

Corrosion inhibition and hydrogen permeation studies of (6R, 7R)-7-[[(2R)-2-amino-2-phenylacetyl]amino]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid on SS 304 in 3.5% NaCl solution-Part I.

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Abstract

The influence of (6R,7R)-7-[[(2R)-2-amino-2-phenylacetyl]amino]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid (APMC) on corrosion and hydrogen permeation through stainless steel 304 in 3.5%NaCl has been studied using weight loss measurements and various electrochemical techniques. The compound is found to be more inhibitive in sea water medium. Potentiodynamic polarization studies clearly indicate that APMC behaves as a cathodic inhibitor. Hydrogen permeation studies and AC impedance measurements also prove an improved performance of the compound in 3.5% NaCl. The adsorption of this compound on the stainless steel surface obeys Temkin's adsorption isotherm.

Keywords : Corrosion inhibitor, impedance, hydrogen permeation, adsorption

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Introduction

Thiourea and its derivatives have been studied for more than four decades because they inhibit the corrosion of steels and are superior to amine-based inhibitors in acid media ¹⁻³. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are potential corrosion inhibitors. While extensive investigations have been carried out on inhibitor properties of thiourea, due attention has not yet been paid to a systematic study of inhibitor action of thiourea derivatives. However, several substituted thiourea have been investigated as corrosion inhibitors ⁴. Most of the effective organic inhibitors have heteroatoms such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface ⁵⁻⁸. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair determines the adsorption of these molecules on the metal surface. All the above studies reveal the one common observation that thiourea derivatives can be regarded as excellent corrosion inhibitors. But studies on the influence of APMC on hydrogen permeation through steel substrate during pickling are very scarce. A good inhibitor should have the following two important requisites: (1) it should have very good inhibition efficiency and (2) it should bring down the hydrogen permeation current to a considerable extent. Some organic compounds give very high values of inhibition efficiency, but they have a negligible effect in reducing the hydrogen permeation current and vice versa. Compounds which come under this class produce hydrogen embrittlement in a later stage by the combination of permeated atomic

hydrogen. This delayed failure creates cracking, pitting, breakage, etc., on the metal surface.

Experimental

SS 304 of size 4 x 1 x 0.020 cm were used for weight loss and hydrogen permeation studies. A SS 304 cylindrical rod embedded in araldite resin with an exposed area of 0.283 cm² was used for galvanostatic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier. [9] Both cathodic and anodic polarisation curves were recorded potentiodynamically (1 mA s⁻¹) using corrosion measurement system BAS Model: 100A computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil, Hg/Hg₂Cl₂/3.5%NaCl was used as auxiliary and reference electrodes, respectively. The hydrogen permeation study was carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell, as described earlier.[4] Double layer capacitance (C_{dl}) and charge transfer resistance values (R_c) were obtained using AC impedance measurements as described in an earlier publication." The surfaces of corroded and corrosion inhibited SS 304 specimens were examined by diffuse reflectance studies in the region 200- 700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan).

Results and Discussion

Weight loss and Gasometrical measurements

Table 1 gives the values of inhibition efficiency for different concentrations of APMC for the corrosion of stainless steel in 3.5 % NaCl obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of steel in neutral media .⁹.

The structure of the compound is given in Figure 1.

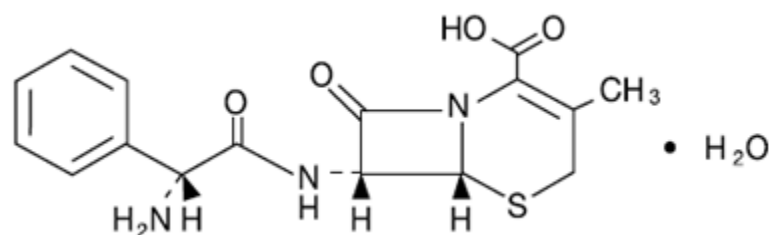


Figure 1. Structure of APMC.

The inhibition of corrosion of brought about by APMC can be due to the following interactions:

1. The interaction between the lone pairs of electrons of the sulfur atom of the organic compound and the positive charge bearing metal surface¹⁰.

2. The interactions between lone pairs of electrons of the nitrogen atoms and the positively charged steel surface ¹¹.

3. The presence of phenyl amino in the inhibitor shows inductive (+I) effect may enhance the electron density on the sulfur atom leading to effective performance ¹².

It is found that there is very good conformity between the values of inhibition efficiency obtained by weight loss and gasometrical methods.

