mannich bases. The corrosion inhibition efficiency offered by the mannich bases in the temperature range 30 to 60 °C after 2 h immersion is given in Table-2. As shown in Table-2, in the presence of the mannich bases, the values of the inhibition efficiency increased with increasing temperature, the maximum IE (%) of about 94.9 % was achieved at 60 °C.

TABLE-2
INHIBITION EFFICIENCY (IE) OBTAINED FROM WEIGHT LOSS MEASUREMENTS OF MILD STEEL IN 5 % HCl CONTAINING 1000 mg/L MANNICH BASES AT DIFFERENT TEMPERATURES

T (°C)	Inhibition efficiency (IE %)					
	LM1	LM2	LM3	LM4	LM5	LSS
30	75.6	79.6	77.7	81.2	73.3	71.3
45	76.0	88.9	91.0	94.1	81.2	82.5
60	83.6	88.4	87.7	94.9	84.6	82.9

Effect of synthetic ratio: Two kinds of corrosion inhibitors which have different synthetic ratio, respectively, 1:1.1:1 and 1:2.2:2 were used for the present study. The result of inhibition for mild steel in 5 % HCl containing 1000 mg/L Mannich base is given in Fig. 2. It can be seen from the Fig. 2 that the effect of synthetic ratio on the rate of inhibition corrosion of mild steel in 5 % HCl solution in the presence of 1000 mg/L corrosion inhibitors containning sodium lignosulphonate Mannich bases and sodium lignosulphonate was investigated at 60 °C. The results reveal that increasing the synthetic ratio does not effect the inhibition efficiency effectively. Therefore, from the viewpoint of efficiency and economy, it is not necessary to increase the ratio of synthesis.

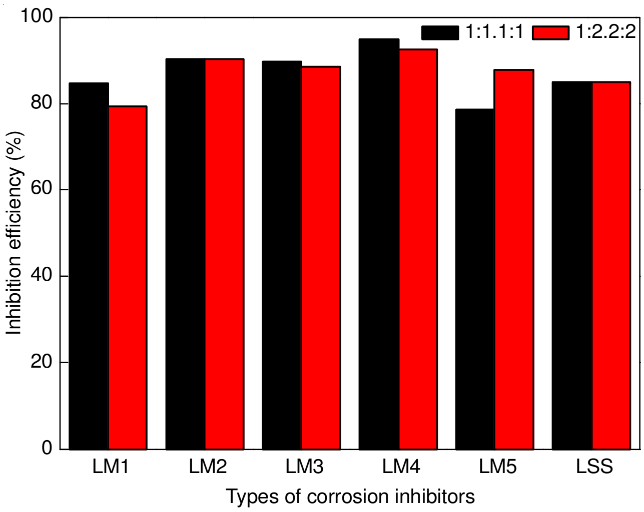


Fig. 2. Inhibition efficiency of different synthetic ratio at 333 K

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 centres, 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 5 % HCl was evaluated from weight loss measurements [θ = IE (%)/100][15] in the temperature range 30 to 60 °C and tested graphically for fitting to a suitable adsorption isotherm.

On consideration of the Langmuir adsorption isotherm[15-17], which is well described by eqn. 3, it has been found that the experimental data gave a straight line graph on a plot of C/θ *versus* C and fitted the adsorption isotherm as shown in Fig. 3.

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

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

Integration[17,18] 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[17,18]. Besides, the adsorption equilibrium constant increases continuously with increasing temperature, therefore, adsorption force also increases. K_{ads} is related to the standard Gibb's free energy of adsorption ΔG_{ads} as per the eqn. 4. Besides, the values of ΔH_0 and ΔS_0 were calculated by eqns. 5 and 6 and are listed in Table-4.

