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Natural onion juice as inhibitor for zinc corrosion

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Abstract

The inhibitive effect of the natural juice of onion bulb on the corrosion of zinc in HCl solution was determined using hydrogen evolution and weight loss measurements as well as potentiostatic technique. Potentiodynamic anodic polarization was used to determine the effect of the juice on pitting corrosion of zinc in NaCl solution. It was found that the presence of onion juice reduces markedly the corrosion rate of zinc in the acid solution. The inhibition efficiency increases as the juice concentration is increased. Moreover, the presence of the juice in NaCl solution shifts the pitting potential toward more positive direction. The inhibitive effect of onion juice was discussed on the basis of adsorption of its components on the metal surface. Such adsorption is found to follows Langmuir adsorption isotherm. Negative values were calculated for the energy of adsorption indicating the spontaneity of the adsorption process. The formation of insoluble complexes as a result of interaction between the juice components and zinc cations was also discussed.

Key Words: Corrosion inhibition – Natural product – Onion – Zinc.

1. Introduction

The addition of corrosion inhibitors is an important method which frequently used to overcome the corrosion of metals and alloys. The compounds used in such treatment must have specific features to be able to acting as corrosion inhibitors. Both organic and inorganic compounds could be used. The inorganic compounds should have an oxidation power to form a passive oxide film on the metal surface, which serve in slowdown the rate of metallic corrosion. Many of these compounds were reported in the literature as corrosion inhibitors, such as the sodium salts of chromate[1,2], molybdate[3-5] and others[6]. On the other hand, the organic compounds which used as corrosion inhibitors are usually adsorbed on the metal surface forming a barrier film for mass and charge transfer. Thus, such compounds should have in their structure, active groups able to establish the adsorption process. Therefore, many of the used organic compounds contain sulfur, oxygen or nitrogen atoms in their structures[7-9].

In such manner, most of the compounds used for corrosion inhibition are very dangerous for human and environment, even in very small concentrations. For this reason, some researches were conducted, recently to use safe naturally occurring substances as corrosion inhibitors for metals and alloys[10-12]. The present work is aimed to study the inhibitive action of the onion juice toward both the general and pitting corrosion of zinc in hydrochloric acid and sodium chloride solutions, respectively.

2. Experimental

Sheets of zinc, with apparent surface area of 16 cm^2, were used in the study of corrosion rate by weight loss measurements. The corrosion rate was calculated on the basis of the apparent surface area. The immersion time was one hour at 25 ± 1 ^{o}C. The results of the weight loss experiments are the mean of three runs, each with a fresh sheet and fresh electrolyte. The percent of inhibition efficiency was calculated using the following equation:

$$IE = [(W_f - W_i) / W_f] \times 100$$

Where W_f and W_i are the weight losses of zinc sheets in the absence and present of onion juice, respectively.

The corrosion rate was also determined by measurement of hydrogen gas evolved during the dissolution of zinc specimens in the acid solution. The reaction vessel used for hydrogen evolution measurements as well as the determination method of zinc dissolution rate, in the tested acid solutions are the same as described elsewhere[13].

For potentiostatic experiments, a cylindrical rod of zinc was embedded in araldite such that the exposed surface area is 1.0 cm^2, and used as working electrode. The electrodes were polished with different grades of emery papers, degreased with acetone and rinsed by distilled water before immersed in the test solution. Potentiostatic polarization experiments were carried out using EG&G model 173 Potentiostat / Galvanostat. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The inhibition efficiency IE was calculated using the following equation:

$$IE = [(I - I_i)/I] \times 100$$

Where I and I_i are the corrosion rates in the free and inhibited acid solutions, respectively.

All chemicals used for preparing the test solutions were of analytical grade and the experiments were carried out at room temperature, 25 ± 1°C.

The swollen bulb of dried onion was divided into small pieces and squeezed between two rotating rolls. The juice was then filtered and used directly in the experiments. Both the freshly prepared juice and that aged, in firmly enclosed bottle at 10 °C, for one month give almost the same results.

