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중탄산소듐 용액에서 납의 부식방지제인 자연산물질들

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Natural Occurring Substances as Corrosion Inhibitors for Tin in Sodium Bicarbonate Solutions

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요 약. 0.1 M 중탄산소듐 용액에서 납전극부식에 대한 로소니아, 감초뿌리 및 카로브 추출물수용액의 부식방지작용에 대한것을 정전류극성방법을 사용해 연구하였다. 이들 물질들의 부식방지작용을 지적해주는 것으로 이들 물질들이 존재할 때 부식속도가 감소하는 것이 발견되었다. 부식방지효율은 추출물농도가 증가하면 증가한다. 이들 추출물의 부식방지작용은 납표면에 이들 추출물이 흡착되어 물질 및 하전이동의 장벽을 만들어 나타내는 것으로 설명되었다. 이들 추출물의 납표면에 흡착은 자발적으로 일어나며, Freundlich 등온흡착을 따르는 것으로 발견되었다. 또한, 변전위양극분극법을 사용해 이들 추출물은 염소를 포함한 용액에서 납의 움푹패이게 하는 부식으로부터 잘 보호해주는 것이 발견되었다.

주제어: 부식방지제, 납, 로소니아, 감초뿌리, 카로브, 자연산물질

ABSTRACT. The inhibitive action of the aqueous extract of lawsonia, licorice root and carob toward the corrosion of tin electrode in 0.1 M NaHCO_3 solutions was investigated using galvanostatic polarization measurements. It was found that the corrosion rate decreases in the presence of these extracts indicating the inhibiting of these compounds. The inhibition efficiency increases with increasing extract concentration. The inhibition action of these extracts was explained in view of adsorption of its compounds onto the tin surface, making a barrier to mass and charge transfer. The adsorption of these extracts on the tin surface was found to be a spontaneous process and follow Freundlich adsorption isotherm. It is also found that these extracts provide a good protection to tin against pitting corrosion in chloride containing solution using potentiodynamic anodic polarization technique.

Keywords: Corrosion inhibitor, Tin, Lawsonia, Licorice root, Carob, Natural products

INTRODUCTION

The corrosion studies of tin are closely related to its wide application in industry. The corrosion behavior of tin and its inhibition has been studied galvanostatically and potentiodynamically in alkaline media.¹⁻¹⁰ Most of corrosion inhibitors are organic compound having hetero atoms in their aromatic or

long carbon chain. However, there is increasing concern about the toxicity of most corrosion inhibitors. The toxic effect does not only affect living organisms but also poison the environment.¹¹ Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors.¹² Inhibitors in this class are those that are environmentally friendly and are gotten from natural product

such as plant extract.¹³ Several studies have been carried out on the inhibition of corrosion of metals by plant extract.¹⁴⁻²⁰

The aim of this work is to study the effect of some natural occurring substances e.g. aqueous extract of lawsonia, licorice root and carob on the corrosion of tin in 0.1 M NaHCO₃ solution using galvanostatic polarization measurements. Moreover, the ability of these compounds to inhibit the pitting corrosion in chloride containing solution was investigated using potentiodynamic anodic polarization technique.

EXPERIMENTAL

The working electrode was made of tin rod (99.999%) axially embedded in Araldite holders to obtain an exposed circular area of 0.53 cm². Before being used, the electrodes were polished successively with different emery papers until 1200 grads, degreased with acetone and then rinsed with distilled water. A Pt foil was used as a counter electrode. The potential was measured against a saturated calomel electrode (SCE) as a reference. All solutions were freshly prepared using analytical grade chemicals and distilled water. Dry lawsonia, licorice root and

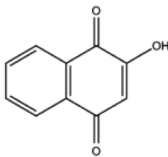
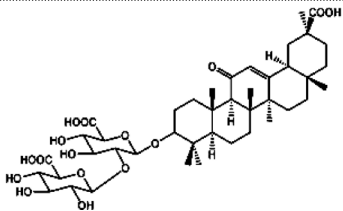
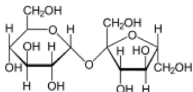
carob were finely divided and extracted in water for 48 h. The filtrate was evaporated in a steam bath and the solid residue was left overnight in open air for complete dryness. The main components of the plants extracts are present in Table 1. A stock solution was prepared, by weight, from the collected solid and used to prepare the desired concentration by dilution. All experiments were carried out at room temperature 25 ± 1 °C. Galvanostatic and potentiodynamic anodic polarization techniques experiments were carried out using a PS remote potentiostat with PS6 software.

RESULTS AND DISCUSSION

Galvanostatic polarization

Fig. 1 represents the anodic and cathodic polarization curves of tin electrode in 0.1 M NaHCO₃ solutions devoid of and containing different concentrations of lawsonia extract. Similar curves were obtained for the other two extracts licorice root and carob extract (not shown) but their corrosion parameters are given in Table 2. Inspection of this figure reveals that the polarization curves shift toward more negative potential and lower current density values upon the addition of the extract. This beha-

Table 1. The main components of the extracts of the plants used as inhibitors.

