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Corrosion Inhibition of copper in sulfuric acid using different surfactants

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ABSTRACT

Four commercial non-ionic surfactant compounds, namely *Bixin, Zenthoxylum almauta, Echitamin, Nyctanthin* were tested as inhibition for corrosion of Copper 0.5 M sulphuric acid solution. Weight loss measurements, potentiostatic polarizatiors and cyclic voltammetry techniques were used in this study. It was found that all the four used compounds act as good inhibitors for acid corrosion of Copper. The inhibition efficiencies obtained by the three techniques were almost the same, and increases with increasing the surfactant concentration. The polarization studies show that all used compounds act also mixed inhibitors. The inhibition action of these surfactants is interpreted in view of their adsorption on the metal surface making a barrier to mass and charge transfer. It was found that the adsorption of compounds follows Longmuir isotherm. The values of free energy of adsorption for them were calcopperlated. It was found that the adsorption process is spontaneous and increases, for different surfactants, in the same direction as inhibition efficiency. The cyclic voltammetry shows that there is only one anodic peak corresponding to the dissolution reaction of electrode. The copperrrent of this dissolution peak was used also for corrosion rate measurements and in evaluation of inhibition efficiencies of the used compounds.

Key words: Corrosion Inhibition, Surfactant, copper and sulphuric acid.

INTRODUCTION

Copper and aluminum is one of the most important metals and is used in a large number of applications. The pure copper has good corrosion resistance and is frequently used as protective coat for metals and alloys. For the same reason, copper used as alloying elements, copper based alloys shows considerable resistance against different type of corrosion. Even the addition of small quantity of copper to an alloy improves its corrosion resistance character. The corrosion resistance of copper is due to the formation of passive film on its surface upon exposure to the corrosive media. Nevertheless, copper could be attacked by acidic media in a considerable rate. Many workers conducted to study the passivation of copper in different acidic media[1-5]. It was reported that the passive film formed on copper surface in low concentration of sulfuric acid. However, it obtained results showed that copper establishes a kind of passivity in which the corrosion current, in the passive potential range, is somewhat higher than those recorded by other passive metals. Because copper is frequently used in contact with acidic solutions, its corrosion rate must be controlled. One of the useful methods of controlling the corrosion process is the addition of corrosion inhibitors.

Many researchers were published in the literature concerning the usage of inhibitors for copper in acidic solution[6-12]. Most of inhibitors are organic compounds containing sulfur or nitrogen in their chemical structures. It was found that this kind of compounds is chemically adsorbed on the copper surface forming a barrier for mass and charge transfer who consequently decreases the rate of corrosion. Unfortunately, most of these compounds are harmful for human health and for the environment. Therefore, additional work should be

conducted to find safe and cheap corrosion inhibitors for copper in acidic solutions. This work devoted to test a series of organic compounds as inhibitor for the copper in sulfuric acid solution. These compounds can be easily synthesized from relative cheap materials. In addition, these compounds are non toxic and have surface active property. Weight loss measurement, cyclic voltammetry techniques were used in the study to evaluate the inhibition efficiency of the tested compounds.

EXPERIMENTAL

Coupons of pure copper with dimensions of 1 x 2 x 0.5 cm were used in weight loss experiments. For potentiostatic polarization technique a cylindrical rod of copper embedded in araldite with an exposed bottom area of 0.5 cm^2 was used. Before each experiment, the electrode was polished to a mirror finish with different grades of emery papers, degreased with acetone and finally rinsed with distilled water. BDH grade sulfuric acid was used for the preparation of the test solution. Weight loss measurements were carried out by the same method as described elsewhere [13]. Each of the copper was immersed, for 24 hours, in 50 ml of 0.5 M sulfuric acid solution containing of surfactants, at 30°C. All electrode cells, with saturated calomel reference electrode and platinum foil counter electrode was used in polarization experiments. Both potentiostatic polarizations a cyclic voltammetry technique were carried out using a PS remote potentiostat with zum PS-6 software for calculation of electrochemical parameters.

