

Electrochemical investigation of anticorrosive effect on mild steel by Phenylalanine dithiocarbamate in 0.5 M sulphuric acid solution

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Abstract:

The dithiocarbamate Phe-dtc was synthesized and investigated electrochemically as potential corrosion inhibitor. Investigations revealed that Phe-dtc is efficient inhibitor with anticorrosive efficiency upto 99% at 298 K. The anodic and cathodic tafel curves showed insignificant change of 17 mV for Phe-dtc governing the compound is mixed-type of inhibitor. With increase in concentrations of Phe-dtc, the rising values of R_{ct} and decreasing value of C_{dl} suggest that Phe-dtc acts via formation of a defensive layer by adsorption at the solution-metal interface.

Introduction

Over the years use of metals and alloys have been increased in our daily life and corrosion of metals remains a global scientific problem. Corrosion affects the metallurgical, chemical, food processing and oil industries as the cleaning and descaling of metals usually involve corrosive acids. The different methods are being employed to minimize the problem of corrosion but are expensive and non-friendly to environment [1]. One such cost effective method is the use of some specific additives known as corrosion inhibitors with the metal or with the surrounding medium which is generally acidic in nature. Organic compounds having S,N,O and conjugation in plane in their structure, are known to behave as good corrosion inhibitors. It is well understood that such compounds adsorb strongly on metal surface and construct a barrier at metal-solution interface thereby prevent the occurrence of redox reaction effectively [2]. The presence of two sulfur atoms and one nitrogen atom in dithiocarbamate (dtc) compound provides strong chelating ability with metal surface and make it to act as an effective corrosion inhibitor [3]. In recent

years dithiocarbamates have been emerged as prominent, environment friendly corrosion inhibitors. Some of the recent studies are reported as here. N. Kicir et.al. assessed ammonium(2,4-dimethylphenyl) dithiocarbamate as effective corrosion inhibitor for MS. The high efficiency and stability in aqueous solution has been attributed to the presence of phenyl group in inhibitor structure [4]. X.H Zhang et.al. revealed that ammonium pyrrolidine dithiocarbamate inhibited corrosion by altering both oxidation and reduction reaction of metal and showed maximum corrosion inhibition efficiency of 95% for in 3 NaCl solution for copper [5]. 1-pyrrolidine dithiocarbamate (PDTC) evaluated as corrosion inhibitor for Aluminium, Copper and Magnesium alloy in NaCl solution by Qafsaoui et.al. and proposed that addition of PDTC increases the galvanic coupling resistance [6]. The corrosion mitigation ability due to formation of stable protective layer of PDTC on copper surface, thereby decreasing both anodic dissolution and oxygen reduction reactions, was explained by Qafsaoui et.al. [7]. Encouraged by these results we have also examined the corrosion mitigation abilities of dithiocarbamate Phe-dtc using electrochemical techniques.

Experimental method

Mild steel strips used in the investigation is of cross section area of 1 cm × 1 cm. The composition of mild steel was determined by EDX spectra analysis which is C = 0.15, S = 0.02, Mn = 1.02, Si = 0.08 and Fe = 98.72. The sample surface was polished before measurements with help of emery paper of grade 100 to 2000 and samples were degreased using acetone, washed with deionized water. The mild steel samples were eventually dried in a vacuum desiccator overnight. The electrochemical workstation (CHI 760D, CH Instruments, USA) was employed to conduct all electrochemical studies. The studies were performed with concentrations 0.01 M, 0.001 M, 0.0001 M and 0.00001 M at optimum temperatures i.e. 298 K to 328 K. In the operating three electrode assembly system, working electrode comprised of low-carbon steel sample with 1cm² of the open area, Pt electrode acted as auxiliary and a saturated calomel electrode (SCE) was used as reference electrodes. EIS studies were done at corrosion potential using frequency range 1Hz – 1kHz with amplitude 0.005 V.

Results and Discussion

Synthesis of Dithiocarbamate:-

The dithiocarbamate namely Sodium(1-carboxy-2-phenylethyl) carbamodithioate (Phe-dtc) was prepared from the recommended procedure [8,9].

Galvanostatic Polarization Studies

The anticorrosive effect on mild steel in 0.5 M sulphuric acid solution was studied with and without different concentrations of Phe-dtc at varied temperatures. To appraise the effect of Phe-dtc on the electrochemical behaviour of mild steel in sulfuric acid, Tafel curve was recorded and shown in Fig.3. Electrochemical parameters for Phe-dtc obtained from the polarization curves are summarized in Table 1.

