

Study on Synthesized Polyamide Surfactant as a Corrosion Inhibitor

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الخلاصة

حضر بولي اميد منشط للسطوح جديد مشتق من مفاعلة سداسي مثيلين ثنائي الامين وثنائي الاثيلين رباعي حامض الخليك وتم تشخيصه بوساطة مطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي. تم إجراء سلسلة من القياسات الكهروكيميائية، بما في ذلك احتمال التآكل والصدأ الانية على عينات الكاربون الصلب المغلفة بمادة البولي اميد في بيئة تأكل مكونة من حامض الهيدروكلوريك بتركيز 0.1 مولاري. وأظهرت النتائج أن مادة البولي اميد يمكن أن تقدم بعض درجات الحماية في بيئات التآكل لمادة الكاربون الصلب من حمض الهيدروكلوريك، والتي يمكن أن تشير إلى الاستخدامات كمواد مضادة للتآكل.

Abstract

The gemini surfactant polyamide derived from Hexa methylene diamine and ethylene diamin tetraacetic acid [(2,2'-1,22-diamino-8,15-dioxo-7,10,13,16-tetraazadocosane-10,13-diyl) diacetic acid] was synthesized according to the previous our work ^[1]. A series of electrochemical measurements, including corrosion potential and corrosion current has been made on polyamide-coated carbon samples in corrosive environment. Results showed that polyamide can offer some degrees of protection in the corrosive environments. The thermodynamic functions of dissolution, activation energy and adsorption processes were calculated and discussed. Adsorption of the inhibitor was found that a follow the Langmuir adsorption isotherm. The corrosion study of this polymer outline that a new surfactant has a good resistant to the corrosion of carbon steel in 1 M solution of HCl.

Keywords: *Surfactant; Polyamide; Corrosion.*

Introduction

Corrosion is one of the most serious problems in the industrial world. In the last few years the use of conducting polymers for protection of metals against corrosion has been investigated ^[2]. Organic surfactants exhibit an inhibition effect in low concentration against the mild steel in sea water ^[3]. If an inhibitor reacts with ferric or ferrous ion to form a sparingly soluble chelate compound, a deposited layer of the compound covers the iron surface, resulting in a high-inhibition effect on iron corrosion^[4].

It was found that an increase in inhibitory action was observed when the concentration of surfactant in the corrosive solution approached the critical micellar concentration (CMC).

Above this value, the efficiency remains constant and there is no further increase with increasing the surfactant concentration ^[5]. The effect of adding surfactants with different types of hydrophilic groups to commercial inhibitor was studied in order to improve their performance as a corrosion inhibition for steel^[6]. In previous studies, they have shown that there is a relationship between inhibitory properties of certain compounds and their hydrophobic character ^[7]. In recent years, preparation of polymer materials either soluble or insoluble in water with various functional groups has been developed, which can adsorb metal ions in aqueous and non-aqueous media. In general, functionalized polymers for metal ion complexation can be prepared either by derivation of a basic polymer (precursor) with the desired ligand or by polymerization of the corresponding ligand derivative ^[8].

The aim of this work was to indicate the effect of surfactants' hydrophilic groups and to clarify the role of these compounds as corrosion inhibitor for carbon steel in 1 M solution of HCl.

Experimental

Materials and Instruments

EDTA, HMDA, acetic anhydride were purchased from Merck and used without any further purification. Pyridine and dimethyl formamide were distilled before use. The infrared spectra were recorded in the 4000-400 cm⁻¹ range from a Fourier transform Shimadzu spectrometer. The materials which used in the present study were carbon steel coupons of rectangular shape in (53.5 × 1.8 × 0.3) cm size having composition 0.3% C, 1.5% Mn, 0.05% p, 0.06% S, 98.39 Fe. The aggressive solutions of (1 M HCl) were prepared by dilution of analytical grade 37% HCl with doubly distilled water.