Potentiodynamic polarization studies

Table 2(a) and 2(b) give values of corrosion kinetic parameters such as Tafel slopes (b_a and b_c), corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency obtained from potentiodynamic polarization curves for stainless steel in 3.5% NaCl containing various concentrations of inhibitor. It can be found from this table that values of Tafel slopes and I_{corr} are very much similar to those reported earlier ^{12,13}. Further it is proved that increasing concentrations of APMC boosts the values of tafel slopes, but the values of cathodic tafel slopes are enhanced to greater extent. So the inhibition of corrosion of stainless steel in salt water is under cathodic control. Values of E_{corr} is shifted to less negative values when different concentrations of inhibitor were used. This could be attributed to the formation of strong adsorbed layer of compound on the surface of SS 304. The presence of increasing concentrations of APMC decreases I_{corr} values in salt water. It can also be seen that most of the values of inhibition efficiency determined by weight loss measurements and potentiodynamic polarization studies are in good agreement to each other.

Hydrogen permeation measurements

Hydrogen permeation measurements results for the dissolution of stainless steel 304 without and with additions of APMC are given in Table 3. It can be visualized from the table that the presence of inhibitor in 3.5%NaCl encourages of the ingress of hydrogen. The enhancement in permeation current might be due to the decomposition of APMC on the SS 304¹⁴. In all the mechanisms suggested so far, invariable the product of decomposition of inhibitor is H₂S, which is evolved on the metal surface. Its formation can be detected by radiometric measurements, if labeled thiourea³⁵ or its derivatives are used¹⁵. The whole process occurs in two steps. In the first step, APMC molecules are adsorbed on the iron metal surface through the interaction of lone pairs of electrons of nitrogen and sulfur. In the second step, the adsorbed molecules of the compound slowly undergoes chemical changes. In general, these type of inhibitor festers with the formation of H₂S by the action of hydrogen evolved on the metal.

Hough et al¹⁶ reported that the enhanced permeation of hydrogen ions through the surface of SS 304 in 3.5% NaCl may be due to the presence of increased number of surface hydrogen atoms. This can be claimed to the inhibition of the combined hydrogen atoms to form hydrogen molecules. TrabANELLI and Zucchi¹⁷ are of opinion that sulfur of hydrogen sulfide acted as negative catalyst for the formation of molecular hydrogen. It can be found from the results that the enhancement of permeation current is greater, if the concentration of inhibitor is more as studied by Lahiri et al¹⁸ who also found that

hydrogen permeation current increases with increase in the concentration of di-ortho tolyl

thiourea.

Impedance studies

The results of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are indicated in table 4. It can be noticed that the values of R_t is found to raise with increase in concentration of inhibitor in salt water. Values of double layer capacitance are seen to be less in the presence of APMC in 3.5% NaCl. It is found that values of C_{dl} are fetched along by increasing concentrations of APMC in salt water medium. This can be ascribed to enhancing the adsorption of compound on SS 304 surface with increase in its concentration.

A plot of surface coverage (θ) versus $\log C$ gives a straight line proving that the adsorption of APMC on the SS 304 surface from both acids follows Temkin's adsorption isotherm. This points to corrosion inhibition by APMC, being a consequence of its adsorption on the metal surface.

Conclusions

1. (6R,7R)-7-[[[(2R)-2-amino-2-phenylacetyl]amino]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid retards the dissolution of SS 304 in 3.5%NaCl.
2. The inhibition of corrosion of steel by the inhibitor is under cathodic control.
3. The presence of inhibitor is found to enhance the extent of hydrogen entry through steel surface.
4. Nyquist plots authenticate the better performance of the compound.

5. The adsorption of the APMC on SS 304 surface obeys Temkin's adsorption isotherm.

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Table 1. Values of inhibition efficiency for the corrosion of SS 304 in 3.5% NaCl in the presence of different concentrations of APMC obtained from weight loss and gasometrical measurements.

Concentration of Inhibitor (mM)	Inhibition efficiency	
	Weight loss Studies	Gasometrical measurements
1	80.2	80.5
5	84.3	84.6
10	90.3	90.5
50	94.3	94.6
100	97.2	97.6

Table 2.a Corrosion kinetic parameters of SS 304 in 3.5%NaCl in the presence of different concentrations of APMC obtained from potentiodynamic polarization studies.

Concentration of Inhibitor (mM)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} mA cm^{-2}	Inhibition efficiency (%)
		b_a	b_c		
Blank	-511	65	117	2.77	---
1	-495	73	126	0.44	84.2
10	-483	74	136	0.29	88.6
50	-477	76	149	0.15	94.0
100	-471	85	164	0.08	95.3

Table 3. Values of permeation current for the corrosion of SS 304 in 3.5% NaCl in the presence of different concentrations of (6R,7R)-7-[(2R)-2-amino-2-phenylacetyl]amino]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid.

Concentration of Inhibitor (mM)	Steady state permeation current (μA)
	1M HCl
Blank	21.9
1	26.6
10	28.5
50	29.0
100	31.8

Table 4. Impedance parameters for the corrosion of SS 304 in salt water in the presence of different concentrations of (6R,7R)-7-[(2R)-2-amino-2-phenylacetyl]amino]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid.

Concentration of Inhibitor (mM)	HCl	
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) $\mu\text{F.cm}^{-2}$
Blank	4.4	242
1	36	174
10	43.5	134.2
50	79.4	118.3
100	89.3	97