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Investigation of Corrosion Inhibition of Quaternary Ammonium Salt on N80 Steel in 5M HCl Solution

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Abstract: Corrosion inhibition of N80 in 5M HCl solution by pyridine quaternary ammonium salt has been studied by weight loss measurements, potentiodynamic test, Tafel polarization and electrochemical impedance. The results show that corrosion rates of N80 steel decrease with increase of inhibitor concentration in 5M HCl solution at temperature 333K and 363K. The adsorption of inhibitor on N80 steel was studied from the results of the weight loss experiment. The adsorption is in conformity with langmuir isothermal adsorption equation at 333 K, the value of indicates the adsorption were both chemical and physical adsorption.

Keywords: Quaternary Ammonium Salt, Inhibitor, N80 Steel, Corrosion, Absorption

1. Introduction

During oil and gas exploitation, acidization is an effective oil well stimulation technique for enhancing oil productivity. Hydrochloric acid is usually used for acidification. Because of the aggressive nature of the acid and high temperature in oil well, severe corrosion attack on tubing and casing may occurred. To reduce the aggressive corrosion of the acid on tubing and casing materials (N80 steel), inhibitors are commonly used during acidization.

Most of corrosion inhibitors are organic compounds containing polar groups (such as, -NH2, -CHO,-COOH,−OH, etc.) [1-3] or hetero atoms (such as, N, O, S, P, etc.) [4-6]. corrosions are mitigated since these inhibitors molecules are easily adsorbed on the metals surface, especially N-heterocyclic compounds，as they act by adsorption on the metal surface, and the adsorption of N-heterocyclic inhibitor takes place through nitrogen heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures. It was a corrosion inhibitor with superior property to inhibit the corrosion of steel in acid solution [7-9].

Corrosion inhibition of quaternary ammonium salts on N80 steel in 5M HCl solution was investigated by weight loss measurements, potentiodynamic polarization and electrochemical impedance. The steel surface of N80 steel was also examined by scanning electron microscope. Meanwhile, the adsorption thermodynamic parameters and corrosion kinetic parameters were calculated according to adsorption theory and corrosion kinetic formula, based on these parameters, the inhibitive mechanism is discussed.

2. Experimental

2.1. Materialsand Test Solutions

Quaternary ammonium salts were synthesised from pyridine and Benzyl chloride by quaterisation reaction at 160~180°C for 6 hours with water condensation. The synthetic route and molecular structures were shown in figure 1.

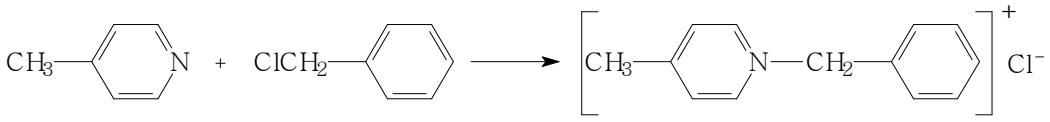

Figure 1. *The synthetic route and molecular structure of pyridine quaternary ammonium salt.*

Tests were performed on N80 steel specimens with following chemical composition (wt.%): C0.240, Si 0.220, Mn1.190,P 0.013, S0.004,Cr 0.036, Mo 0.021,Ni 0.028 and Fe balance. The 5M HCl solution was prepared by dilution of analytical grade 37% HCl with double distilled water.

2.2. Preparation of Electrodes

The working electrode was a cylindrical disc cut from an oil well steel (N80).The metal disc was coated with epoxy resin except its bottom surface with area of 1.0 cm^2. The surface of working electrode was mechanically abraded using different grades of sand papers, which ended with the 1200 grade. The disc was cleaned by distilled water, ethanol, respectively, finally dried with a filter paper.