RESULTS AND DISCUSSION

Weight loss measurements

The losses of weight of copper sheets due to their immersion in solution of 0.5 M sulfuric acid containing different concentrations of the inhibitors were measured. It was found that the addition of any the used all compounds lowers the weight loss of the copper sheet than its value in the acid solution. This result indicates the all the natural products act as inhibitor for the corrosion of metals in acidic solution. The inhibitive action could be attributed to the adsorption of their molecules on the copper surface, forming a barrier between the bar metal and the corrosive environment. The surface activity of natural compounds as well as the presence of function group, in their structures facilitates such adsorption. The surfactant molecules adsorb on the surface via their functional group. Since the compounds mixed in to the solution they repel aggressive anions away form the metal surface and therefore inhibit the corrosion reaction. The inhibition efficiencies of different concentrations of the compounds are given in Table-1. The inhibition efficiency was calculated using the following equation:

$$IE\% = [(w_f - w_i) / w_f] \times 100$$

Where w_f and w_i are weight loss of metals in free and inhibited acid media respectively.

Inspection of Table-1 reveals that the inhibition efficiency increases as the inhibitor

Table 1: Dependence of IE% of the inhibitors of their concentration as revealed from weight loss measurements

Concentration of inhibitor	Bixin	Zentheloxylum almauta	Echitamine	Nyctanthin
50 ppm	49.58	57.43	78.9	82.9
100 ppm	68.9	71.6	84.32	90.67
200 ppm	80.21	81.65	94.1	95.34
300 ppm	88.123	90.24	95.7	98.10
400 ppm	92.30	94.6	96.12	98.673

concentration is increased. This behavior could be attributed to the increases of the metal surface area covered by the adsorbed inhibitor molecules with the increasing inhibitor concentration. Furthermore, data of Table-1 show that the extent of inhibition of different compounds on their structures. The inhibition efficiency increases in the following order.

Bixin < Zenthoxlum almauta < Echitamine < Nyctanthin

This sequence reflects the effect of type of the unit present in the compound and their inhibitive action.

Potentiostatic Polarization

Fig.- 1.1 represents the anodic and cathodic polarization curves of copper electrode in 0.5 M sulfuric acid solution containing different concentrations of inhibitor. Similar curves were also obtained for the other inhibitors. Analysis of fig. 1.1

Table 2: Electrochemical parameters of Cu corrosion in free and inhibited 0.5 M sulfuric acid solutions

Inhibitor Concentration/ppm		E_{corr} Mv	I_{corr} mA/cm²	(β_a)	-(β_c)	IE%	Θ
0.0	Bixin	-280	12.89	296	768		
50		-80	6.56	199	546	49.1	0.49
100		-61	4.123	199	505	68	0.68
200		-52	2.68	167	398	79.2	0.79
300		-48	1.123	156	368	91.2	0.912
400		-29	1.124	178	340	91.5	91.5
600		-18	1.124	159	329	91.5	91.5
1.0	Zenthoxylum Alatuma	-280	12.89	296	768		
50		-98	5.432	165	498	57.8	0.57
100		-84	3.4325	145	476	73.4	0.73
200		-76	2.1678	133	450	83.2	0.83
300		-69	1.3980	121	405	89.1	0.89
400		-63	0.9867	120	401	92.3	0.92
600		-54	0.9861	116	389	92.3	0.92
2.0	Echitamine	-280	12.80	296	768		
50		-100	3.45	153	410	73.2	0.73
100		-92	2.912	146	356	77.4	0.77
200		-82	1.8970	157	342	85.5	0.85
300		-62	1.2180	169	322	90.5	0.90
400		-54	0.8189	168	301	90.7	0.907
600		-44	0.6231	162	289	95.1	0.95
4.0	Nyctanthin	-280	12.89	296	768		
50		-108	3.0237	142	410	76.5	0.76
100		-98	1.1876	144	356	90.7	0.90
200		-89	1.0970	158	342	91.4	0.91
300		-68	1.0180	169	322	92.1	0.92
400		-54	0.6142	171	301	95.2	0.95
600		-45	0.4123	171	289	96.8	0.96

find that both the anodic and cathodic polarization curves are shifted to less current density values in the presence of inhibitors. This behavior suggests that the inhibition action of the compounds. The extant of the shift in current density increases with increasing of the concentration of compounds.

