

Study of 2-Diethylamino Ethanol as an effective inhibitor for steel in hydrochloric acid and its synergistic effect with Hexamine

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Abstract

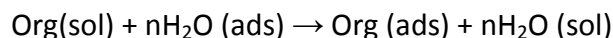
The inhibition effects of 2-Diethylamino Ethanol (2DEAE) and hexamine (HA) on the corrosion of mild steel in HCl solution was studied using tafel polarisation and electrochemical impedance measurements. For 2DEAE an optimum in the inhibition efficiency was observed at a concentration close to 200 ppm, which was ascribed to the formation of hemi-micellar aggregates that provoke inhibitor desorption from the metal/solution interface at higher concentrations. However, a monotonous increase in inhibition efficiency was observed as a function of concentration in the case of HA. Upon mixing HA and 2DEAE, concentration regions showing synergistic and antagonistic inhibition behavior were identified, and it was concluded that electrostatic interactions between adsorbate ions were likely responsible for both phenomena.

Keywords: 2-Diethylamino Ethanol, Corrosion Inhibitor, Synergism, Potentiodynamic, EIS

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1. Introduction:

Acid solutions are widely used for various purposes such as acid pickling, industrial cleaning, oil-well acid in oil industry and petrochemical processes [1, 2]. By developing these processes, corrosion of equipment has always been a major trouble for almost all mentioned industries. Hydrochloric acid is one of the most widely used agents in industry. Application of organic inhibitors is a known way for controlling corrosion in many industries. By adsorption on the metal surface, these inhibitors form a protective layer that will remove corrosive species from the metal/ solution interface and protect the metal [3]. Inhibitors protection depends on several factors acting together such as solution properties, metal characteristics in the solution and physiochemical properties of the inhibitor [4,5]. If these factors match properly in a certain solution/ metal system, H₂O molecules would replace with inhibitor molecules on the metal surface [6]:



It can be written that a polar group containing atoms such nitrogen, sulfur or oxygen exists in most of the organic active inhibitors [7-8]. In oil and gas industry, usually steel parts are in long term contacts with different acids and their relative products.

In this research, the effect of 2DEAE inhibitor (2-Diethylamino Ethanol) on corrosion of mild steel was evaluated in a 1 M hydrochloric acid (HCl) using potentiodynamic polarization and Electrochemical impedance spectroscopy(EIS). For this purpose, the average of corrosion rates in the presence and absence of 2DEAE were determined. In addition, the effect of Hexamine on corrosion inhibition of the samples was studied. Finally, for optimizing 2DEAE performance, synergistic effects of Hexamine were investigated using electrochemical tests.

2. Experimental:

2.1. Materials:

Hydrochloric acid (HCl 1M) was prepared by addition of analytical grade 35- 37% HCl to deionized water. Hexamine and 2DEAE were supplied from Merck Co. Fig. 1 shows the molecular structure of the investigated inhibitors.

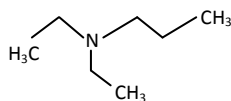


Fig. 1. Molecular structure of 2DEAE

The steel samples used had the following composition (in wt %); C: 0.085, Mn: 1.20, S: 0.33, Ni: 0.11, Cr: 0.06, Cu: 0.18, Si: 0.04 and Fe balance. Prior the polarization tests, the specimens were polished with emery papers up to 1200# and then were washed with double- distilled water.

2.2. Potentiodynamic and EIS tests:

Potentiodynamic and impedance measurements were carried out at open circuit potential (E_{ocp}) with a saturated calomel electrode (SCE) and a platinum electrode as reference and auxiliary electrode, respectively. Polarization curves were plotted using a computer controlled potentiostat (EG&G Model 273A) at a scan rate of 0.6 mV/sec. Electrochemical experiments were carried out after 1 hours of immersion of the samples in the solution. Corrosion current densities are reported from the polarization curves by linear extrapolation of the Tafel curves at points 50 mV more positive and more negative, respectively, than E_{ocp} . Correction of the curves for IR-drop was not required in view of the high electrical conductivity of the strongly acidic solutions.