3. Results

3.1. Hydrogen evolution measurements

The dissolution reaction of zinc in 0.1 M HCl solutions devoid of and containing different concentrations (volume percent) of onion juice (J) was studied using hydrogen evolution method. Fig (1) represents the relationship between the volume of hydrogen evolved during the corrosion reaction and the reaction time. Inspection of Fig (1) reveals that, there is a linear relationship between hydrogen volume and reaction time. The addition of onion juice reduces markedly the rate of hydrogen evolution. The rate of hydrogen evolution decreases as the added juice concentration is increased. The slopes of the obtained straight lines, which represent the rates of corrosion reaction, were used to determine the inhibition efficiencies of the used juice concentrations. The calculated inhibition efficiencies are given in Table (1).

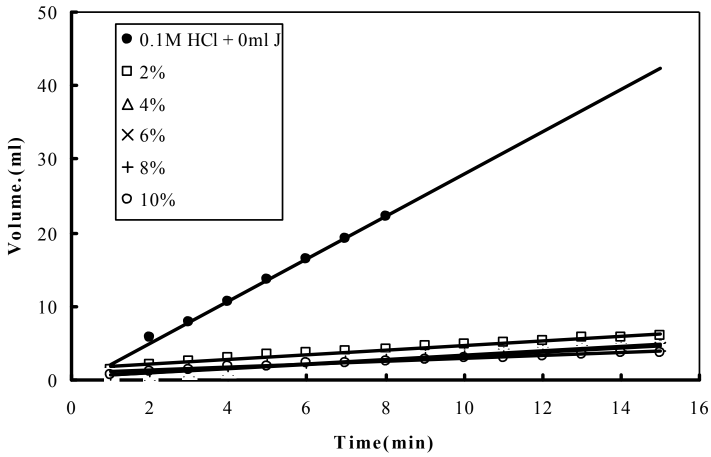


Fig.(1): Hydrogen evolution curves of zinc in 0.1M HCl solutions devoid of and containing different concentrations of J .

3.2. Weight loss measurements

The weight losses of zinc sheets due to their exposure to 0.1 M HCl solutions devoid of and containing different concentrations of onion juice were determined. Table (1) contains the calculated inhibition efficiencies as a function of juice concentration. Inspection of Table (1) reveals that onion juice acts as good corrosion inhibitor for acid corrosion of zinc. The inhibition efficiency increases as the juice concentration is increased.

Table (1): Inhibition efficiencies and θ values as revealed from hydrogen evolution and weight loss measurements.

Conc., vol%	**H_2 evolution.**		**Wt. loss**	
	IE%	**θ**	**IE%**	**θ**
2	89.73	0.89	65.13	0.65
4	90.18	0.90	81.54	0.81
6	92.14	0.92	82.21	0.82
8	92.87	0.92	84.32	0.84
10	89.73	0.89	86.27	0.86

3.3. Potentiostatic technique

Fig (2) represents the anodic and cathodic polarization curves of zinc electrode in solutions of 0.1M HCl devoid of and containing different concentrations (v%) of onion juice. Inspection of the figure reveals that the presence of onion juice shifts the anodic curves toward more noble direction and cathodic ones towards more active direction. This behavior indicates that the addition of onion juice inhibits the corrosion of zinc in the acidic medium.

The corrosion parameters of zinc in the free and inhibited acid solutions were obtained from the curves of Fig (2) and given in Table (2). Several remarks could be noticed in Table (2). The presence of onion juice shifts the corrosion potential, slightly, toward more noble direction. It follows that, the presence of onion juice has a little effect on the corrosion mechanism. On the other hand, the corrosion current decreases in presence of the juice suggesting its inhibitive effect. The inhibition efficiency increases as the juice concentration is increased. The high values of inhibition efficiencies reveal that the juice performs as good inhibitor for acid corrosion of zinc. Moreover, the addition of juice decreases both the anodic and cathodic Tafel constants. This result suggests that the onion juice acts as mixed inhibitor.

