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Corrosion Inhibition Effects of Sodium Dodecyl Sulfonate on Zinc Surface in Nitric Acid Solution

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Abstract

In order to study the alkyl sulfonate anion surfactant's corrosion inhibition and adsorption on zinc in nitric acid, the corrosion inhibition of sodium dodecyl sulfonate on zinc in 3wt % Nitric acid was weight under different temperatures and different concentrations of sodium dodecyl sulfonate by weight-loss method and electrochemical method. Results obtained from weight-loss method reveal that the rule of adsorption conforms with Langmuir's isotherm in 0~300mg•dm^{-3} concentration. Electrochemical polarization curve showed Sodium dodecyl sulfonate had corrosion inhibition effects both on the anodic reaction and the cathodal reaction. In the experiment, the data of weight-loss method were analyzed with Sekine method and electrochemical data were treated with Tafel line extension. Some thermodynamic parameters(ΔH^0,ΔS^0,ΔG^0), electrochemical parameters (E_{corr}, I_{corr})and dynamic parameters as activate energy were obtained.

Keywords: Nitric acid; Zinc; Sodium Dodecyl Sulfonate; Adsorption; Polarization

Introduction

In the 1950's, aniline and aniline derivations had been found effectively on corrosion inhibitors for the zinc in nitric acid, after the 1970's alkyl sulfonate oleate could retard the dissolution rate of zinc in nitric acid solution [1]. Since the 2000's, Vashi, R.T discovered that the ethanolamine and ethanolamine derivations have highly corrosion inhibition effects in 0.01mol·dm^{-3} HNO_3 and in 0.01 mol·dm^{-3} HNO_3+HCl binary mixture solution at 301K[2,3]. Since then, Vashi,R.T used chloroanilines to inhibit corrosion of zinc in 0.05 mg•dm^{-3}HNO_3[4]. People wanted to find some effective and non-hazard inhibitors.

Sodium dodecyl sulfonate (SDS) has good adsorbability on the liquid-solid interface and the effective inhibition rate reaches to 85% in 3 wt % HNO_3 at 293K on the concentration of 300 mg•dm^{-3}. The adsorption of such organic compounds has been attributed to different factors such as altering the nature of the corrosion products, chemisorption, rearranging the potential of the surface or changing the resistance. An extensive review of the literatures about the adsorption of

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alkyl sulfonate anion have been performed[5,6,7], but very few studies about the zinc surface in nitric acid reported.

The aim of the present work is to study the inhibition corrosion effects of SDS on zinc in nitric acid solution.

Experimental

Materials

All the chemicals used were of AR grade. The solutions were prepared in triply distilled water. The percentage composition of the zinc samples used was as follows: Pb0.004, Fe0.002, Cu0.001, Zn the remainder.

Weight-loss measurement

The specimen sheet of 20mm×30mm×2mm was abraded with emery paper No.1000 and successively washed with distilled water, alcohol, and acetone. The temperature was in the range of 293-323K. and specimens were immersed in a 100 dm^3 solution with the desired concentrations for 1h. The experimental data were analyzed with Sekine method[8].

Electrochemical polarization

A specimen electrode of 1cm^2 area was used as a working electrode. The assistant electrode consisted of a platinum wire, and the potential was measured by a saturated calomel electrode. The test solution was aerated for 40min before running. The electrode was abraded with wet emery paper of No.1200 grade and was washed by acetone and alcohol. The scanning scope of the potential was -2V to 0.2V and the scanning rate of the potential was conducted at 60 mV /min. The electrochemical data were analyzed with extension method of the Tafel line.

Results and Discussion

Relationship between weight loss of zinc and concentration of SDS at different temperature is shown in **Fig.1**.In general, the corrosion weight loss increased with increasing the temperatures. At any temperature, inhibition effect by SDS is evident on the concentrations under 100mol/L. When the content increase to the certain value, the tend $\Delta W \sim C$ level off and the weight-loss basically unchanged.