Inhibitors used	Main component	Molecular formula	Chemical structure formula	Iupac name	Ref.
Lawsonia	Lawsone	C ₁₀ H ₆ O ₃		2-Hydroxy-1,4-naphthoquinone	21
Licorice root	Glycyrrhizin	C ₄₂ H ₆₂ O ₁₆		(3-β,20-β)-20-Carboxy-11-oxo-30-norolean-12-en-3-yl 2-O-β-D-glucopyranuronosyl-α-D-glucopyranosiduronic acid	22
Carob	Sucrose	C ₁₂ H ₂₂ O ₁₁		Sucrose	23

avior reflects the inhibitive action of lawsonia extract. The corrosion parameters of tin electrode in the free and inhibited NaHCO_3 solutions were obtained from the curves of Fig. 1 and given in Table 2. The data in Table 2 show that the corrosion potential shifts to more negative values as the concentration of added extract is increased. Moreover the corrosion current density decreases markedly on addition of the extract indicating the inhibiting effect of these extracts. The inhibition efficiency increases with increasing extract concentration.

Further inspection of Table 2 reveals that, both the anodic and cathodic Tafel constants increase

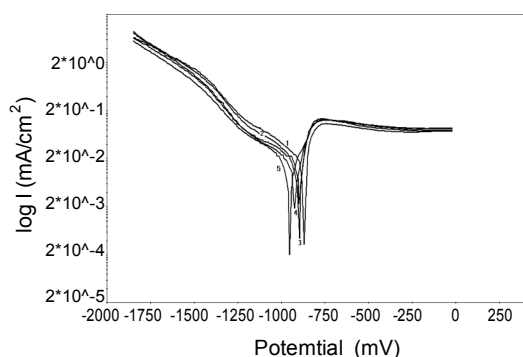


Fig. 1. Galvanostatic polarization curves for tin electrode in 0.1 M NaHCO_3 containing different concentrations of lawsonia extract 1- 0, 2- 500, 3- 1000, 4- 1500 and 5- 2000 ppm.

with increasing extract concentration. This result suggests that the presence of these extracts affect the anodic dissolution of tin as well as the cathodic reduction of hydrogen ions. Therefore, it could be concluded that the molecules of the extract adsorb onto both anodic and cathodic sites of tin surface. This behavior indicates that the extracts act as mixed inhibitors.

Adsorption behavior

The inhibitive action of the extract of lawsonia, licorice root and carob toward the corrosion of tin in 0.1 M NaHCO_3 solution could be attributed to the adsorption of its components (Table 1) on the tin surface. It is important to mention here that the compounds in Table 1 do not represent the whole composition of the used extracts. However, these compounds are expected to do most of the inhibition work supported by the other constituents. The adsorbed layer acts as a barrier between the tin surface and the aggressive solution, leading to a decrease in the corrosion rate. The degree of surface coverage (θ) which represents the part of metal surface covered by inhibitor molecules was calculated using the following equation:

$$\theta = 1 - (I_{\text{add}}/I_{\text{free}}) \quad (1)$$

The values of (θ) have been shown in Table 2. The

Table 2. Electrochemical parameters obtained from galvanostatic polarization measurements of tin electrode in 0.1 M NaHCO_3 solution containing different concentrations of plants extracts.

Inhibitor	Inh. conc. (ppm)	β_a mV. dec ⁻¹	β_c mV. dec ⁻¹	E_{corr} mV (SCE)	I_{corr} $\mu\text{A}/\text{cm}^2$	θ	%IE
Free	0	119.45	-336.46	-868	7.843	-	-
Lawsonia	500	70	-255	-889	4.655	0.4064	40.64
	1000	74	-173	-876	3.539	0.5487	54.87
	1500	84	-142	-923	2.969	0.6214	62.14
	2000	84	-121	-952	2.142	0.7268	72.68
Licorice root	500	119	-177	-968	4.702	0.4004	40.04
	1000	76	-160	-967	3.805	0.5148	51.48
	1500	79	-143	-963	3.118	0.6024	60.24
	2000	86	-112	-920	2.471	0.6849	68.49
Carob	500	82	-220	-894	5.157	0.3425	34.25
	1000	83	-203	-895	4.556	0.4191	41.91
	1500	88	-162	-895	3.971	0.4936	49.36
	2000	97	-111	-895	3.607	0.5460	54.60

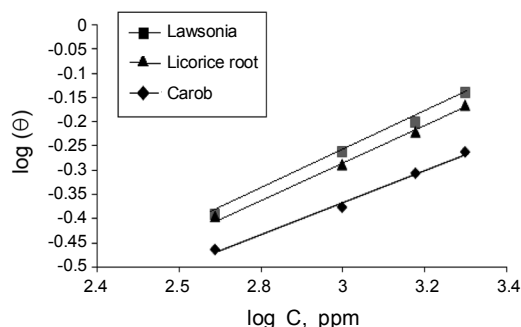


Fig. 2. The relation between $\log(\theta)$ and $\log C$, ppm for tin electrode in 0.1 M NaHCO_3 .