As seen from the Table 1, the notable alteration was found in b_a and b_c for variation in Phe-dtc concentration, this indicates that the inhibitor affected both polarization reactions [10, 11]. Maximum E_{corr} value change for Phe-dtc is 28 mV (Table 1) at 298 K, which concluded that Phe-dtc is of a mixed-type inhibitor. This also depicts that inhibition mechanism follows geometrical blocking of the reaction sites by adsorbing Phe-dtc at mild steel surface [13].

The values in Table 1 also indicate that the inhibition efficiencies (IE) increases with the concentration of Phe-dtc but decreases with rising temperature due to the desorption of some adsorbed inhibitor molecules. [14].

Electrochemical Impedance Spectroscopy studies:

It is clear from the Nyquist plot and Bode plots of acidic solutions that with addition of concentration of Phe-dtc from 10^{-5} M to 10^{-2} M, impedance response (single depressed capacitive loop) increases in comparison to blank acid solution [15, 16].

As seen from Table 2, the R_{ct} values of inhibited solution are increasing with the concentration of Phe-dtc. A corroding system will be slow when it possesses a larger charge transfer resistance [17]. The values of decreasing C_{dl} with increase in amount of Phe-dtc suggests an increase in thickness of the electrical double layer and acts via adsorption at the metal-solution interface.

Conclusion

Dithiocarbamate compound Sodium(1-carboxy-2-phenylethyl) carbamodithioate (Phe-dtc) showed effective inhibition performance for the corrosion of MS in 0.5 M H_2SO_4 solutions. The IE increases as inhibitor concentration goes from 10^{-5} M to 10^{-2} M and gets decreased at elevated temperatures due to desorption of inhibitor molecules from the mild steel surface. Phe-dtc is of mixed-type inhibitor shown by insignificant change in the Tafel slope values. The inhibition action is due to formation of a defensive layer at MS surface by adsorption of Phe-dtc supported with high R_{ct} values.

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Caption of Figures

Fig. 1. Structure of Phenylalanine dithiocarbamate (Phe-dtc)

Fig. 2. Galvanostatic polarization curves for mild steel in 0.5 M H₂SO₄ containing different concentrations of (Phe-dtc) at various temperatures

Fig. 3. Bodes and Nyquist curves for mild steel in 0.5 M H₂SO₄ containing different concentrations of (Phe-dtc) at various temperatures

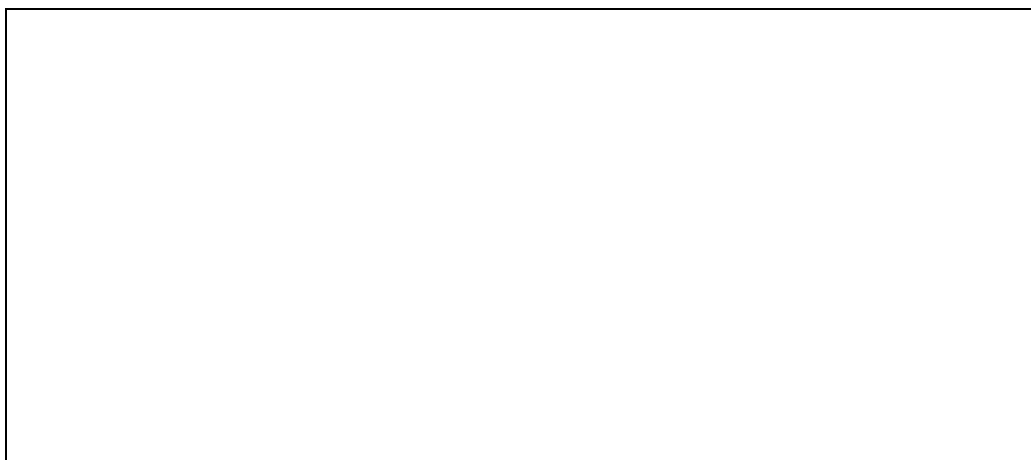


Fig. 1. Structure of Phenylalanine dithiocarbamate (Phe-dtc): Sodium(1-carboxy-2-phenylethyl) carbamodithioate

