

Research Article

Corrosion Inhibition Effect of 4-(2-Diethylamino-Ethylsulfonyl)-Phthalonitrile and 4,5-Bis(Hexylsulfonyl)-Phthalonitrile

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Inhibition of stainless steel corrosion in a 3.0 M NaCl solution by 4-(2-diethylamino-ethylsulfonyl)-phthalonitrile (DAESPN) and 4,5-bis(hexylsulfonyl)-phthalonitrile (Bis-HSPN) was investigated by polarization and electrochemical impedance spectroscopy (EIS) measurements. The values of cathodic (β_c) and anodic (β_a) Tafel slopes, i_{corr} , E_{corr} , corrosion rate (CR), and inhibition efficiencies (IE%) obtained from polarization curves and polarization resistance (R_p), double-layer capacitance (C_{dl}), specific capacitance (C_{sp}) values were obtained from EIS. Double-layer capacitance differences in the presence and absence of inhibitors were also obtained from EIS measurements as suggested in the literature in order to investigate the interaction of them with metal surface. Results show that both DAESPN and Bis-HSPN are effective in cathodic reaction. Impedance measurements suggest higher surface coverage for DAESPN. The interaction between the inhibitor and the stainless steel was investigated by the adsorption isotherm. Langmuir adsorption isotherm K_{ads} was applied and ΔG values were obtained and found as 4.32×10^{-4} , 1.17×10^{-4} and 9.2 kJ, 12.5 kJ for DAESPN and Bis-HSPN, respectively, which suggests the electrostatic interaction between charged metal surface and charged organic molecules.

1. Introduction

Stainless steel is used in a wide range of industrial applications. Corrosion of steel and its inhibition in chloride solution have attracted the attention of a number of investigators [1–4]. Because of its aggressiveness, inhibitors are used to reduce the rate of dissolution of metals. Compounds containing nitrogen, sulfur, and oxygen are being used for this purpose [5]. The most effective and efficient inhibitors are organic compounds with π bonds in their structures. The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to be adsorbed on the metal surface, which consists of the replacement of water molecule at a corroding interface. The adsorption of these compounds is influenced by the electronic structure of the inhibiting molecules [6, 7] and also by the steric factors, aromaticity, electron density at the donor atoms, and the presence of functional groups [8–13]. EIS is a useful

technique to evaluate the effect of sorption of inhibitors on the protection [14]. Double-layer capacitance differences in the presence and absence of inhibitors obtained from EIS measurements can be used in order to investigate the interaction of them with metal surface [15].

Thermodynamic parameters of the corrosion process play an important role to define the spontaneity of the conversion of the metal to corrosion products that can form in the corrosion environments to which the metal is exposed [16, 17].

In the present investigation, the corrosion inhibition behaviour of 4-(2-diethylamino-ethylsulfonyl)-phthalonitrile (DAESPN) and 4,5-bis(hexylsulfonyl)-phthalonitrile (Bis-HSPN) on stainless steel in 3.0 M NaCl solution was investigated using two different techniques: potentiodynamic polarisation curves and electrochemical impedance spectroscopy. The inhibitor efficiency was investigated at different inhibitor concentrations.

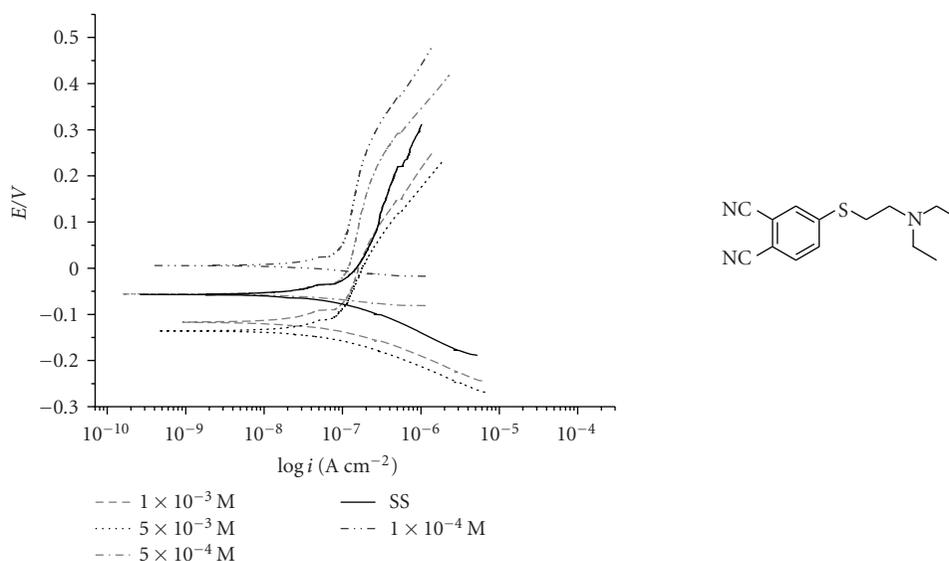


FIGURE 1: Polarization curves of stainless steel in the presence and absence of different concentrations of 4-(2-diethylamino-ethylsulfanyl)-phthalonitrile (DAESPN) in 3.0 M NaCl medium.