Table 3. Equilibrium constant and the adsorption free energy of the inhibitors adsorbed on the surface of tin electrode in 0.1 M NaHCO_3 .

Inhibitor type	K	ΔG_{ads}^0 Cal. mol^{-1}
Lawsonia	0.0327	-355.21
Licorice root	0.0385	-452.5
Carob	0.0432	-521.18

degree of surface coverage was found to increase with increasing concentration of additives. Attempts were made to fit θ values to various isotherms including Langmuir, Freundlich, Temkin and Frumkin. By far, the best fit was obtained with Freundlich isotherm:

$$\log \theta = \log K + n \log C \quad (2)$$

Fig. 2 represents the relation between $\log(\theta)$ and $\log [\text{Inhibitor}]$. Linear correlations are obtained for all compounds suggesting that the Freundlich adsorption isotherm is obeyed. The calculated values for the equilibrium constant of adsorption were listed in Table 3. The values of ΔG_{ads}^0 were calculated and listed in Table 3 from the following equation:

$$K = 1/55.5 \exp(-\Delta G_{\text{ads}}^0 / RT) \quad (3)$$

The standard free energy change of adsorption is associated with water adsorption/desorption equilibrium which forms an important part in the overall free energy changes of adsorption. The negative values of ΔG_{ads}^0 obtained have indicated that the ad-

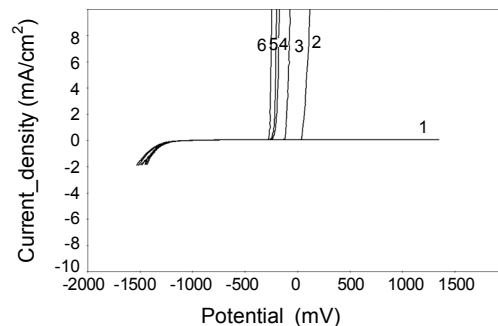


Fig. 3. Polarization curves for tin electrode at scan rate 1 mV/sec in 0.1 M NaHCO_3 and different concentrations of NaCl (1) 0 (2) 0.1 M (3) 0.3 M (4) 0.5 M (5) 0.6 M (6) 1 M.

sorption process of these compounds on the metal surface is spontaneous one.

Potentiodynamic anodic polarization

The effect of the NaCl concentration in the pitting corrosion of tin electrode in 0.1 M NaHCO_3 solution was examined by potentiodynamic anodic polarization technique.

Fig. 3 shows the potentiodynamic anodic polarization curves of tin electrode in 0.1 M NaHCO_3 using different concentrations of NaCl at scan rate 1 mV/sec. The slow scan rate permits that the pitting initiation occurs at less positive potential.²² It is clear from the results that in the concentration range of NaCl studied the metal does not exhibit an active-transition. However, on increasing the concentration of Cl^- ion, there is a sudden and marked increase of current density at a definite potential indicating the passivity breakdown and initiation of pitting corrosion.²³ The potential at which the sudden rise takes place is defined as the pitting potential (E_{pit}). The higher concentration of Cl^- ions; the higher is the shift of pitting potential towards the active direction. The breakdown of passivity could be attributed to the adsorption of chloride ions on the passive film formed on the tin surface, which create an electrostatic field across film/solution interface.^{24,25} Thus, when the electrostatic field reaches a certain value, the adsorbed anions begin to penetrate into the passive film and the pitting corrosion is initiated.

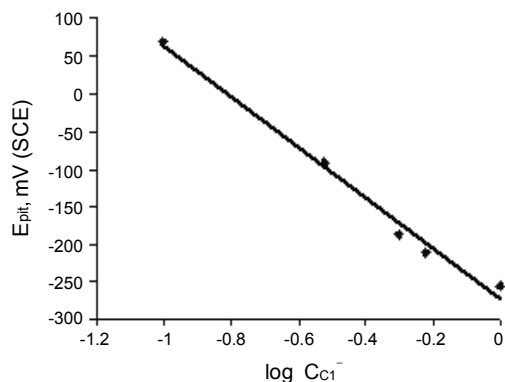


Fig. 4. The relation between the pitting potential (E_{pit}) and $\log C_{Cl^-}$.