The value of corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic Tafel constant (β_a) and cathodic constant (β_c), exclude from polarization curves are given in Table- 2.0. Inspection of Table – 2.0 given an idea that the corrosion potential of copper and aluminium in acidic solution is largely shifted to less negative values upon addition of the compounds. The magnitude of this shift increases with increasing of the associated of natural product like Bixin, Zenthoxylum almatum, echitamine and Nyctanthin, and with the increasing of the additives concentration.

On the other hand current density is greatly reduced upon addition of any of the four inhibitors. These results suggest the inhibitive effects of the tested compounds. The data in Table 2 reveals that the values of inhibition efficiency obtained by polarization technique are comparable to those obtained by weight loss measurements. The inhibition efficiency increases with increasing of concentration of compounds. The efficiency could be recognized in table 2 that the inhibition efficiency

Table 3: Cyclic voltammetry of Cu in 0.5 M sulfuric acid solutions containing different natural products. V= 10 mv/sec

Inhibitor concentration/ppm		E_pMv	I_pmA	IE%
00	Bixin	256	160	
50		288	88	45
100		346	56	65
200		350	44	72
300		388	38	76
400		405	32	80
600		458	26	83
0.0	Zenthoxylum Alatuma	256	160	
50		300	78	51
100		340	45	71.8
200		366	36	77.5
300		398	28	82.5
400		422	22	86.25
600		470	18	88.7
0.0	Echitamine	256	160	
50		305	64	60
100		376	40	75
200		401	30	81.25
300		430	22	86.25
400		468	18	88.7
600		479	14	91.25
0.0	Nyctanthin	256	160	
50		312	50	68
100		390	28	82.5
200		426	22	86.25
300		468	16	90
400		488	08	95
600		494	04	97.5

of the compounds increases in the following order:

Bixin < Zenthoxlum almauta < Echitamine < Nyctanthin

It is of interest to note that this sequence is the same like that obtained by weight loss measurements. Further, inspection of Table- 2.0 reveals that the addition of increasing concentration of compounds decreases both the anodic and cathodic Tafel constants. This result indicates that the non ionic surfactants act as mixed inhibitors. This means that the surfactant molecules are adsorbed on both the anodic and cathodic sites resulting in an inhibition of both anodic dissolution and cathodic reduction reactions. The greater the metal surface area occupied by adsorbed molecules, the higher the inhibition efficiency. A parameter (è) which represents the fraction of the metal surface covered by adsorbed using the following equation:

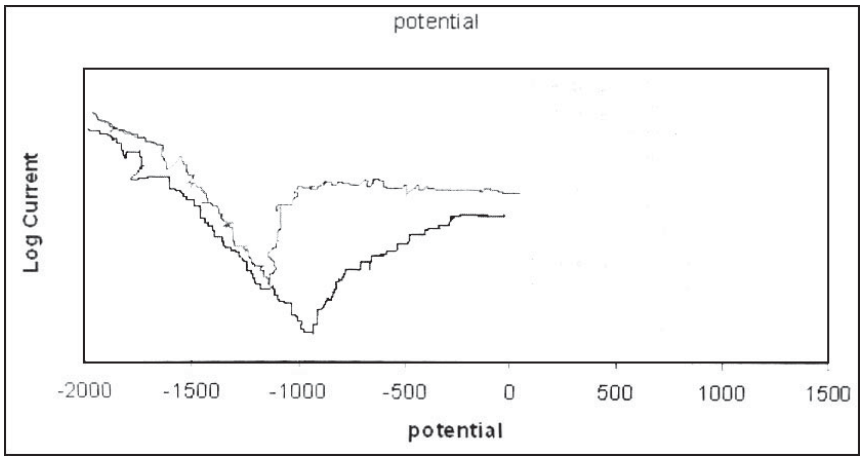

Fig. 1: Polarization curves of Copper in 0.5 M sulfuric acid containing different concentration of Surfactants

