Amino Acids as Corrosion Inhibitors for Corrosion of Admiralty Brass in Sulphuric Acid Solution

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The corrosion behaviour of admiralty brass electrode in 0.1 M H_2SO_4 solution in the presence of four amino acid compounds (glycine, L-phenylalanine, L-tyrosine and L-histidine) has been studied using weight loss and polarization measurements. It was found that, the inhibition efficiency of these compounds depends on their concentration and their chemical structures. The effect of temperature on the rate of corrosion in the presence and absence of the inhibitors was also studied. Some thermodynamic function were computed.

Copper - base alloys have received relatively little attention although they are extensively used as heat exchanger tubes in refinery systems using water as coolant [1,2]. These alloys have much less tendency to corrode and foul on the water side than steel tubes. But on the process side, the presence of acidic conditions may accelerate the corrosion of these alloys. Pitting and stress corrosion failure of admiralty brass condenser tubes were investigated and the effect of some adverse water additives and constituents was discussed [3].

The most important method for protecting materials against corrosion is use of inhibitors [4,5]. Unfortunately, many corrosion inhibitors used in aqueous heating and cooling systems are health hazards [6]. Many proven inhibitors with toxic properties include aromatic and nitrogen containing heterocyclic compounds which find applications in pickling process and in the oil and gas industry [7]. Amino acids are non toxic and relatively cheap. The aim of this study is to investigate the inhibition properties of some of these.

EXPERIMENTAL :

The bottom end of admiralty brass rod of composition 70% Cu, 29% Zn and 1% Sn (surface area 0.42 cm^2) was the specimen. Prior to each experiment, the electrode was successively abraded with 1, 0, 00 grade emery paper, degreased with acetone, rinsed under running water and finally dried between two filter papers.

i) Weightloss Measurements

Experiments were carried out in open beakers to minimize the effect of heat evolved. Duplicate experiments were carried out and the weight loss averaged. The method is fully described earlier [8].

ii) Polarization Measurements

Current from a constant current device (Potentiostatic, Galvanostatic model 253),

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was impressed on the specimen using 3 electrode cell (specimen, Pt wire and SCE). Corrosion potential was recorded using a digital pH-meter (Type C.G. 822). Details of the experimental procedure, electrolytic cell and electrical circuit are fully described earlier [9].

The corrosion rate (R_{corr}) in millimeter per year (MPY) can be expressed by the equation [10]

$$R_{corr} = \frac{0.13\ i_{corr}\ W_e}{d} \qquad ....(1)$$

where i_{corr} is the corrosion current density in $\mu A.cm^{-2}$. W_e is the equivalent weight of the corroding species and d is the density.

The inhibitors studied are the four amino acids - glycine, L-phenylalanine, L-tyrosine and L-histidine. All chemicals used were of A.R. grade.

RESULTS AND DISCUSSION

Weight Loss Measurements

Admiralty brass were exposed for 3-hours in naturally aerated 0.1 M H_2SO_4 with and without addition of the inhibitors. From the amount of loss in weight, the corrosion rates were determined and the Inhibition efficiency (I.E.) at each inhibitor concentration was calculated using the equation.

$$I.E. = \left[1 - \frac{R_{add}}{R_{free}} \right] x\ 100 \qquad ... (2)$$

where R_{add} and R_{free} are the corrosion rates of admiralty electrode in presence of the inhibitors and its absence. The results are collected in Table 1. It is clear that, the inhibition efficiency of these inhibitors decreases in the following order: histidine > tyrosine > alanine > glycine.

Polarization Measurements

The effect of addition of increasing concentrations of these inhibitors on the anodic and cathodic polarization of admiralty brass was studied in 0.1 M H_2SO_4 at 30°C. Fig. 1 shows this effect of histidine as a typical case. Similar curves were obtained for the other compounds.