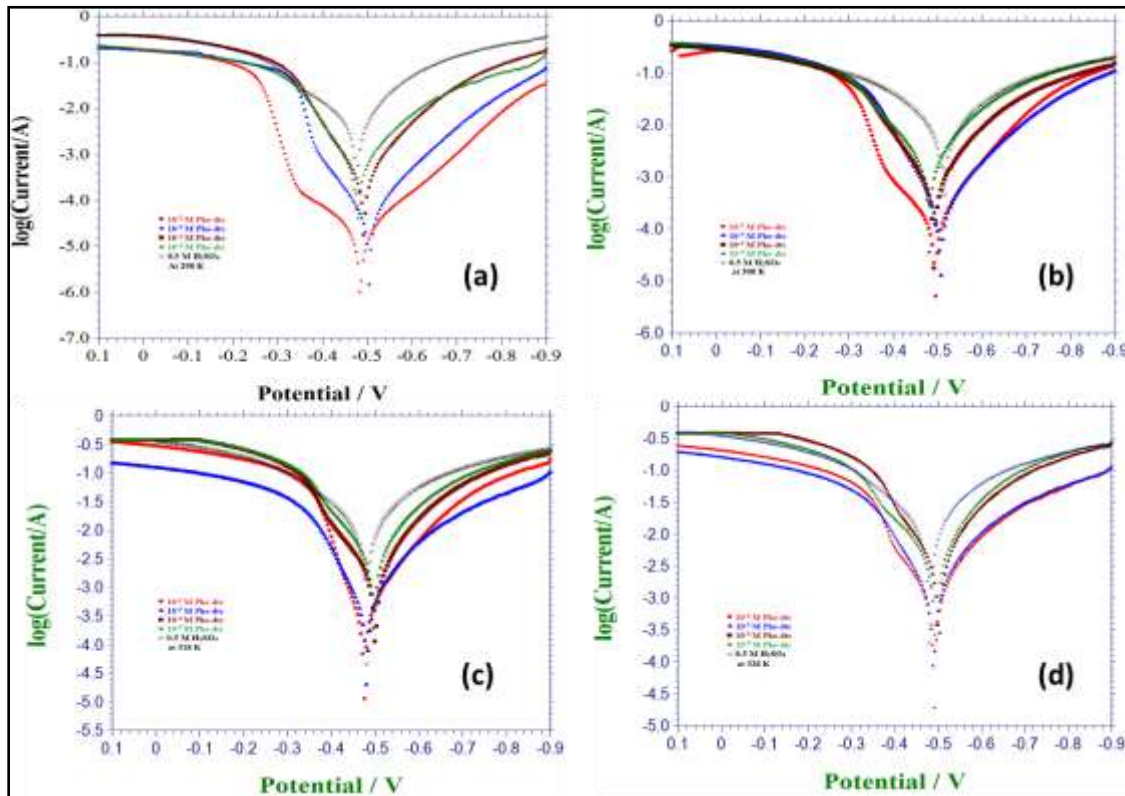


Fig.2. Galvanostatic polarization curves for mild steel in 0.5 M H₂SO₄ containing different concentrations of (Phe-dtc) at various temperatures.