The inhibition efficiency (IE) was determined by the following relationship:

$$IE = \left(1 - \frac{C.R_{inh}}{C.R_{blank}}\right) \times 100 \quad (1)$$

In which $C.R_{inh}$ and $C.R_{blank}$ are the corrosion rates of steel with and without the presence of inhibitor, respectively.

3. Results and discussion

For investigating the effect of 2DEAE on corrosion of the samples, polarization tests in different concentration of the inhibitor were employed. The obtained results were depicted in Fig. 2. It is observed that the presence of 2DEAE shifts the Tafel curves to the left. The results of Fig. 2 are summarized in Table 1.

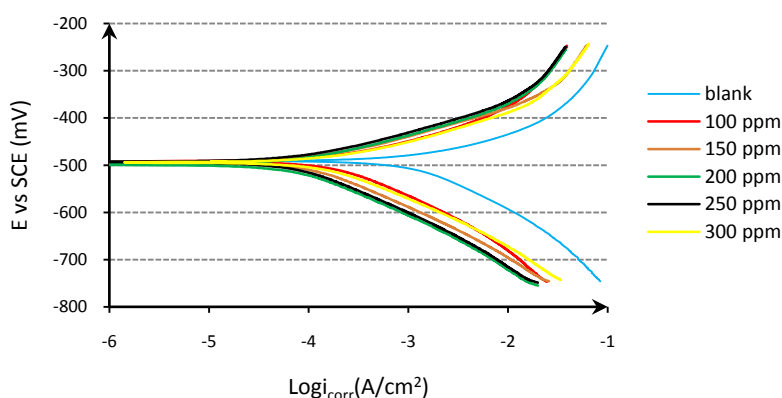


Fig. 2. Potentiodynamic polarization curves for mild steel samples in 1M HCl containing different concentrations of 2DEAE

Table1. Polarization parameters for specimens in 1M HCl in presence of different concentration of 2DEAE and blank solution.

C(ppm)	E_{corr} vs SCE(mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	β_c (mV/dec)	C.R (mpy)
0	-489.5	572.2	112	180	92.7
100	-492.1	240.7	71.26	109.5	38.90
150	-495.8	181.8	71.06	116.3	32.33
200	-500.7	144.4	68.13	101.6	26.8
250	-493.2	158.2	73.14	105.1	31.5
300	-494.9	209.1	64.58	97.84	32.78

Based on Table 1, it was observed that by adding 2DEAE to HCl up to 200ppm, corrosion rate decreased to 26.8 mpy. But more enhancing of 2DEAE (300 ppm) increased corrosion rate. Thus, it can be deduced that the optimum inhibition by 2DEAE in HCl solution was 200 ppm.

Increasing 2DEAE concentration beyond 200 ppm results in a diminished corrosion protection. This behavior can be attributed to the formation of so-called hemi- micelles on the surface. At concentrations of the surfactant close to or beyond the critical micelle concentration (cmc), the withdrawal of adsorbate back into the solution bulk probably becomes thermodynamically favorable [9].

Corrosion potential (E_{corr}) shifted toward more negative potentials in the presence of 2DEAE, which can ascribe cathodic characteristics of this inhibitor. But, by considering simultaneous decrease in anodic and cathodic slopes in Tafel curves, it can be stated that 2DEAE is a mixed inhibitor. Thus, by adsorbing on the cathodic and anodic zones at the same time, the inhibitor restrains the corrosion attack and decreases its rate [10].

For more complete studies about the effects of 2DEAE on mild steel corrosion, electrochemical impedance spectroscopy (EIS) was performed in a 1 M HCl by introducing different amounts of 2DEAE. The Nyquist representation of EIS data obtained before and after the addition of 2DEAE was shown in Fig. 3.