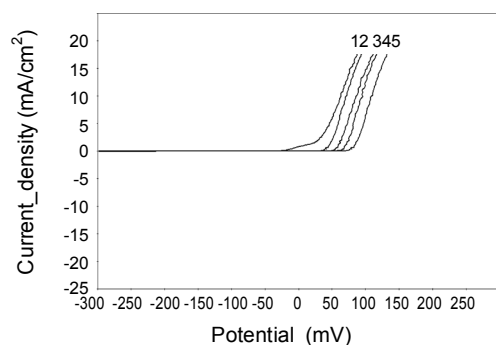


Fig. 5. Polarization curves for tin electrode in 0.1 M $\text{NaHCO}_3 + 0.1$ M NaCl containing different concentrations of lawsonia extract at scan rate 1 mV/sec (1) 0, (2) 500, (3) 1000, (4) 1500 and (5) 2000 ppm.

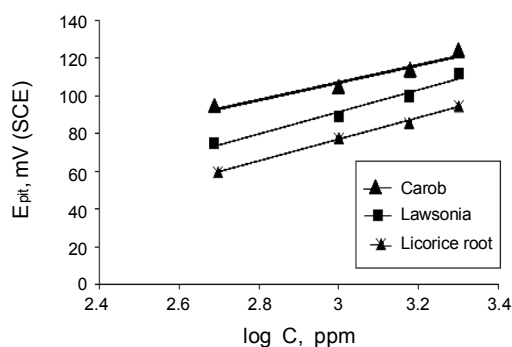


Fig. 6. The relation between the pitting potential (E_{pit}) and $\log C$, ppm.

The dependence of E_{pit} with the concentration of Cl^- ion is shown in Fig. 4. The relation gives straight line curve in the following form:²⁶

$$E_{pit} = a_1 - b_1 \log C_{Cl^-} \quad (4)$$

where, a_1 and b_1 are constants depending on both the nature and type of the aggressive anion and of the electrode.

The effect of increasing the concentrations of lawsonia extract on the potentiodynamic anodic polarization of tin in [0.1 M $\text{NaHCO}_3 + 0.1$ M NaCl] at scan rate of 1 mV/sec is illustrated in Fig. 5. It was found that increasing the concentration of lawsonia causes a shift of the pitting potential into noble direction indicating an increased resistance to pitting attack. Similar curves were obtained for the two extract licorice root and carob (not shown). Straight line relationship between E_{pit} and $\log C_{inh.}$ (Fig. 6) is obtained according to the equation:

$$E_{pit} = a_1 + b_2 \log C_{inh.} \quad (5)$$

where, a_1 and b_2 are constants which depend on both the type of additive and the nature of the electrode.

Mechanism of Inhibition

Natural products act as an easy and cheap way to forbidden or retarding the electrochemical corrosion reaction. It can be gained and extracted by simple aqueous media from many wastes of agriculture plants and seeds without any over much cost with the comparison of synthetic organic materials. The use of these products in many times does not cause any pollution and toxic to the environment. In addition, the fact available on the application of natural products as restrainer in pickling or polishing processes.²⁷ Moreover, the advantage of natural products, it can be easily obtained from cheap plants and/or by products (peels, seeds, etc.) remaining in the caning industry, but also, these extracts always contain more than one organic products, these contents of natural product are made it as effective inhibitors in retarding the dissolution of metals.

Lawsonia extract. The main components of Lawsonia extract are hydroxyl aromatic compounds such as tannin and lawsone. The inhibitive action of tannin was attributed to formation of a passivating layer of tannate on metal surface. Tannin is also known

to form complex compounds with different metal cations, especially in the basic medium. Therefore, formation of tannin complexes may be responsible for the observed inhibition in the alkaline medium.

The other constituent of the extract is lawsone which is present in higher amount. Lawsone molecule is a ligand that can chelate with tin to form complex compounds, which adsorbed on the metal surface lead to corrosion inhibition.

Licorice root extract. The chemical structure of this extract contains poly aromatic compounds contained glycyrrhizin. This compound presents in licorice root are horizontally adsorbed on the tin surface due to the presence of more one active centre in the compound. The strong adsorption process leads to increase the inhibition efficiency.

Carob extract. The carob extract contains mainly sucrose compound. The inhibition of this extract can be explained in view of adsorption of sucrose compounds on the tin surface making a barrier for mass and charge transfers. This arrangement leads to protection of the metal surface from the attack of the aggressive anions. The degree of protection increases with increasing of the surface fraction occupied by the adsorbed molecules, which increases as the extract concentration is increased.

CONCLUSION

1. The extract of lawsonia, licorice root and carob act as an inhibitors for corrosion of tin electrode in 0.1 M NaHCO₃.
2. The inhibition action of these extracts was attributed to the adsorption on the tin surface.
3. These extracts act as mixed inhibitors.
4. The adsorption of these extracts follow Freundlich isotherm.
5. These extracts inhibit the pitting corrosion of tin in chloride containing solutions.

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