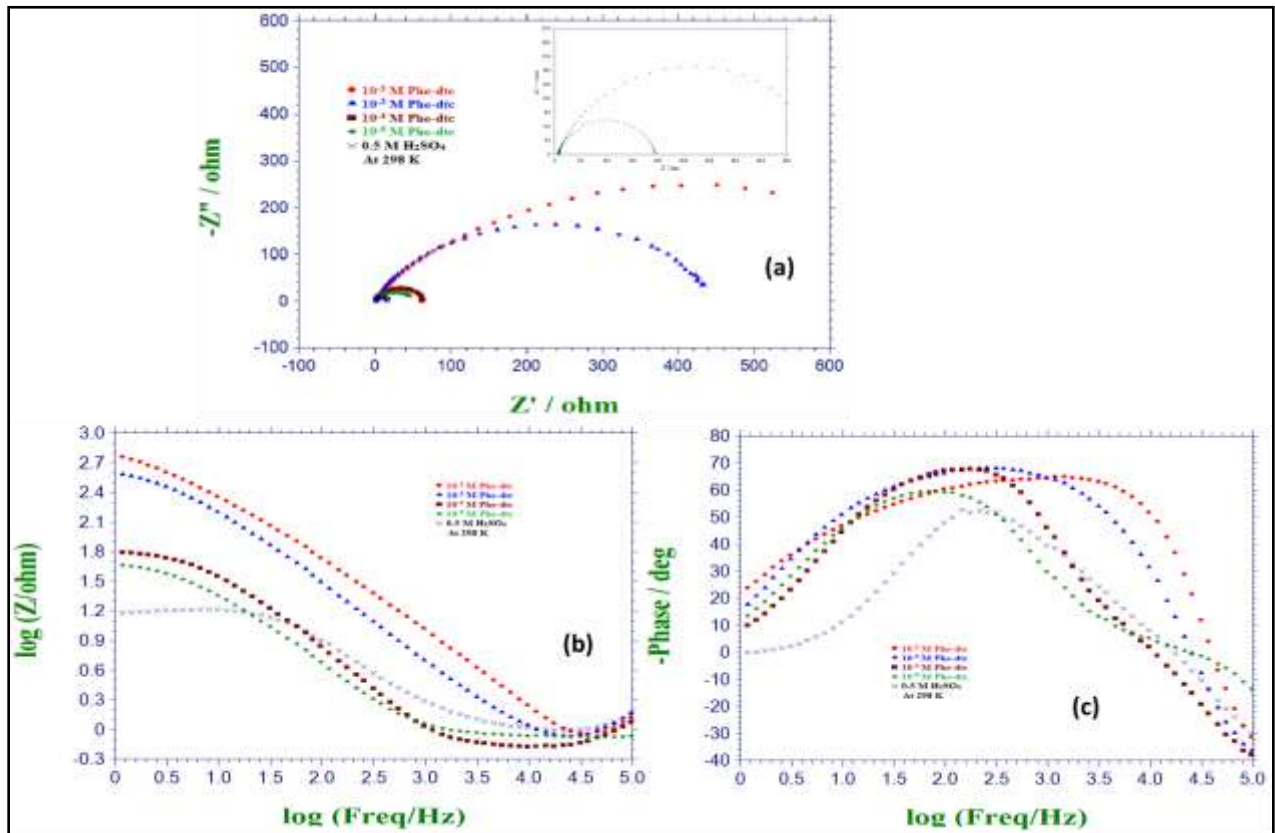


Fig.3. Bodes and Nyquist curves for mild steel in 0.5 M H_2SO_4 containing different concentrations of (Phe-dtc) at various temperatures.

Table 1. Galvanostatic polarization parameters for the corrosion of mild steel in 0.5 M H₂SO₄ containing different concentration of (Phe-dtc)

Temp. (K)	Conc. (M)	-E _{corr} (mV vs. SCE)	b _c (mV/decade)	b _a (mV/decade)	I _{corr} (mA cm ⁻²)	I.E. (%)
298	10 ⁻²	486	129	167	0.02458	99
	10 ⁻³	505	101	76	0.04714	99
	10 ⁻⁴	493	96	65	0.2954	94
	10 ⁻⁵	478	109	69	0.49	90
	0	477	124	155	5.29	-
308	10 ⁻²	495	97	93	0.1462	98
	10 ⁻³	507	108	67	0.2317	97
	10 ⁻⁴	493	107	83	0.7182	91
	10 ⁻⁵	480	118	111	1.97	76
	0	514	155	154	8.336	-
318	10 ⁻²	475	101	49	0.2957	97
	10 ⁻³	481	118	72	0.4883	96
	10 ⁻⁴	501	115	98	1.886	85
	10 ⁻⁵	497	128	107	3.821	70
	0	480	164	174	13.01	-
328	10 ⁻²	492	134	80	1.102	92
	10 ⁻³	489	135	91	1.416	90
	10 ⁻⁴	502	134	92	3.959	74
	10 ⁻⁵	494	125	148	4.861	68
	0	480	170	177	15.43	-

Table 2. Impedance parameters for the corrosion of mild steel in 0.5 M H₂SO₄ containing different concentration of (Phe-dtc)

Conc. (M)	R _{ct} (Ω cm ⁻²)	f _{max} (Hz)	C _{dl} (μF cm ⁻²)	I.E. (%)
10 ⁻²	882.74	248.72	0.7248	98.41
10 ⁻³	465.30	164.12	2.084	96.99
10 ⁻⁴	64.085	26.39	94.10	78.21
10 ⁻⁵	52.74	18.83	160.26	73.53
Blank	13.96	7.193	1584	-