It is apparent from these figures that SDS at low concentrations was confirmed to inhibit the corrosion rates by adsorbing on the zinc surface. Therefore, the adsorption at concentration lower than 100 mol·dm^{-3} , which gives excellent inhibition effect. It is investigated to determine whether it follows the Langmuir isotherm. Assuming that the inhibitor forms a monomolecular layer on the zinc surface at the maximum inhibition of corrosion weight loss, the values of surface coverage(θ) of the inhibitor is unity. The θ value can be calculated from the following equation:

$$\theta = (\Delta W_0 - \Delta W) / (\Delta W_0 - \Delta W_m) \quad (1)$$

where ΔW_0 and ΔW are the values of weight loss without and with addition of inhibitor,

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respectively; and ΔW_m is the corrosion weight loss, which gives the maximum inhibition efficiency. A correlation between θ and the concentration (C) of inhibitor in the electrolyte can be represented by the Langmuir adsorption isotherm.

$$\theta = KC/(1+KC) \qquad (2)$$

Rearranging Equation(2),

$$C/\theta = 1/K + C \qquad (3)$$

If the hypothesis above is true, the data of C/θ and C fit straight line with the slope nearly equals to 1.0 and the intercept is $1/K$. Many factors have effects on the weight loss of zinc in the in nitric acid solution, not only the SDS adsorption on the surface of zinc, but also the surface state of zinc, the zinc corrosion electricity, multilayer adsorption occurred, and some other disturbed factors. So it's not exact to use the weight loss method to calculate the values of coverage(θ), that couldn't reveal the SDS adsorption condition on the surface of zinc exactly; so the correction factor is introduced to revise the equation:

$$f\theta = KC/(1+KC)$$

And then: $C/\theta = f/K + fC$

It can be seen that the C/θ and C also fit the straight line, but the slope changes into f and the intercept is f/K, and the condition which the slope doesn't equal to 1.0, is also applicable. So this equation is more suitable and exact.

Where K is the constant of adsorption. The relation between C/θ and C at different temperatures is shown in **Fig.2**. The plots at each temperature were found to yield a straight line, and their slopes have the same trend. Consequently, the adsorption of SDS on the zinc surface at low concentrations follows the Langmuir adsorption isotherm.

The θ value is believed to be equal to the K value of Equation (2). Since the K value at each temperature is determined from the intercept in **Figure.2** and **Table 1**. The adsorption heat (ΔH) can be obtained from the K^0 value applied to the van't Hoff equation:

$$\int d\ln K^0 = \int \frac{\Delta H}{RT^2} dT + B$$

$$\Delta H = \Delta H^0 + aT + bT^2$$

And then: $\ln K^0 = -\frac{\Delta H^0}{RT} + \frac{a}{R}\ln T + \frac{b}{R}T + B \qquad (4)$

where ΔH is the adsorption heat, determined by the temperature, B is the constant. The value of $\ln K^0$ was calculated from the data listed in **Table 1**. The plots of $\ln K^0$ against the temperature (T) yield a curve, and the relation between ΔH and T was obtained from the equation: $\Delta H = \Delta H^0 + aT + bT^2$ = -52.08-895.2T+2.544T^2, through this equation, the adsorption heat was calculated in different temperatures (**Figure3**).

where R and T are constant and absolute temperature, respectively. The ΔG^0 value under different K value has been reported according to Equation (5). The changes of standard entropy were calculated from the simple relationship:

$$\Delta G^0 = -RT\ln k \qquad (5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (6)$$

The calculated values are shown in **Table 2**. It is clear that reaction runs self-movingly for $\Delta G^0<0$. Adsorption entropy $\Delta S^0<0$ illuminates that the adsorption process which takes place on the surface of zinc is decreasing-entropy exothermal process.

Efficiency of corrosion inhibition is decreased with rising the temperature, because the adsorption ability is weaken on zinc with increasing temperature. Reaction of $\Delta H^0<0$ are exothermic.