TABLE 1: Corrosion values SS in the presence and absence of different concentrations of DAESPN and Bis-HSPN in 3.0 M NaCl medium.

Electrode	Concentration M	E_{corr} mV	I_{corr} μA	β_a , mV/dec	β_c , mV/dec	IE%	CR, $\times 10^3$ mmpy
Bare	—	-56	0.418	453.2	93.2	—	5.0
DAESPN	1×10^{-3}	-116	0.273	406.5	67.9	34.6	3.3
Bis-HSPN	1×10^{-3}	-4	0.171	358.9	81.4	59.0	2.1
DAESPN	5×10^{-3}	-135	0.253	354.0	67.8	39.4	3.1
Bis-HSPN	5×10^{-3}	-75	0.381	823.4	75.2	24.0	4.6
DAESPN	5×10^{-4}	-55	0.305	636.7	43.8	27.0	3.7
Bis-HSPN	5×10^{-4}	40	0.226	577.2	24.8	46.0	2.7
DAESPN	1×10^{-4}	6	0.278	663.4	37.7	33.4	3.3
Bis-HSPN	1×10^{-4}	18	0.293	1002.8	25.4	30.0	3.5

2. Experimental

The working electrode for electrochemistry measurements was prepared from a cylindrical stainless steel rod (99.99%) with area of 0.2 cm^2 . The aggressive environment used was 3.0 M NaCl solution prepared from analytical reagent-grade chemicals and deionized water. All other chemicals were of AR grade, and the solutions were prepared using deionized water. Electrochemical polarisation curves and electrochemical impedance spectroscopy measurements were performed in a three-electrode cell using a PAR 2263 model potentiostat.

All potential values were reported versus Ag/AgCl. The working electrode was mechanically polished on wet silicon carbide (SiC) papers (400, 600, 1200 grid), rinsed with deionized water, degreased with acetone and ethanol, and dried at room temperature. It was then polarised $\pm 250 \text{ mV}$ from equilibrium potential at 1 mV/s for electrochemistry polarisation curve tests. The EIS experiments were performed at open circuit potential over a frequency range of $1 \text{ MHz} - 1 \text{ mHz}$, and effect of starting point was also tested in the range of $10 \text{ mHz} - 10 \text{ kHz}$ in order to see if there is any differences in measurements if it is started from low

frequency through higher frequency and vice versa. The sinusoidal potential perturbation was 10 mV in amplitude. The cell was open to air, and the measurement was conducted at room temperature.

3. Result and Discussion

Tafel-extrapolation measurements were done in the potentials region $\pm 250 \text{ mV}$ from corrosion potential, E_{corr} . Figures 1 and 2 show typical polarization curves for SS in 3.0 M NaCl solutions with and without inhibitors of (DAESPN and Bis-HSPN), respectively. The corresponding corrosion potentials (E_{corr}), corrosion currents, (i_{corr}), anodic Tafel slopes (β_a), and cathodic Tafel slopes (β_c) at different inhibitor concentrations are listed in Table 1.

As it can be seen from Table 1, addition of inhibitor prevents the corrosion up to 60 percent. Inhibitor concentration has only a small effect on inhibition since the corrosion currents do not change significantly by changing concentrations. However increase in concentration shifts the corrosion potential to the more cathodic values. Corrosion rates (CRs) have also calculated as mmpy for practical