2.3. Weight Loss Study

The N80 steel specimens used in the weight loss study were cut into desired dimension and the surface preparation was carried out with emery paper grade 600 and 1200, then it was washed with distilled water and acetone and finally dried with cool air. The initial weight of each specimen was noted before immersion using an analytical balance (precision:±0.1 mg). Then the specimens were immersed in 5 M HCl solutions with different concentrations of inhibitors at 333K and 363K for 4h. After immersion, the specimens were washed and reweighed.

The inhibition efficiency IE%, surface coverage degree θ and corrosion rate V_{corr} were obtained by

$$IE\%=(W_0-W)/\ W_0\times100 \quad (1)$$

$$\theta=(W_0-W)/\ W_0 \quad (2)$$

$$V_{corr}=(W_0-W)/st \quad (3)$$

W_0 and W are the weight losses in the absence and presence of the inhibitor, respectively,s is samples surface area, t is immersion time, the unit of V_{corr} is mm y^{-1}.

2.4. Electrochemical Measurements

The electrochemical experiments were performed with PARSTAT 2273 Potentiostat/Galvanostat in a classical three-electrodes cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) coupled to a fine luggin capillary as the reference electrode. The working electrode (WE) was prepared as showed in 2.2. EIS measurement was carried out in 100 kHz-0.1Hz frequency range at open circuit potential (OCP) disturbed with amplitude of 10 mV. The potentiodynamic polarization curves were obtained from -250 mV to +250 mV(versus OCP) with a scan rate of 0.5 mV/s, the data were collected and analyzed by electrochemical software. The inhibition efficiency for each concentration of inhibitors is calculated by

$$IE\%=(I_{corr}-I_{corr(inh)})/I_{corr}\times100 \quad (4)$$

I_{corr} and $I_{corr(inh)}$ were the corrosion current density with and without of inhibitors, respectively.

For EIS measurement, IE(%) was defined as:$IE\%=(R_{ct}-R^0_{ct})/I_{corr}\times100(5)R_{ct}$ and R^0_{ct} were the charge transfer resistance with and without inhibitors, respectively.

2.5. Surface Analysis

The surface morphology of the N80 steel samples after immersion in HCl solution in the presence and absence of the inhibitor, was investigated by using JSM-5600LV scanning electron microscope.

3. Results and Discussion

3.1. Weight Loss Study

The values of corrosion rates and inhibition eficiencies obtained from the mass loss study for different inhibitor concentrations in 5 M HCl solution at 333Kand 363K are summarized in table 1.It was found that the corrosion rates decrease with increase of inhibitor concentration. It is evident from the Table 1 that when the inhibitor concentration is 6.0 mM, the corrosion rates of N80 steel at 333K and 363K decreased from122.77 mm/y to 0.920 mm/y and from341.54 mm/y to 5.976 mm/y respectively, the inhibition efficiencies reaches a maximum value of 99.25%. Table 1 also shows that inhibition efficiency decreases with the experimental temperature, which can be attributed to desorption of inhibitor from the N80 steel surface at the higher temperatures.

Table 1. *Corrosion parameters for N80 steel in 5 M HCl solutions with different concentrations of inhibitors.*

T K	C mM	W_0-W mg·cm-2	V_{corr} mm·y-1	IE %	θ
	Blank	43.732	122.77	—	—
	0.02	8.304	23.315	81.01	0.8101
	0.2	2.720	7.636	93.78	0.9378
333	0.4	1.596	4.48	96.35	0.9635
	2.0	0.695	1.952	98.41	0.9841
	4.0	0.476	1.338	98.91	0.9891
	6.0	0.327	0.920	99.25	0.9925
	Blank	121.65	341.54	—	—
	0.02	28.867	81.044	76.27	0.7627
	0.2	14.573	40.914	88.02	0.8802
363	0.4	8.211	23.053	93.25	0.9325
	2.0	4.050	11.372	96.67	0.9667
	4.0	2.943	8.264	97.58	0.9758
	6.0	2.128	5.976	98.25	0.9825