The electrochemical polarization curves of Zinc in 3 wt % HNO_3 solution at different temperatures are shown in **Figure.4** to **Figure7**. The experimental data were analyzed with extension method of the Tafel line. The corrosion potential E_{corr}, the corrosion electric current I_{corr} and the efficiency of corrosion inhibition are listed in **Table 3,** respectively. It is clear that the corrosion potential of zinc in the presence and absence of SDS has been changed when the temperature increases. SDS is a hybrid type inhibitor[9] by suppressing the anodic and the cathodal corrosion. The efficiency of corrosion inhibitor decreased with increasing the temperature.

The values of corrosion current which are proportional to I_{corr} obtained at different temperatures and the Arrhenius activation energy Ea[10], could be calculated from the following equation:

$$\text{Log k} = -\text{Ea}/2.3\text{RT} + \text{C} \qquad (7)$$

where K is the slope of straight lines which yielded by using log I_{corr} against $1/T$ **(Fig 8)**. It can be seen that the presence of inhibitor enhances the activation energy as shown in **Table 4** and retards the dissolution of zinc in HNO_3 solution.

Conclusions

The rule of adsorption conforms with Langmuir isotherm. Oxygen of SDS structure adsorbed on the zinc surface and alkyl formed hydrophobe membrane. The result leads that zinc and HNO_3 solution are separated to retard the dissolution of zinc in HNO_3 solution. Corrosion potential of zinc in the presence and absence of SDS with increasing temperature has been changed, but there is little difference between corrosion potentials in the presence and absence of inhibitor. SDS is hybrid type inhibitor and both relieve the anodic's corrosion and the cathodal's corrosion. Through increasing the activation energy, SDS makes the dissolution of zinc in HNO_3 solution difficult.

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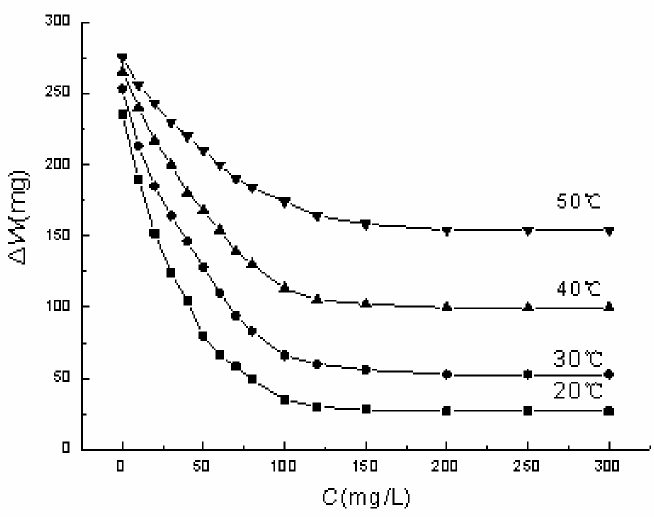

Fig.1. Relationship between weight loss of zinc and concentration of SDS at different temperature

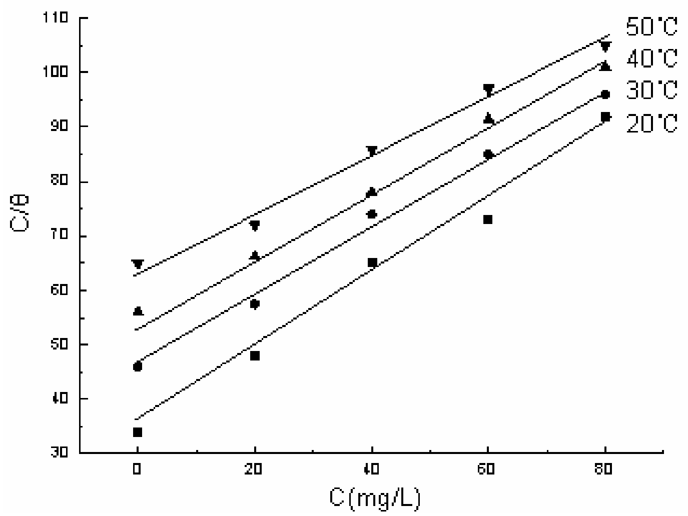

Fig.2. Langmuir adsorption isotherm of SDS on zinc surface at different temperatures