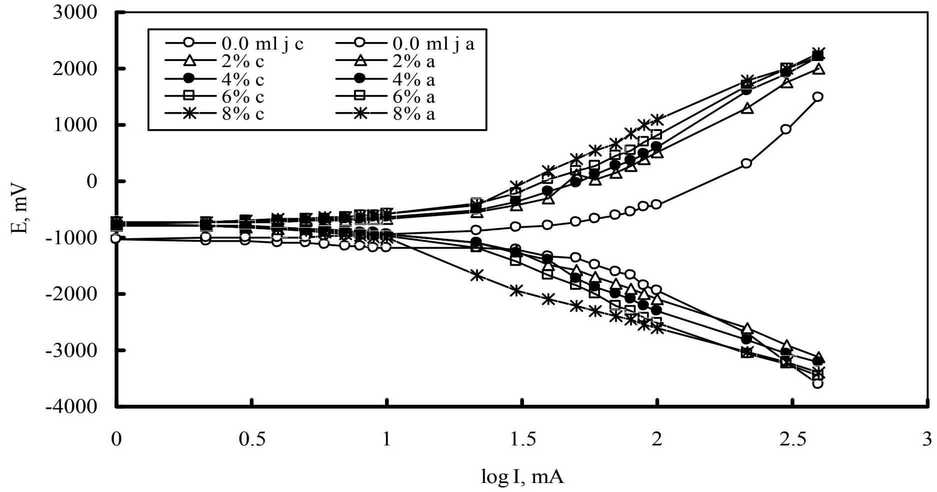


Fig (2): Polarization curves of zinc in 0.1M HCl solutions devoide of and containing different concentrations of onion juice.

Table (2): Corrosion parameters of zinc in free and inhibited 0.1 M HCl solutions.

Solution	E_{corr} mV	β_a mV/decade	β_c mV/decade	I_{corr} mA/cm^2	IE	θ
Free acid	-1100	3191	-2944	54.95	-----	-----
2%	-1090	2215	-1651	19.95	63.69	0.6369
4%	-1080	2266	-1752	19.05	65.33	0.6533
6%	-1050	2192	-1793	15.13	72.46	0.7246
8%	-1000	2119	-1285	8.51	84.51	0.8451
10%	-1050	2100	-1165	8.38	84.74	0.8474

3.4. Pitting corrosion

Fig (3) represents the potentiodynamic anodic polarization curves of 3.5% NaCl solutions devoid of and containing different concentrations of onion juice. The potentiodynamic polarization was performed at scanning rate of 1.0 mV/sec.

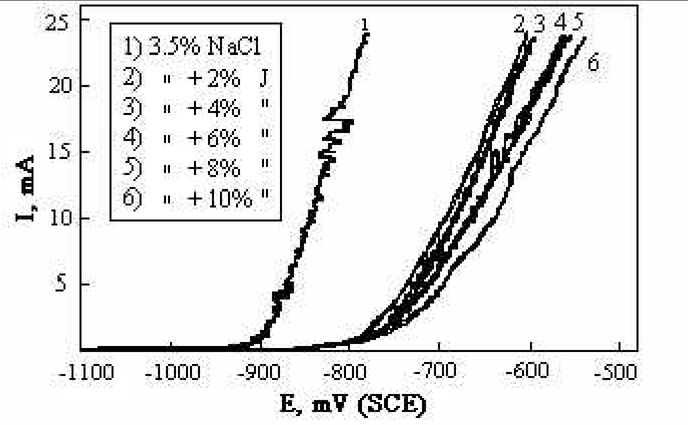


Fig (3): Potentiodynamic anodic polarization curves of 3.5% NaCl solutions devoid of and containing different concentrations of onion juice.