Inhibitor Preparation

EDTA-hexamethylene diamine (polyamide) was prepared as in previous our work ^[1] by mixed of (0.51 gm, 0.001 mole) of (EDTA-DA) that dissolved in 10 ml of toluene with (0.33 gm, 0.002 mole) of HMDA in a 100 mL-flask equipped with a condenser and a magnetic stirrer. The reaction was carried out at 45°C for 7hr. After that the product was drying under rotary evaporator then, purified by recrystallization with acetone. The formation reactions of poly amide was given in

Results and Discussion

Adsorption Isotherm

The adsorption isotherm can be outline the basic information of the interaction between the inhibitor and the carbon steel surface. Several attempts were made to fit various isotherms including Langmuir isotherms, Temkin, Frumkin, Freundlich, Bockriss, and Flory – Huggins [9]. In the present study we applied the best fitted by Langmuir adsorption isotherm. According to this isotherm, the surface coverage (θ) is related to the inhibitor concentration (C) by [10]:

$$\frac{\theta}{1-\theta} = K_{\text{ads}} \cdot C \quad \dots\dots\dots(1)$$

Rearranging and integration of eq.(1) gives:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad \dots\dots\dots(2)$$

The **Figure 1** shows a fitted straight line which is obtained from the plots of C/θ versus C with slopes close to 1 and the parameters are listed in **Table 1**. The strong correlation ($R^2 > 0.99$) suggest that the adsorption of the inhibitor on carbon steel surface obeyed the Langmuir adsorption isotherm. Also, the **Table 1** shows that the adsorption equilibrium constant (K_{ads}) value decreases with increasing of temperature, which indicates that, it is easily and strongly adsorbed on the carbon steel surface for the inhibitor at relatively lower temperature. But when the temperature was relatively higher, the adsorbed inhibitor tended to desorb from the carbon steel surface [11].

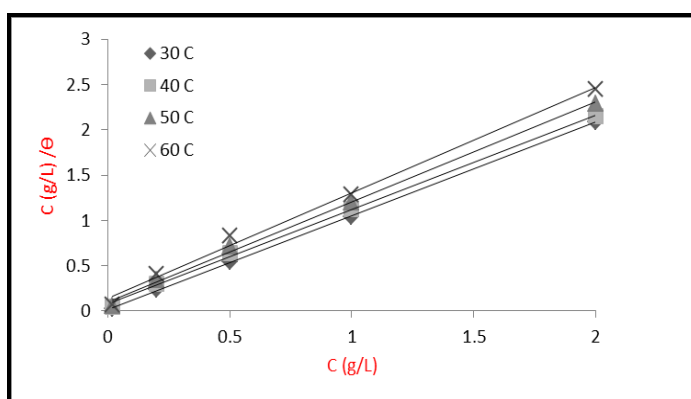


Fig. 1: Langmuir adsorption isotherm model of polyamide in 1 M HCl solution on carbon steel surface at different temperatures.

Table 1: Adsorption parameters for polyamide obtained from Langmuir adsorption isotherm at different temperatures.

<i>Temperature</i>	<i>Adsorption parameters</i>			
<i>°C</i>	<i>R²</i>	<i>Slope</i>	<i>Intercept</i>	<i>K_{ads}</i>
30	0.894	1.032	0.017	47.983
40	0.963	1.047	0.063	12.984
50	0.996	1.105	0.102	10.853
60	0.953	1.198	0.152	7.789

Thermodynamic Functions of the Adsorption Process

The standard free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) can be obtained from the following equation ^[12].

$$\Delta G^{\circ}_{\text{ads}} = -R T \text{Ln. } K_{\text{ads}} \quad \dots \dots (3)$$

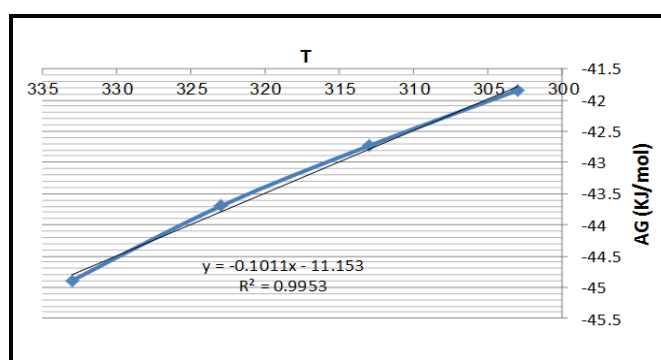
Where (K_{ads}) is the constant of adsorption. The adsorption heat ($\Delta H^{\circ}_{\text{ads}}$) and entropy ($\Delta S^{\circ}_{\text{ads}}$) can be obtained by the thermodynamic basic equation ^[13].