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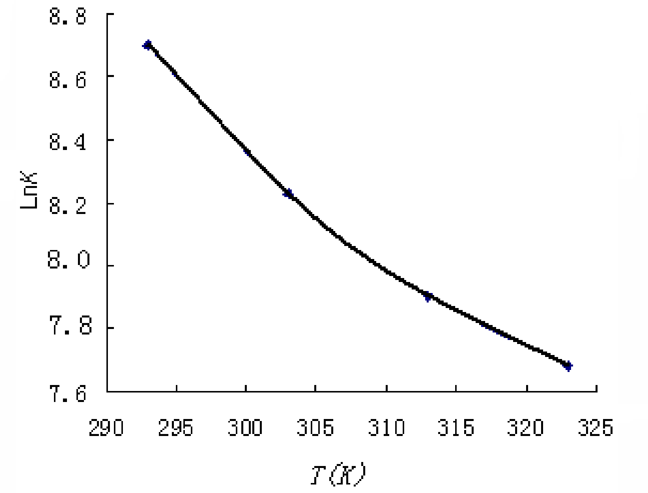

Fig .3. Arrhenius plots of zinc in 3% HNO_3 in the presence of SDS

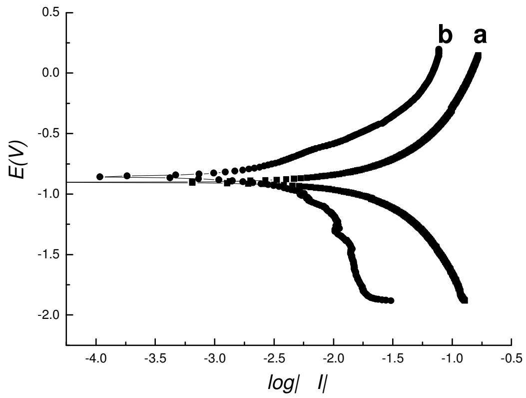

Fig.4. Polarization curves of zinc in HNO_3 at 20℃ (a) without inhibitor (b) 100mg•dm^{-3}SDS

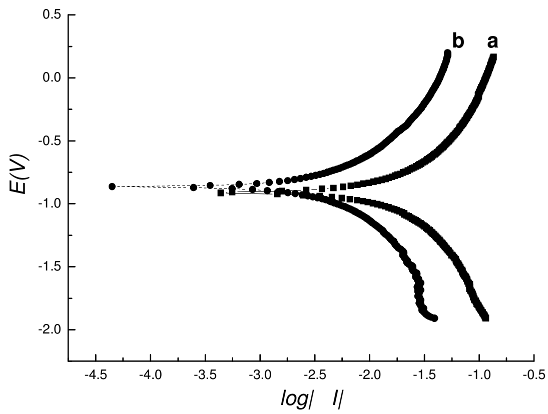

Fig.5. Polarization curves of zinc in HNO_3 at 30℃ (a) without inhibitor (b)100 mg•dm^{-3}SDS

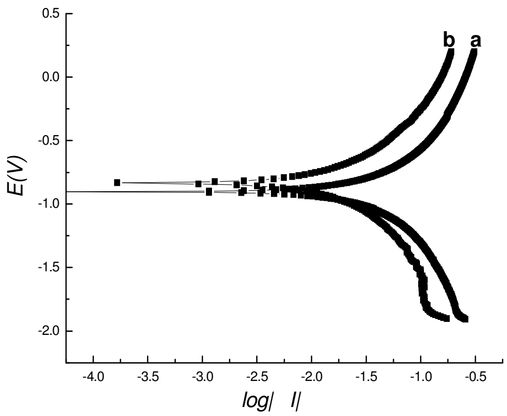

Fig.6. Polarization curves of zinc in HNO_3 at 40℃ (a) without inhibitor (b) 100 mg•dm^{-3}SDS