3.2. Scanning Electron Microscopy

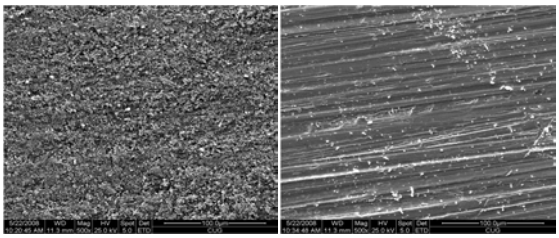

Figure 2. *Scanning electron microscopy of of N80 steel samples after immersion in 5 M HCl(a)without inhibitor (b) with 2.061mM inhibitor.*

Surface examination using SEM (figure 2) was carried out to investigate the effect of inhibitor on the surface morphology of the N80 steel. The surface morphology of the N80 steel specimen after immersion in 5M HCl solution at 333K with no additives for 4 h were shown in figure 2(a).The micrograph reveals that the surface was strongly damaged in the absence of inhibitor. The surface morphology of the N80 steel specimen after immersion in 5 M HCl solution at 333K with 2.0 mM of inhibitor was shown in figure 2(b), it can be seen that the rate of corrosion is suppressed in the presence of inhibitors. It is revealed that there is a good protective film adsorbed on specimens surface, which is responsible for the inhibition of corrosion.

3.3. Potentiodynamic Test

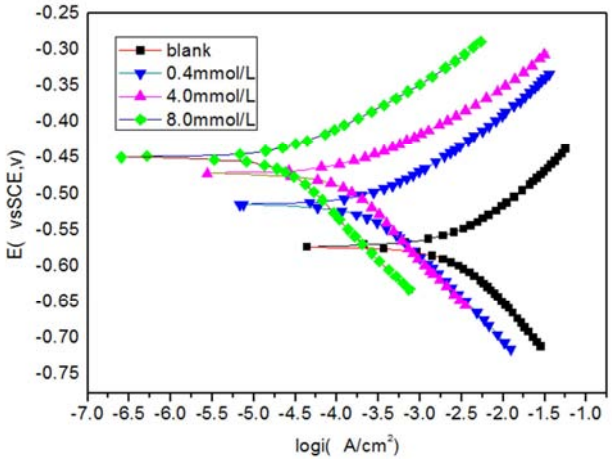

Figure 3. *Potentiodynamic curves of N80 steel in 5 M HCl with different concentrations of inhibitor at 333 K.*

The potentiodynamic curves of N80 steel in 5 M HCl with different concentrations of inhibitors at 333K are shown in figure 3.As seen in figure 3, anodic and cathodic current decreases with the increasing concentration of corrosion inhibitors, this effect is attributed to the adsorption of the inhibitor on the active sites of the metal surface. The similar shape of anodic and cathodic curves with different concentration of inhibitor indicated that the mechanisms of the cathodic hydrogen reduction and anodic metal dissolving did not change.

Table 2 gives the values of corrosion current, corrosion potential, cathodic and anodic tafel slopes, percentage inhibition efficiency are obtained by the anodic and cathodic regions of the tafel plots. It is obvious from table 2 that the slopes of the cathodic (b_a) tafel lines remain almost the same with differentconcentration of inhibitor, but the cathodic slope (b_c) increased after addition of inhibitor. The potentiodynamic curves moves in a more anodic direction, the corrosion potential moved about 124 mV (from -573.2 mV to-449.4 mV) with inhibitor concentration increase from 0 mM to 8 mM. The positive potential shift and large b_c indicated a mixed type in electrochemical mechanism of this system.

The corrosion current density I_{corr} reduces from 532.0μA·cm^{-2} to 7.0μA·cm^{-2} after addition of inhibitor in HCl to 8mM, and the inhibition efficiency is as high as 98.7%. It indicates that corrosion rate of N80 steel in 5 M HCl decreases and present inhibitive effect.