$$\Delta G^{\circ}_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} - T\Delta S^{\circ}_{\text{ads}} \quad \dots \dots \dots (4)$$

Figure 2 shows the variation of $\Delta G^{\circ}_{\text{ads}}$ versus T. A straight line was obtained, the slope gives $\Delta S^{\circ}_{\text{ads}}$ and the intercept leads to $\Delta H^{\circ}_{\text{ads}}$. All the values of the thermodynamic parameters for the adsorption of polymer surfactant are listed in **Table 2**. The negative value of ($\Delta G^{\circ}_{\text{ads}}$) suggest that the adsorption of inhibitor molecules on carbon steel surface is a spontaneous process. Generally, values of ($\Delta G^{\circ}_{\text{ads}}$) up to (-20 kJ mol^{-1}) are consistent with the electrostatic interaction between the charged molecules and charged metal (physical adsorption) while those more negative than (-40 kJ mol^{-1}) involve sharing or charge transfer to form a coordinate bond (chemisorptions) ⁽¹⁴⁾. The value of ($\Delta G^{\circ}_{\text{ads}}$) for the polyamide was around (-40 kJ mol^{-1}) therefore; that the adsorption mechanism of it on carbon steel surface in 1 M HCl solution was chemisorptions. An exothermic adsorption process ($\Delta H^{\circ}_{\text{ads}} < 0$) may involve either physisorption or chemisorptions or a mixture of both processes ^[15]. Also, the negative value of ($\Delta H^{\circ}_{\text{ads}}$) shows that the adsorption is exothermal with an ordered phenomenon ascribed by the negative values of ($\Delta S^{\circ}_{\text{ads}}$).

Table 2: Thermodynamic parameters for the adsorption of polyamide on carbon steel surface in 1 M HCl solution at different temperatures.

<i>Temp.</i> <i>T</i>	<i>K_{ads}</i> <i>(L/g)</i>	ΔG°_{ads} <i>(kJ mol⁻¹)</i>	ΔH°_{ads} <i>(kJ mol⁻¹)</i>	ΔS°_{ads} <i>(kJ mol⁻¹ K⁻¹)</i>
303	12.72	-41.843	-50.83	-0.0863
313	5.874	-42.730		-0.0784
323	4.742	-43.698		-0.0832
333	3.953	-44.889		-0.0794

**Fig. 2:** The variation of ΔG°_{ads} versus T.

Thermodynamic Activation Functions of the Corrosion Process

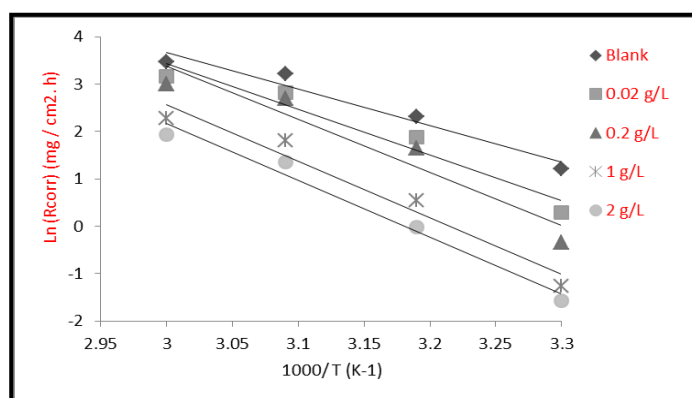
The adsorption phenomenon has been successfully explained by thermodynamic parameter, to further elucidate the inhibition properties of inhibitor (polyamide), the kinetic model was another useful tool to explain the mechanism of corrosion inhibition for the inhibitor. The activation parameters for the corrosion process were calculated from Arrhenius equation ^[16]:

$$R_{\text{corr}} = A \exp \left(-\frac{E_a}{RT} \right) \quad \dots\dots\dots(5)$$

Where; E_a represent the apparent activation energy, R the gas constant, A the pre – exponential factor and R_{corr} is the corrosion rate. Arrhenius plots for the corrosion rate of carbon steel were given in **Figure 3**. Values of E_a for carbon steel in 1 M HCl with polyamide at different concentrations were calculated by linear regression between $\ln R_{\text{corr}}$ and $1/T$. results were shown in **Table 3**.

Table 3: Activation parameters for the dissolution of carbon steel in 1 M solution of HCl with different concentrations of polyamide.