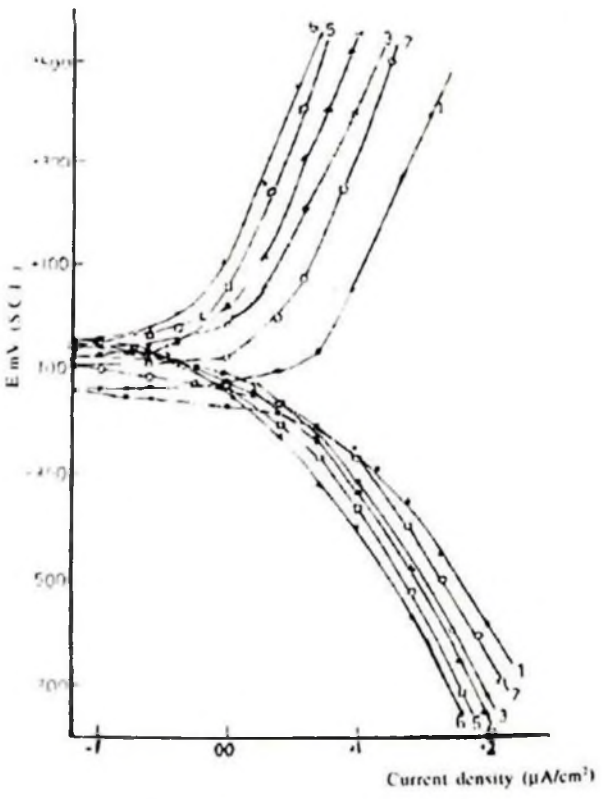


Fig 1 Anodic & Cathodic Polarization Curves
Specimen Admiralty Brass; Temp. 30°C
Medium 0.1 M Sulphuric acid Solution containing Different concentrations of Histidine
1 0.0 ppm; 2 100 ppm; 3 300 ppm;
4 500 ppm; 5 700 ppm; 6 900 ppm

Table 1

Corrosion potential (E_{corr}), corrosion current density (i_{corr}) exchange current density (i_o), rate of corrosion (R_{corr}), inhibition efficiency (I.E) from polarization and weight loss measurements

Specimen: Admiralty Brass;
Medium 0.1 M H_2SO_4 containing different concentration of inhibitors.

Inhib.conc. ppm	E_{corr} mV SCE	i_{corr} μA.cm^{-2}	i_o μA.cm^{-2}	R_{corr} mpy	% I.E. From polarisation	wt loss
Inhibitor: Glycine						
0.00	-145	6.309	4.365	6.328	-	-
100	-133	4.002	2.754	4.014	36.562	35.242
300	-125	3.019	2.089	3.028	52.149	51.032
500	-116	1.650	1.318	1.655	73.846	70.732
700	-108	1.380	0.955	1.384	78.128	75.003
900	- 96	1.258	0.660	1.262	80.056	79.112
Inhibitor: Phenylalanine						
0.00	-145	6.309	4.365	6.238	-	-
100	-125	3.681	2.630	3.692	41.656	42.522
300	-119	2.830	1.995	2.637	58.328	56.112
500	-116	1.659	1.585	1.669	73.704	72.003
700	-105	1.338	1.148	1.342	80.056	78.113
900	-101	1.047	1.023	1.050	83.861	82.165
Inhibitor: Tyrosine						
0.00	-145	6.309	4.365	6.328	-	-
100	-122	2.884	1.659	2.892	54.282	53.565
300	-116	1.819	1.513	1.824	71.75	70.166
500	-108	1.513	0.955	1.517	76.027	75.024
700	-104	1.258	0.794	1.262	80.056	79.523
900	- 99	0.955	0.631	0.958	84.861	83.224
Inhibitor: Histidine						
0.00	-145	6.309	4.365	6.328	-	-
100	-118	3.981	3.162	3.993	58.328	5.215
300	-109	1.819	2.089	1.824	71.175	70.024
500	-105	1.317	1.585	1.351	78.650	78.650
700	- 98	1.223	1.258	1.226	80.625	79.342
900	- 92	0.902	1.049	0.904	85.714	88.671

The corrosion current density was determined by extrapolating anodic and cathodic Tafel lines to the free corrosion potential values. The exchange current density was determined from the intersection of the linear parts of the cathodic curves with the reversible potential of hydrogen on Pt in the same solution [11].

The inhibition efficiency was calculated from polarization measurement from the following equation:

$$I.E = 100 \left[1 - \frac{R_{add}}{R_{free}} \right]$$

where R_{add} and R_{free} are the corrosion rates in presence and absence of the inhibitors.

Table 1 shows the effect of the inhibitor concentrations on the corrosion parameters. The data shows clearly that with increase in the concentrations of the additives, E_{corr} shifts to less negative values; i_{corr} and hence R_{corr} decrease and I.E. increases indicating the inhibiting effect of these compounds.

The order of inhibition efficiency obtained from polarization studies is the same as in weight loss measurement: histidine > tyrosine > phenylalanine > glycine.

The inhibition efficiency of additives depends on several factors including charge density, number of adsorption sites, molecular size and mode of interaction with the metal surface. The inhibition of admiralty brass by amino acid compounds

Table 2

Effect of Temperatures on the Corrosion Parameters

Specimen: Admiralty Brass;
Medium: 0.1 M H_2SO_4 without/with inhibitors
reference electrode SCE.