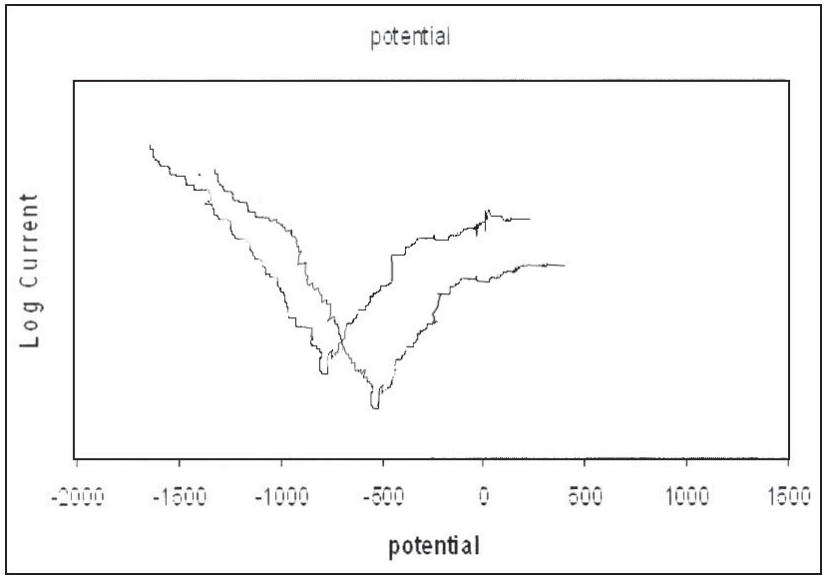

Fig. 2: Polarization curves of Al in 0.5 M sulfuric acid containing different concentration of surfactant

$$\Theta = [(I_f - I_i) / I_f]$$

Where I_f and I_i are the corrosion currents in free and inhibited acid solutions, the values of è corresponding to different concentrations of natural products are given in Table 2.

Plotting of log θ/(1-θ) versus logarithm of concentration of natural products give straight lines with the slop the value close to unity for the compounds, but the values are deviated from unity. These results suggest that the adsorption of the compounds on Copper surface follows Longmuir adsorption isotherm. This isotherm postulates that there is no kind of interaction force that could arise between the molecules adsorbed at metal surface. Thus, the free energy of adsorption of the molecule is independent on the value of θ.

The following equations describe the Langmir adsorption isotherm [14]:

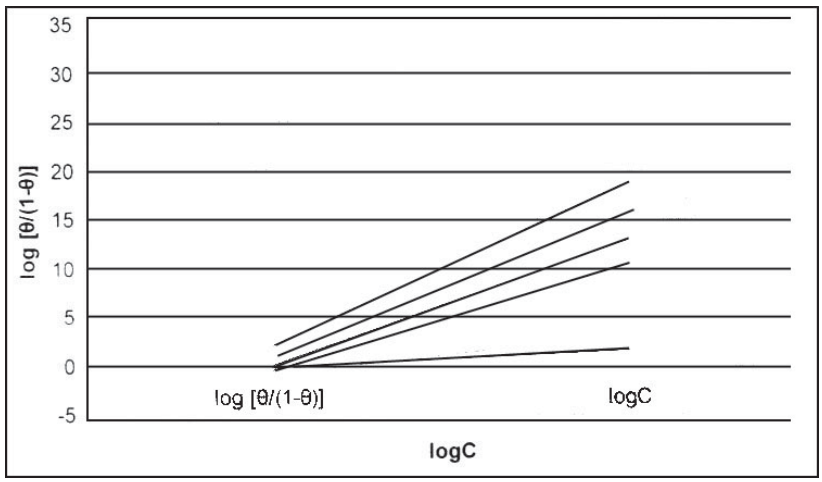

Fig. 3: Isotherms of different natural products

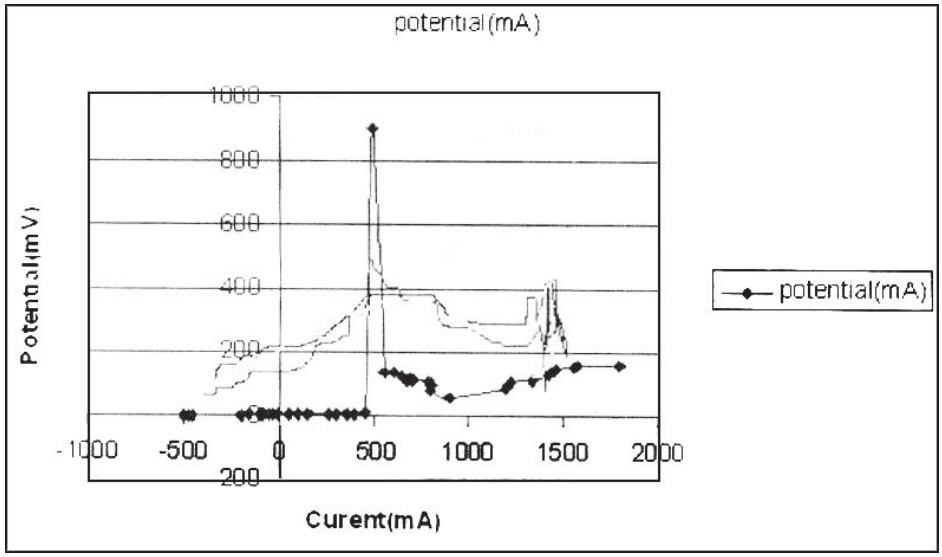

Fig. 4: Cyclic voltammetry of Copper in 0.5 M sulfuric acid solutions containing different natural produces. V = 10 mv/sec

$$\text{Log } [\theta/(1-\theta)] = \log C + \log K$$

Where

$$\text{Log } K = -1.74-[\Delta G^0/2.303\ RT]$$

Thus, the values of free energy of adsorption (ΔG^0) are calculated using these equations. It was found that ΔG^0 values are -198, -209, -1004, -1200 joule for Bixin, Zenthoxylum almatua, Echitamine and for Nyctanthin respectively. It is very important to mention here that the calculated ΔG^0 values are not related to any standard weight of the natural products, such as mole. This is because the calculated values are based on the data extracted from Fig-2, where the concentration is expressed by ppm unit, whereas the value of R in the equation is expressed by cal/mole. Thus, the obtained values of ΔG^0 do not refer to the actual values of the free energies of adsorption. However, these values comparison that the adsorption is spontaneous process.

Cyclic voltammetry

Fig. 3 represents the cyclic voltammetry curves analysis of copper corrosion in 0.5 M on sulfuric acid solution containing different concentration of natural products, traced at scanning rate of 10 mv/sec, between hydrogen and oxygen evolution potentials. Similarly curves also obtained for different more compounds but not shown here. Inspection of figure-3 reveals that there is only one large anodic peak and no peaks for cathodic loop. Some authors[6,15-17] reported that copper gives a small anodic peak in addition to large one and other[11] recorded a very small cathodic peak. However, we determine the appearance of a small anodic peak by using voltage scanning rate smaller than the 10 mv/sec. It was determine that the large anodic peak obtained due to the formation of oxide of cooper. Thus, this peak is responsible for the passivation of copper in sulfuric acid solution. So, the dissolution of copper take place at its potential and analysis in the formation of passive layer, which retards the rate of copper corrosion in sulfuric acid solution. The presence of such type of dissolution peak makes it possible to use its current to represent the corrosion rate of copper, and its potential as the corrosion potential. With the analysis of figure 3 is found that in acidic media the anodic peak current largely decreased. This behavior is in contrast with the other recorded inhibitor[6,11], which increases anodic peak current upon their addition. It was observed that the all compounds enhance the passivation and consequently lead to more saving of copper against the corrosion peak. However, it could be observed that the addition of compounds decreases both the current of the passive current. This behavior to conclude that the adsorptions of molecules of inhibitors prevent the dissolution of copper and act as passive layer better than the oxide film. That mean, other compounds act through enhancement of copper dissolution and produces a thick layer of passive oxide, the natural compounds act through adsorption on the cooper surface preventing directly dissolution of copper. This is the reason of the observe higher inhibition efficiency of natural products.

Potentials and current of anodic peak, in 0.5 M solution containing different concentration of natural plant extracts, as well as the inhibition efficiencies calculated from the peak current, are represent in Table-3 reveals that the peak potential, which refers to corrosion potential, is shifted toward more noble direction in the presence of natural products. The magnitude of potential shift increases as the concentration of inhibitor is increased. This behavior is in agreement with that observed in the potentiostatic technique, although the difference in the absolute values of the potential. On the other hand, the peak current is greatly reduced as a result of addition of extract of natural products, indicating the inhibition efficiencies calculated from the cyclic voltammetry technique, are comparable with those calculating by weight loss and potentiostatic techniques.

CONCLUSIONS

- The tested compounds established a very good inhibition for copper corrosion in sulfuric acid.
- These compounds inhibit the copper corrosion by adsorption on its surface and act better than passive oxide film.

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