Inspection of the figure reveals that the current remains constant at almost zero value as the potential is increased toward the noble direction. However, the current jumps to a much higher value at a specific potential value that depends on the solution composition. This specific potential value denotes the pitting potential. Inspection of the curves of Fig (3) reveals that the addition of onion juice shifts the pitting potential to more noble direction. This behavior indicates that the juice acts as inhibitor of pitting corrosion of zinc. Table (3) contains the values of pitting potential corresponding to the solution composition. The values of Table (3) reveal also that the pitting corrosion potential shifts to more noble value as the added concentration of onion juice is increased. The magnitude of potential shift reaches about 200 mV, indicating that the onion juice performs as a good inhibitor for pitting corrosion of zinc.

Table (3): Pitting potentials of zinc in free and inhibited 3.5% NaCl solutions.

Solution	Free	2%	4%	6%	8%	10%
E_{pitt}	-905	-791	-782	-770	-758	-716

4. **Discussion**

Mechanism of inhibition

Onion juice contains proteins, lipids, carbohydrates and fibers. The juice is characterized by the presence of two sulfur-containing amino acids (glutamyl peptides), namely S-(1-propenyl)-L-cysteine sulfoxide and S-2-carboxypropyl glutathione. The two glutamyl peptides are accumulated in the stored bulbs and their concentrations reach 2.1 and 0.4 mg per gm of onion bulb[14-17]. These peptides undergo enzymatic hydrolysis if the bulb is injured and thus their concentrations are reduced. However, such hydrolysis is inhibited by cooling or in aqueous solutions.

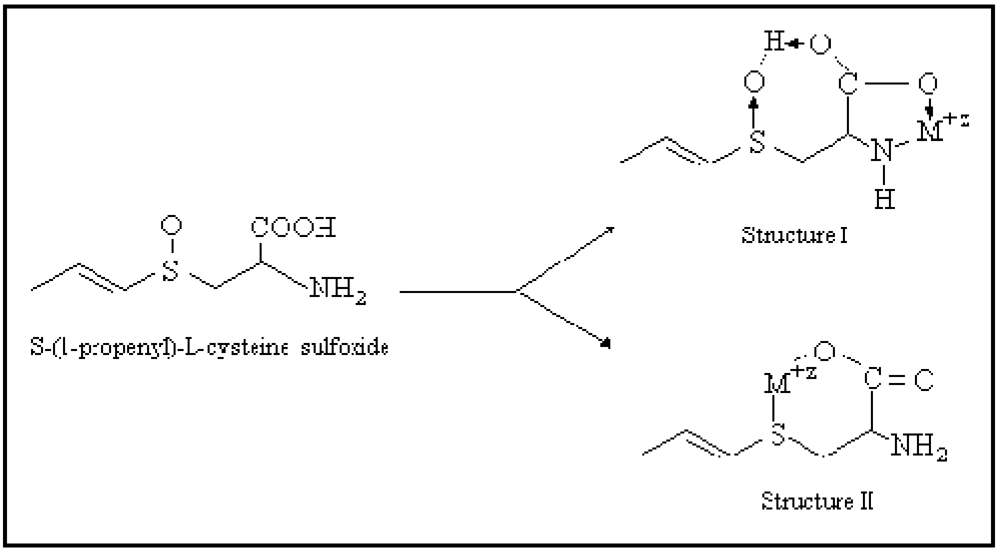
The inhibiting action of onion juice to zinc corrosion could be attributed to the adsorption of its components on the metal surface. The adsorbed molecules form a barrier between the aggressive medium and the metal surface. The inhibition efficiency is directly related by the fraction of surface covered by the adsorbed molecules (θ). Therefore, θ was calculated as IE/100 and its values corresponding to different juice concentrations were given in tables (1) and (2). Inspection of these tables reveals that, the value of θ increases as the additive concentration is increased. The nature of the relationship between the additive concentration and θ determines the mode of molecules adsorption. It was found that the additive concentration is directly proportional to C/θ. Thus, plotting C against C/θ, for the three used techniques, gave straight lines with slope values of almost one (Fig 4). This result suggests that the adsorption of onion juice components on zinc surface in the acidic medium follows Langmuir adsorption isotherm which could be represented as following:

$$C/\theta = C + 1/k$$

Where k is the adsorption constant. Langmuir isotherm postulates that there is no interaction between the adsorbed molecules and hence the free energy of adsorption, ΔG_{ads}, is independent on θ value. The free energy of adsorption could be calculated using the following equation[18]:

$$\log k = - 1.74 - [\Delta G_{ads} / 2.303 RT]$$

Values of -10.56, -14.06 and - 8.84 KJ were obtained for ΔG_{ads} using weight loss, hydrogen evolution and potentiostatic techniques, respectively. The negative sign indicates that the adsorption of the juice compounds on zinc surface in the acidic medium is a spontaneous process. However, it should be mentioned here that, these values do not represent the exact values of ΔG_{ads} since the juice concentration was expressed by volume percent not by molar unit. Nevertheless, In spite of this argument, these values still valid to be used as an indication for spontaneity of the adsorption process. Moreover, the calculated values of free energy of adsorption suggest a physical adsorption of the juice compounds on zinc surface.



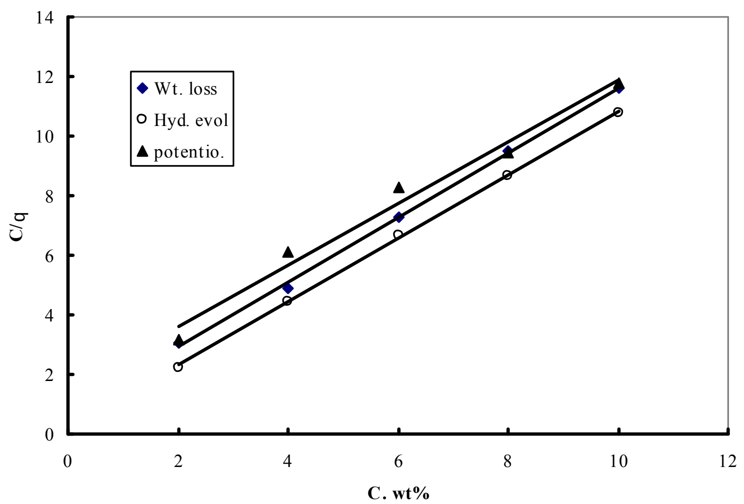


Fig (4): Adsorption isotherm of onion extract on zinc surface determined using different techniques.

Fig (5): Structures of possible formed complexes.

The molecules adsorbed on the zinc surface have the ability to interact, chemically, with the dissolved zinc ions. Thus, those molecules with active centers in their structures can produce complexes as a result of such interaction. The formation of insoluble complex compounds upon addition of onion juice to zinc ions is confirmed in the present work by conductometric titration. The results indicate that a 1:1 complex is formed in the acidic solution. The main component present in onion juice is S-(1-propenyl)-L-cysteine sulfoxide. The formation of two different complexes is possible as revealed from Fig (5). A five-membered ring contains a coordination bond is formed in structure (I). On the other hand, the weak S-O bond could be broken and the structure (II) with a six-membered ring is formed. The released oxygen can react with the metal cations forming oxide compound. Obviously, structure (II) is the more stable structure and its formation enhances the formation of passive oxide layer. Thus, the complex of structure (II) is more preferable to be formed. The presence of insoluble complex layer on the metal surface makes a compact barrier for mass and charge transfer. The formation of such barrier leads to decreasing the rate of zinc dissolution and thus increasing the inhibition efficiency of onion juice.

5. Conclusions

- Onion juice acts as inhibitor for acid corrosion of zinc.
- The presence of onion juice increases the pitting resistance of zinc.
- The adsorption of onion components on zinc surface is spontaneous and follows Langmuir isotherm.
- The components of onion juice react with dissolved zinc cations forming insoluble complex compounds.

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