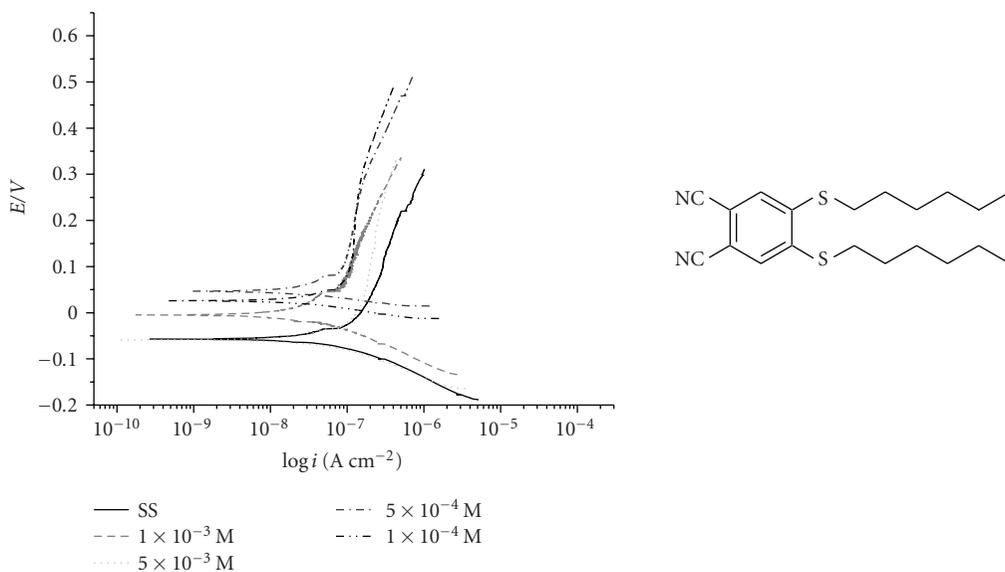


FIGURE 2: Polarization curves of stainless steel in the presence and absence of different concentrations of 4,5-bis(hexylsulfonyl)-phthalonitrile (Bis-HSPN) in 3.0 M NaCl medium.

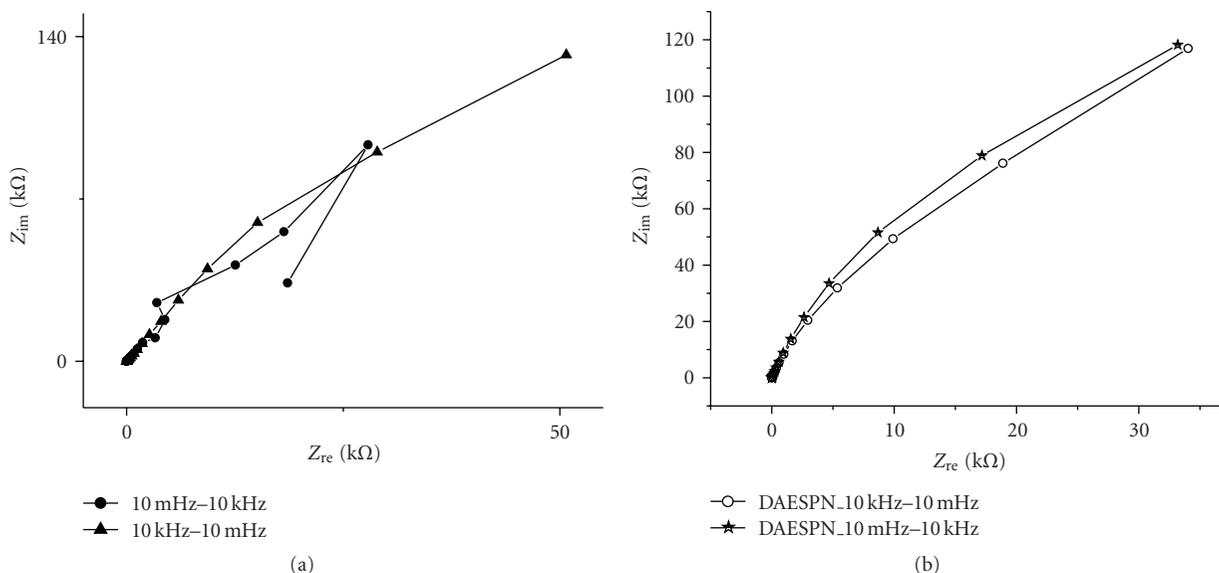


FIGURE 3: Nyquist plot of SS in the absence and presence of 1×10^{-3} M DAESPN in 3.0 M NaCl medium.

application, and results show that using 1×10^{-3} M Bis-HSPN produced the lowest corrosion rates for SS.

Impedance spectra of electrodes in the absence and presence of inhibitors were obtained in the frequency range of 1 MHz–1 mHz. Effect of starting point was also tested in the range of 10 mHz–10 kHz. In the first run, impedance spectrum was recorded by starting from low frequency (10 mHz), then frequency was increased up to 10 kHz. In the second run measurements were recorded in the reverse direction. Although bare electrode has some deviation when the direction changed (Figure 3(a)), in the presence of DAESPN the electrode becomes more stable that Nyquist plots are almost the same in both direction (Figure 3(b)). This result indicates that presence of inhibitor stabilizes the

surface. The frequency in which the phase angle is equal to -45 degrees commonly indicates Warburg diffusion. The absence and presence of inhibitor electrodes show Warburg type impedance behaviour in the range of 100 mHz–100 kHz (Figure 4, inset).

Specific capacitance (C_{sp}), double layer capacitance (C_{dl}), and phase angle degree were calculated from the impedance measurements for different inhibitor concentration and summarized in Table 2. The highest specific capacitance value was obtained for 5×10^{-3} M Bis-HSPN.