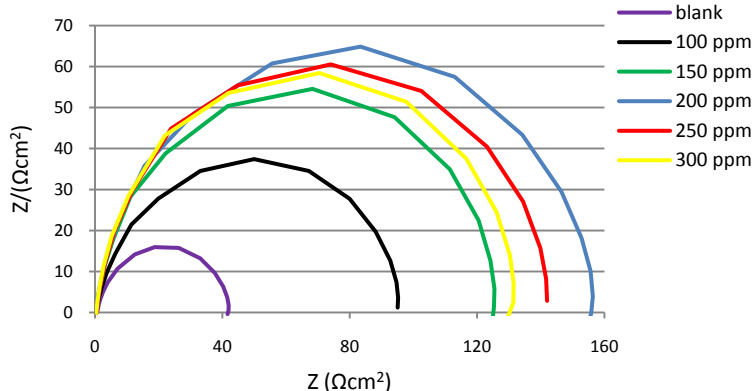


Fig. 3. Nyquist plots for specimens in solutions containing different concentrations of 2DEAE.

The Nyquist curves reveal that addition of 2DEAE to HCl up to 200ppm results in increasing semi- circles diameter. Thus, the maximum polarization resistance (R_p) of the specimens was observed in 200ppm.

Table2. Impedance parameters with corresponding inhibition efficiency for the corrosion of mild steel in 1M HCl at different concentrations of 2DEAE.

C	R_p (Ω)	CPE-T($\Omega^{-1}\text{Cm}^{-1}$)	n	C_{dl} (μFcm^{-2})
Blank	42	480	0.91	275.3
100	94.4	415	0.92	256.2
150	126.4	395	0.911	232.0
200	154.2	338	0.904	193.2
250	142	371	0.915	224.3
300	131.1	368	0.92	229.3

Also it is observed that by adding 2DEAE in HCl solution up to 200ppm, R_p increases from 42 Ω to 154 Ω , but further increasing of the inhibitor leads to decreasing of polarization resistance.

Electrical equivalent circuits are commonly used to analyzing and interpreting of EIS data. The selected circuit should match completely with obtained experimental data. The equivalent circuit reflects physical characteristics of the electrode surface such as film uniformity, double layer properties and different layers of a film.

Based on Fig. 3, EIS curves with and without the presence of 2DEAE contain a semi- circle due to a double layer capacitor (C_{dl}) that is in parallel to a polarization resistance (R_p) in the equivalent circuit.

Therefore, the equivalent circuit of Fig. 4 was used to fit completely the experimental data of fig. 3. In this figure, C_{dl} represents the absorbed ions in electrical double layer, R_p is charge transfer resistance and R_s shows the solution resistance.

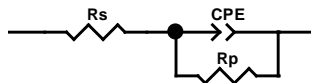


Fig. 4. The equivalent circuit used to fit the impedance spectra.

In the obtained Nyquist curves, a crushing effect can be observed and the curves demonstrate a deviation from the ideal shape. So the C_{dl} in Fig. 4 was mathematically simulated using CPE (constant phase element). The CPE values are calculated by following equation [11]:

$$CPE = Y_0 (\omega)^{n-1} \quad (2)$$

In which Y_0 is CPE constant, ω is angular frequency in maximum imaginary impedance and n is power of CPE. The closer n to 1, the closer CPE behavior to the capacitor will be.

Several reasons have been mentioned for the crushing loops in EIS curves such as decreasing of corrosion rate during test, effect of ions adsorption and desorption in low frequencies and instability in the potential [12].

It is obvious that CPE values decreased by increasing the concentration of 2DEAE to 200ppm. This can be explained by considering the adsorption of the inhibitor on the surface and replacing with H_2O molecules or hydroxyl (OH^-) ions in electrical double layer, since the inhibitor dielectric coefficient is lower than that of H_2O and OH^- [13,14]. So by the formation of a protective layer, contacting of corrosive ions to the steel surface is hindered.

According to Helmholtz equation [15]:

$$C = K \frac{\epsilon_0 A}{d} \quad (3)$$

In which d is the thickness of the protective layer, K the dielectric constant of the medium, ϵ_0 the vacuum permittivity and A is the effective surface area of the electrode, and by considering K , A and ϵ_0 as constant parameters, reducing C_{dl} with raising 2DEAE concentration is related to increase in the thickness of the protective film.

Influence of Hexamine

So far, in several investigations, effects of Hexamine have been studied in HCl [16,17]. But for comparison purposes, in this study, polarization tests were performed in different concentrations of Hexamine. Tafel curves obtained and related data were shown in figure 5 and table 3, respectively.