Additives	Conc. (g/L)	E_a (kJ mol ⁻¹)	ΔH_a° (kJ mol ⁻¹)	ΔS_a° (kJ mol ⁻¹ K ⁻¹)	$E_a - \Delta H_a^\circ$
Blank polymer	0.0	61.794	64.583	-27.942	2.31
	0.02	79.365	72.489	15.469	2.31
	0.2	91.859	90.359	63.743	2.31
	0.5	101.385	94.580	79.805	2.31
	1	98.385	96.396	65.938	2.31
	2	100.648	97.985	62.695	2.31

**Fig. 3:** Arrhenius plots of $\ln(R_{\text{corr}})$ versus $1/T$ for carbon steel in 1 M HCl solution with polymer at different concentrations.

Conclusion

The gemini surfactant was synthesized. A series of electrochemical measurements, including corrosion potential and corrosion current has been made on polyamide-coated iron samples in corrosive environment 1 M solution of HCl. It was found that corrosion potential of the polyamide-coated samples was shifted toward noble potentials indicating better performance of decrease in corrosion current. Also from this study the following results can be drawn: Firstly, the inhibition efficiency increases with increase in the concentration of the inhibitor and decreases with an increase in temperature. Secondly, the surfactant polyamide is adsorptive inhibitor and their adsorption obeys the Langmuir's adsorption isotherm. Finally, thermodynamic adsorption parameters such as $\Delta G_{\text{ads}}^\circ$, $\Delta H_{\text{ads}}^\circ$ and $\Delta S_{\text{ads}}^\circ$, show that the inhibitor are adsorbed by a spontaneous exothermic process and a chemisorptions process can be suggested for the inhibitor.

References

- 1) Hussain M. Sh. and Khalaf U.J.[2014]: Anticorrosive properties of polyamide on the carbon steel. Journal of Basrah researches (sciences)., 2A, 40.
- 2) McAndrew T.P.[1997] : Corrosion of polyaniline-coated steel in high pH electrolytes.Trends Polym. Science, 5, 7–11.
- 3) G.B. Hatch G.B. and P.H. Ralsto P.H.[1972]: Cathodic Protection and Isolation Solve Corrosion Problems of Oxygen Corrosion Control in Flood Waters. Materials Protection and Performance, Vol. 11.39.
- 4) Truesdell J.W. M.R. and Van De Mark M.R.[1982]:[Chelating-Polymer Adsorption Effects on Corrosion of Steel](#). J. Electrochem. Soc., Vol. 129 , 2673.
- 5) Hettiarachchi S., Chan Y.W., Wilson R.B. Jr R.B. and Agarwala V.S.[1989].Corrosion,Vol. 45, 30.
- 6) Pebere N., M. Duprat M. and F.J. DabosiF.J.[1988].Applied Electrochem.18 ,225.
- 7) Growcock F.B.[1987]: Inhibition of Steel Corrosion in HCl by Derivatives of Cinnamaldehyde. Society of Petroleum Engineers of AIME, Richardson, TX, USA SPE16265 . 248.
- 8) Warshawsky A.[1988]: Polymeric ligands in hydrometallurgy. In: Syntheses and Separations using Functional Polymers ,Sherington D.C. and Hodge P. (Eds.), John Wiley, Chichester.325-332.
- 9) James A.O. and Akaranta O.[2009].. African J. Pure and Applied Chemistry. 3, 262 – 168.
- 10)Milic S.M. and M. M. Antonijevic M.M.[2009].Corrosion Science. 51, 28 – 34.
- 11)Zhang D., Cai Q., He X., Gao L. and G. Kim.[2009].Corrosion Science 51, 2349 – 2354.
- 12)Aljourani J., Raeissi K. and Golozar M.[2009].Corrosion Science .51, 1836 – 1843.
- 13)Herrag L., Chetouani A., Elkadiri S., Hammouti B., and Aouniti A.[2008]. Portugaliae Electrochimica Acta. 26,211 – 220.
- 14)Zhang S., Tao Z., Li W., and Hou B.[2009]. Applies Surface Science.255, 6757 – 6763.
- 15)Mohana K.M. and Badiea A.M.[2008]. Corrosion Science . 50, 2939 – 2947.
- 16)Larabi L., Benali O., and HarekY.[2006]. Portugaliae Electrochimica Acta.24, 337 – 346.