Basic information on the interaction between the inhibitor and the stainless steel can be provided by the adsorption. The degree of surface coverage (θ) for different concentrations of DAESPN and Bis-HSPN can be obtained

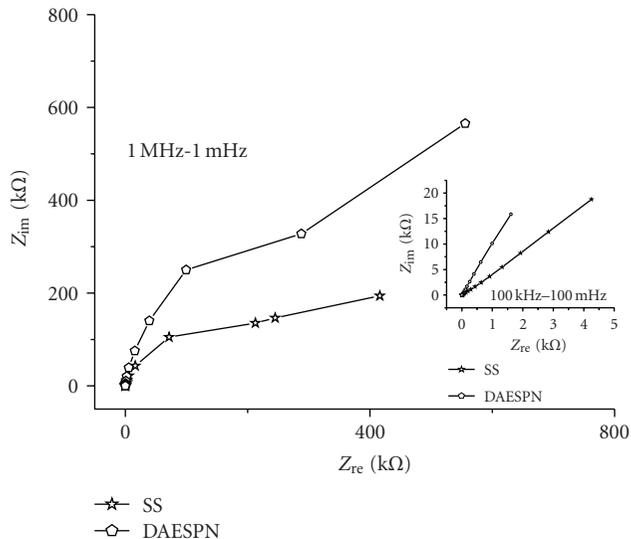


FIGURE 4: Nyquist plot of SS in the presence of 1×10^{-3} M DAESP in 3.0 M NaCl medium at different frequency range.

from the alternative current impedance study, using the following equation as suggested in the literature [18]:

$$\theta = \frac{C_{dl}(\theta = 0) - C_{dl}\theta}{C_{dl}(\theta = 0) - C_{dl}(\theta = 1)}, \quad (1)$$

where $C_{dl}(\theta = 0)$ and $C_{dl}(\theta = 1)$ are the double-layer capacitances (per unit area) of the inhibitor-free and entirely inhibitor covered surfaces, respectively; C_{dl}, θ is the composite total double-layer capacitance for any intermediate coverage θ . Higher θ values were obtained for DAESP than the values obtained at the same concentrations of Bis-HSPN.

With regard to the Langmuir adsorption isotherm the surface coverage θ of the inhibitor on the steel surface is related to the concentration (C_{in}) of the inhibitor (M) in the bulk of the solution according to the following equation [19–21]:

$$\theta = \frac{K_{ads}C_{in}}{1 + K_{ads}C_{in}}, \quad (2)$$

where K_{ads} is the equilibrium constant for the adsorption/desorption process. This equation can be rearranged to

$$\frac{C_{in}}{\theta} = \frac{1}{K_{ads}} + C_{in}. \quad (3)$$

From the intercepts of the straight lines on the C_{in}/θ -axis, K_{ads} can be calculated which is related to free energy of adsorption, ΔG_{ads}° as given by

$$\Delta G_{ads}^{\circ} = -RT \ln(55.5K_{ads}). \quad (4)$$

4. Conclusion

Two different types of phthalonitrile were used as inhibitors for SS corrosion in NaCl medium. Results show that both

TABLE 2: Specific (C_{sp}) and double layer capacitance (C_{dl}), phase angle and surface coverage values for SS electrode in the presence and absence of different concentrations of DAESP and Bis-HSPN in 3.0 M NaCl medium.

	Concentration M	C_{sp} , μF	$C_{dl} * 10^4$ F	Phase angle	θ
Bare	—	161.6	3.50	72	—
DAESP	1×10^{-3}	112.0	4.36	80	0.43
Bis-HSPN	1×10^{-3}	95.7	3.25	78	0.13
DAESP	5×10^{-3}	132.8	5.50	82	1.00
Bis-HSPN	5×10^{-3}	137.8	3.11	70	0.20
DAESP	5×10^{-4}	123.0	5.10	80	0.80
Bis-HSPN	5×10^{-4}	101.1	3.10	75	0.20
DAESP	1×10^{-4}	95.0	2.80	74	0.35
Bis-HSPN	1×10^{-4}	87.3	2.10	74	0.70

DAESP and Bis-HSPN inhibited the corrosion. Increase in concentration results a cathodic shift in corrosion potential indicating inhibitors are effective in cathodic reaction. Impedance measurements suggest that presence of inhibitors protect the electrode. The interaction between the inhibitor and the stainless steel investigated by the adsorption isotherm. Higher θ values suggest higher surface coverage for DAESP. Langmuir adsorption isotherm was applied. K_{ads} and ΔG values were obtained and found as 4.32×10^{-4} , 1.17×10^{-4} and 9.2 kJ, 12.5 kJ for DAESP and Bis-HSPN, respectively. This results indicates the electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution rather than charge sharing or charge transfer between the metal surface and organic molecules.

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