Temp. °C	E_{corr} mV	i_{cor} μA.cm^{-2}	i_o μA.cm^{-2}	R_{corr} mpy	I.E. %
No Inhibitor					
30	-145	6.309	4.365	6.328	-
40	-148	6.725	4.532	6.745	-
50	-155	7.213	4.932	7.235	-
60	-160	7.815	5.221	7.838	-
70	-166	8.432	6.232	8.457	-
Inhibitor: Glycine 700 PPM					
30	-108	1.380	0.955	1.384	78.128
40	-103	1.513	1.585	1.517	76.024
50	-100	1.659	1.737	1.664	73.704
60	- 96	1.778	1.905	1.783	71.823
70	- 94	1.901	2.089	1.906	69.879
Inhibitor: Phenylalanine 700 PPM					
30	-105	1.338	1.148	1.342	80.056
40	-102	1.448	1.202	1.450	77.619
50	- 98	1.579	1.380	1.583	76.557
60	- 96	1.695	1.737	1.700	73.704
70	- 92	1.818	1.955	1.824	71.168
Inhibitor: Tyrosine 700 PPM					
30	-104	1.258	0.794	1.262	80.056
40	-101	1.290	0.955	1.294	79.551
50	- 96	1.379	1.049	1.383	78.142
60	- 92	1.475	1.148	1.479	76.620
70	- 88	1.595	1.318	1.599	74.730
Inhibitor: Histidine 700 PPM					
30	- 98	1.223	1.258	1.226	80.625
40	- 94	1.258	1.380	1.262	80.056
50	- 90	1.312	1.737	1.316	79.203
60	- 87	1.395	1.905	1.399	77.890
70	- 82	1.475	2.089	1.479	76.626

is expected to occur through adsorption on the metal surface *via* the carboxylate groups. The adsorption of the carboxylate group on the metal surface would depend essentially on its charge density.

Histidine is more efficient as inhibitor because of the presence of highly donating imidazol group. This group increases the charge density on the adsorbing centre of the molecule. The other compounds are less inhibitive because of the comparative lower basicity of the carboxylate group in these compounds.

Effect of Temperatures

The effect of temperature on the corrosion parameters, E_{corr}, I_{corr}, I_o and I.E. was studied in 0.1 M H_2SO_4 in the temperature range 30-70°C in absence and presence of 700 ppm of every additive. The results were listed in Table 2.

The temperature has almost no effect on the general shape of the polarization curves. An inspection of Table 2 shows that as the temperature increased, the corrosion

Table 3

Activation energy (E_a), enthalpy change ($\Delta H'$), entropy change ($\Delta S'$) and change in free energy of activation ($\Delta G'$)

Specimen: Admiralty Brass
Medium: 0.1M H_2SO_4 without /with of different inhibitors ; Temperature Varying

Temp.°K	303	313	323	333	343
Glycine 700 PPM					
E_a kJ.mol^{-1}			9.573		
$\Delta H'$ kJ.mol^{-1}	12.092	12.175	12.258	12.342	12.425
$-\Delta S'$ kJ.mol^{-1}	0.1897	0.1905	0.1912	0.1916	0.1921
$\Delta G'$ kJ.mol^{-1}	69.601	71.815	74.068	76.160	78.313
Phenyl alanine 700 PPM					
E_a kJ.mol^{-1}			8.616		
$\Delta H'$ kJ.mol^{-1}	11.135	11.218	11.301	11.384	11.467
$-\Delta S'$ kJ.mol^{-1}	0.2058	0.2060	0.2063	0.2068	0.2072
$\Delta G'$ kJ.mol^{-1}	73.206	75.697	77.952	80.258	82.562
Tyrosine 700 PPM					
Ea kJ.mol^{-1}			6.127		
$\Delta H'$ kJ.mol^{-1}	8.646	8.729	8.812	8.895	8.978
$-\Delta S'$ kJ.mol^{-1}	0.2140	0.2143	0.2144	0.21146	0.2148
$\Delta G'$ kJ.mol^{-1}	73.498	75.815	78.086	80.387	82.687
Histidine 700 PPM					
E_a kJ.mol^{-1}			4.78		
$\Delta H'$ kJ.mol^{-1}	7.299	7.382	7.465	7.548	7.832
$-\Delta S'$ kJ.mol^{-1}	0.2192	0.2197	0.2202	0.2204	0.2205
$\Delta G'$ kJ.mol^{-1}	73.725	76.174	78.583	80.928	83.287

potential (E_{corr}) shifts in the negative direction and the value of corrosion current density and hence the corrosion rate increase. This proves that the inhibition occurs through the adsorption of the additives on the metal surface. Desorption is aided by increase in temperature.

The activation energy of the corrosion process is related to R_{Corr} by the following equation [12]:

$$R_{corr} = A \exp\left[\frac{-E_a}{RT}\right] \quad .....(4)$$

where E_a is the activation energy, A is the Arrehenius constant, R is the gas constant and T is the absolute temperature. A plot of log R_{corr} *vs* 1/T was found to be linear in all cases; the value of E_a can be obtained from the slope of the straight line. The value of E_a obtained in 0.1 M H_2SO_4 is equal 7.27 kJ.mol^{-1}. The values for the compounds studied are listed in Table 3.

Thermodynamic Parameters

The activation parameters - free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) - were calculated using the well known relationships [13,14] and are listed in Table 3. The positive values of free energy of activation ΔG^* indicated the adsorption on the surface of the specimen to be non spontaneous. The positive value of ΔH^* shows the adsorption process is endothermic in nature. The negative value of ΔS^* indicate an increase in order with rising of temperatures.

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