Table 2. *Potentiodynamic parameters of N80 steel in 5 M HCl with different concentrations of inhibitorat 333 K.*

C mM	E_{corr} mV	b_c mV·dec^{-1}	b_a mV·dec^{-1}	I_{corr} μA·cm^{-2}	IE %
Blank	-573.2	75.4	54.8	532.0	-
0.4	-514.5	90.7	55.2	52.2	90.2
4.0	-471.2	121.2	47.6	30.4	94.3
8.0	-449.4	113.5	45.5	7.0	98.7

3.4. Electrochemical Impedance

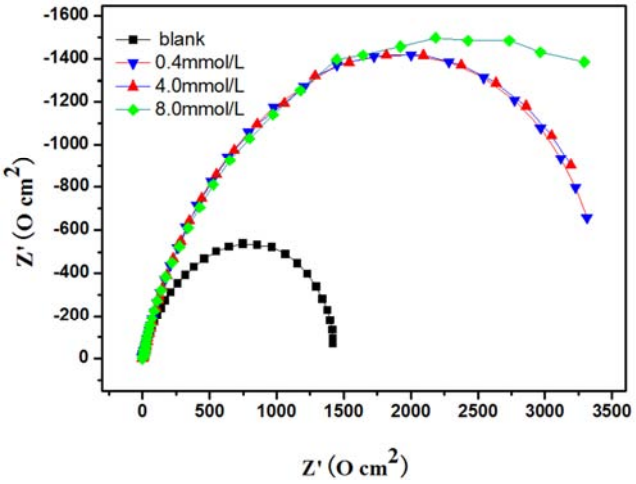

Figure 4. *Nyquist diagrams for N80 steel in 5 mol/LHCl with diferent concentrations of inhibitor.*

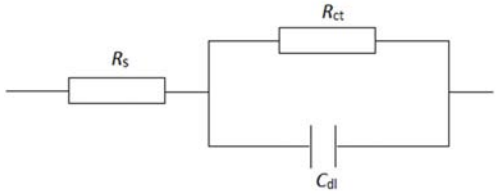

Figure 5. *Equivalent circuit fitted for N80 steel in 5 mol/LHC1with inhibitor at 333K.*

Electrochemical impedance measurements were carried over the frequency range from 100 kHz to 0.1 Hz at open circuit potential. The nyquist representations of impedance

behaviour of N80 steel in 5 M HCl with and without addition of various concentrations of inhibitor are given in figure 4,equivalent circuit fitted for N80 steel in 5 M HC1with inhibitor at 333K was shown in figure 5,electrochemical impedance parameters and the corresponding inhibition efficiencies,the fitted data was shown in Table 3, R_s , R_{ct} and C_{dl} were the solution resistance, charge transfer resistance and interfacial double layer capacitance respectively.

Table 3. *Electrochemical impedance parameters and the corresponding inhibition eficiencies of N80 steel in 5 M HCl with diferentconcentrations of inhibitor.*

C mM	R_{ct} Ω•cm^2	C_{dl} μF•cm^{-2}	IE %
Blank	461	620.20	-
0.4	3770	475.14	87.8
4.0	3886	364.32	88.1
8.0	4658	290.67	90.1

It is seen that addition of inhibitor increases the values of R_{ct} and reduces the C_{dl}. The decrease in C_{dl} is attributed to increase in thickness of electronic double layer [10]. The increase in R_{ct} value is attributed to the formation of protective film on the metal/solution interface [11-12]. The EIS diagrams confirm the higher protection with increasing the concentration of the inhibitor, which is related to adsorption of the inhibitor on the metal surface.

3.5. Adsorption Isotherm and Thermodynamic Parameter

The adsorption of surfactants at metal/solution interfaces can markedly change the corrosion resisting properties of metals. The efficiency of corrosion inhibitors mainly depends on their adsorption ability on the metal surface, so, it is essential to know the mode of adsorption and the adsorption isotherm of corrosion inhibitors.