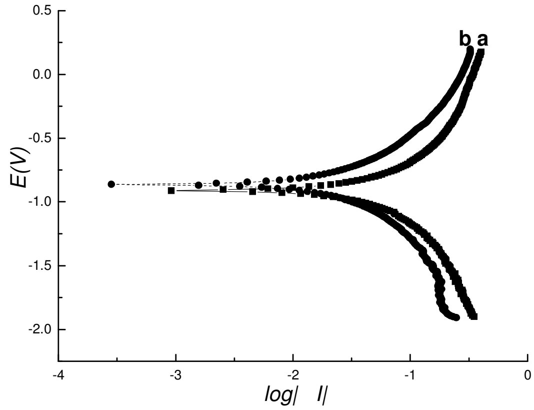

Fig.7. Polarization curves of zinc in HNO_3 at 50℃(a) without inhibitor (b) 100 mg•dm^{-3}SDS

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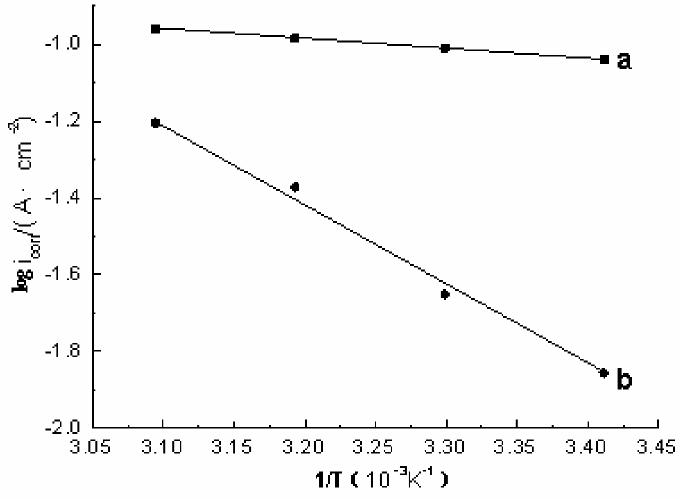

Fig.8. log i_{corr} ~ 1/T

Table 1 The relations between temperature and some other parameters (Inhibition Efficiency= IE)

Temperature	Correlation	*f* /*K*	Slope *f*	*K* (×10³)	IE (%)
20	0.9944	34.05	0.7051	5.651	87.50
30	0.9972	46.20	0.6375	3.753	78.49
40	0.9987	55.48	0.5762	2.825	61.73
50	0.9898	64.61	0.5150	2.168	43.06

Table 2 Thermodynamic parameters increment of the adsorption process

temperature	ΔH^0	ΔG^0	ΔS^0
20	-44.19	-21.07	-78.87
30	-38.00	-20.75	-56.90
40	-31.30	-20.69	-33.88
50	-24.33	-20.63	-11.45

Table3 Parameters for corrosion of zinc in HNO_3 solution at different temperatures

temperature (℃)		E_{corr}/V	I_{corr}/(A·cm^{-2})	IE/%
20	Without inhibitor	-1.031	0.0912	84.78

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	With SDS	-0.9472	0.0139	
30	Without inhibitor	-0.9893	0.0974	77.06
	With SDS	-0.9926	0.0223	
40	Without inhibitor	-0.9685	0.1035	58.96
	With SDS	-0.9093	0.0425	
50	Without inhibitor	-0.9364	0.1097	43.13
	With SDS	-0.8991	0.0624	

Table 4 Activation energies of zinc in the presence and absence of inhibition

solution	Slope K	Correlation Coefficent R	Ea(kJ/mol)
HNO_3	-0.2512	0.9998	4.803
SDS	-2.119	0.9964	40.52