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (4)$$

TABLE-3
(c/θ)-c LINEAR REGRESSION PARAMETERS OF DIMETHYLAMINE MANNICH BASES

T (°C)	Correlation index	Slope	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

TABLE-4
THERMODYNAMIC PARAMETERS FOR ADSORPTION OF SODIUM LIGNOSULPHONATE MANNICH BASES ON MILD STEEL IN 5% HCl SOLUTIONS AT DIFFERENT TEMPERATURES FROM LANGMUIR ADSORPTION ISOTHERM

T (°C)	ΔG_0 (KJ/mol)	ΔH_0 (KJ/mol)	ΔS_0 (J/mol K)
30	-29.72	11.20	134.99
40	-31.57	11.20	136.60
50	-32.74	11.20	135.99
60	-33.89	11.20	135.34

where, R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution (mol/L).

$$\ln K = \frac{-\Delta H_0}{RT} + \text{constant t} \quad (5)$$

where, ΔH_0 is the adsorption enthalpy:

$$\Delta S_0 = (\Delta H_0 - \Delta G_0)/T \quad (6)$$

where, ΔS_0 is the adsorption entropy.

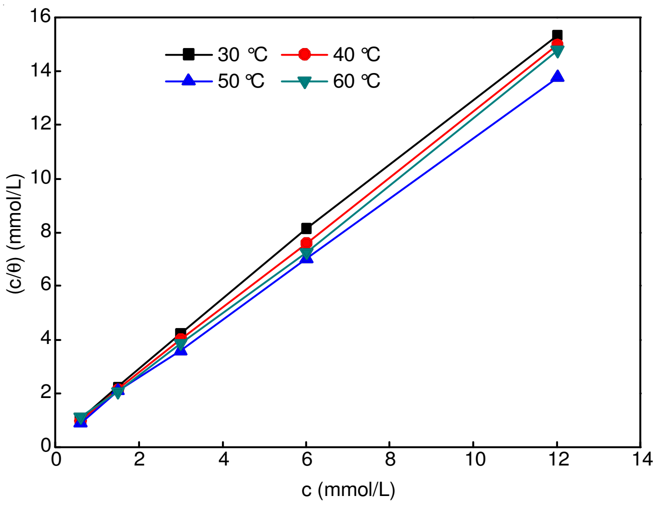


Fig. 3. Langmuir adsorption isotherm of mannich base LM4 on mild steel in 0.5 % HCl at different temperatures

From Table-4, the negative values of ΔG_{ads} suggest that the adsorption of inhibitor molecules onto steel surface is a spontaneous phenomenon. More negative values of ΔG_{ads} suggest the strong interaction of the inhibitor molecules with the metal surface. Generally, values of ΔG_{ads} up to -20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption) while those negative values higher than -40 kJ/mol involve sharing or transfer of electrons from theinhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption)[18-20]. In the present study the value of ΔG_{ads} is about -20 to -40 kJ/mol which supports physisorption and chemisorption of Mannich bases on mild steel. The value of ΔH_0 provides further information about the mechanism of corrosion inhibition. The positive value of ΔH_0 indicates that adsorption process is endothermic. An exothermic adsorption process may be chemisorption or physisorption or mixture of both, whereas endothermic process is attributed to chemisorption. In the present work, the positive value of ΔH_{ads} indicates that the mannich base extracts adsorb on the mild steel surface through physisorption and chemisorption. In short, the adsorption process of this study is spontaneous, endothermic and entropy increase process.

Conclusions

In this study of the inhibitory effect of an eco-friendly inhibitor, lignosulphonate Mannich base, on the corrosion of mild steel in 5 % HCl *via* weight loss method, the following conclusions may be drawn:

• The inhibition efficiencies of the Mannich bases are greater than that of sodium lignosulphonate and the results determined the optimal raw material effect of mole ratio, lignin sulfonate:methanal:amine = 1: 1.1: 1.

• IE of these compounds increased with an increase in the concentration of the inhibitors, the maximum IE (%) of 94.9 % was achieved by LM4 at 1000 mg/L.

• The result showed that the inhibition efficiency has increased with the increasing temperature, the maximum IE (%) of 94.9 % was achieved at 60 °C.

• The adsorption of these compounds on the steel surface was consistent with the Langmuir adsorption isotherm. Besides, the adsorption process is spontaneous, endothermic and entropy increase process.

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