The surface coverage values are evaluated using corrosion rate values obtained from the weight loss method. Attempts were made to fit the θ values to various isotherms, including Langmuir, Frumkin and Temkin isotherm. By far, the best fit is obtained with the Langmuir isotherm. Langmuir adsorption isotherm is described by the following equations:

$$C_{inh}/\theta = C_{inh}+1/K_{ads} \quad (6)$$

Where C_{inh} is inhibitor concentration, θ is the degree of the coverage on the metal surface and K_{ads} is the equilibrium constant for the adsorption–desorption process.

In order to clarify the nature and the strength of adsorption, the experimental results have been fitted on the assumption that the adsorption isotherm of corrosion inhibitors corresponds to the form of langmuir isotherm, the results of data fitting is presented graphically in figure 6.The correlation coefficient(R^2=0.9999)is close to one confirm this assumption. The average value of K_{ads} have been found to be 5.99×10^4 M^{-1} indicating that the adsorbed inhibitor molecules form monolayer on the mild steel surface and there is no interaction among the adsorbed inhibitor molecules [13]. The standard free energy of adsorption ($\triangle G^0_{ads}$) values of inhibitors are obtained from the following equation and the value of $\triangle G^0_{ads}$ is calculated as-34.07 kJ mol^{-1} at 333 K.

$$\triangle G^0_{ads} = -RT\ln(55.5K_{ads}) \quad (7)$$

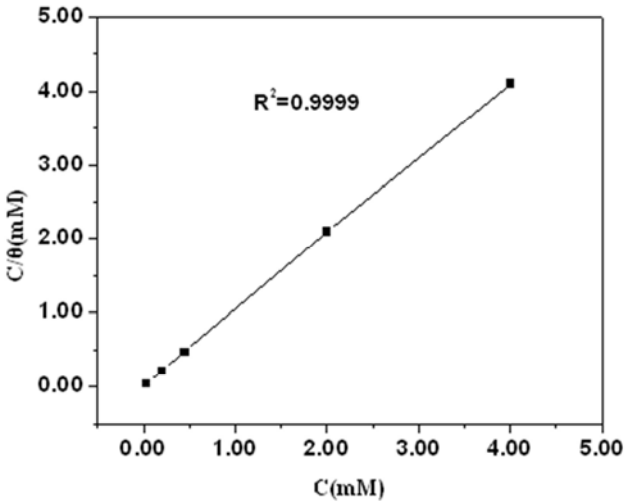

Figure 6. *Langmiur adsorption plots of N80 steel in 5 M HCl with diferent concentrations of inhibitor at 333 K.*

Generally the negative values of standard free energy of adsorption indicate spontaneous adsorption of inhibitor on mild steel surface. The standard free energy of adsorption values of -20 kJ mol^{-1} or less negative are associated with physical adsorption of inhibitor, if the value is-40 kJ mol^{-1} or more negative, it indicated that the adsorption of inhibitor on the steel surface is chemical adsorption [14–15]. The values of standard free energy of adsorption are between -20 kJ mol^{-1} and -40kJ mol^{-1}, it can be concluded that the adsorption takes place through both chemical and physical adsorption [16].

4. Conclusion

Weight loss study showed that the inhibition efficiency of quaternary ammonium salt increases with increase in inhibitor concentration, the inhibition efficiencies reaches a maximum value of 99.25%. Potentiodynamic polarization proved that quaternary ammonium salt is an efficient corrosion inhibitor having mixed type of inhibition property. Electrochemical impedance showed that addition of inhibitor increases the values of R_{ct} and reduces the C_{dl} on account of the formation of protective film on the metal/solution interface. The adsorption of inhibitor on N80 is in conformity with langmuir isothermal adsorption equation at 333 K, the value of $\triangle G^0_{ads}$ indicates the adsorption were both chemical and physical adsorption.

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