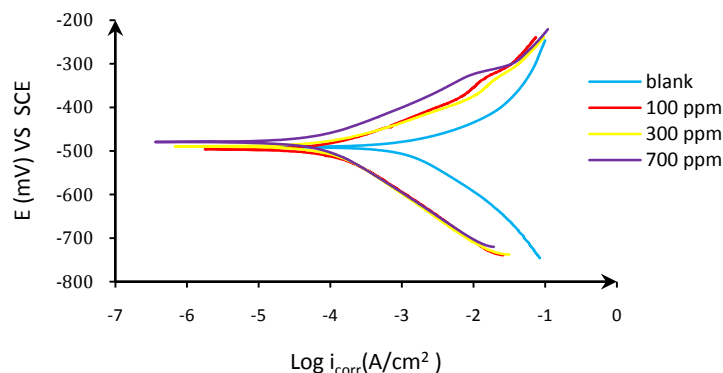


Fig. 5. Polarization curves for specimens in 1M HCl in the absence and presence of different concentrations of Hexamine.

Table3. Tafel polarization parameters for the corrosion of specimen 1M HCl in the presence of different concentrations of HA

Concentration(ppm)	E (mv)	$I_{corr}(\mu A/cm^2)$	$\beta_a(mV/dec)$	$\beta_c(mV/dec)$	C.R (mpy)
0	-498.5	572.2	112	180	92.7
100	-496.7	138.3	79.8	112.5	21.5
300	-490.1	100.8	55.1	109.3	15.8
700	-481.5	80.3	53.3	106.3	12.7

Results clearly show that corrosion rate decreases with the enhancement of hexamine in the solution. As the other similar studies reported, this decrease in corrosion rate is related to the formation of a protective layer and physical adsorption of Hexamine on the metal surface [18].

Effect of Hexamine on 2DEAE

For studying the effect of Hexamine on the inhibition efficiency of 2DEAE in HCl, polarization tests at different concentrations of Hexamine and 2DEAE were performed.

Figure 6 shows the inhibition efficiency of 100 and 200 ppm of 2DEAE in the presence of different concentrations of hexamine.

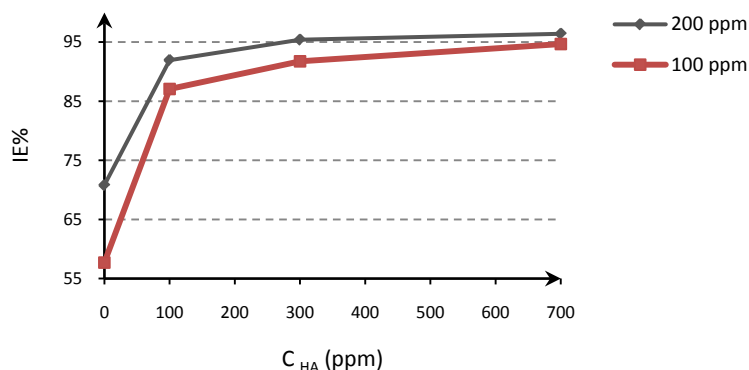


Fig. 6. Relation between inhibition efficiency and concentration of hexamine at fixed values of 2DEAE

As it can be seen, addition of 100 ppm of hexamine to the solution containing 2DEAE results in higher corrosion efficiencies. IE increases from 55% to 87% in the presence of 100 ppm of 2DEAE, and reaches to 95% by increasing hexamine concentration. But the maximum inhibition in the presence of 2DEAE, acting alone, is about 70%. Therefore, low amount of the inhibitor is sufficient to achieve low corrosion rates.

According to the figure 6, no decrease in IE is observed at the presence of two inhibitors in the solution. It means that, there is no antagonistic effect in this case. On the other hand, enhancing inhibition efficiency couldn't be necessarily a reason for synergistic effect of two inhibitors and could be resulted from a simple additive adsorption.

Generally for assessing the combined effect of two inhibitors, S and H, the synergism parameter is used. This parameter is defined as follows [19]:

(4)

$$S = \frac{1 - \eta_D - \eta_H - \eta_D \eta_H}{1 - \eta_{DH}}$$

Where η_D and η_H are the inhibition efficiencies observed with 2DEAE and Hexamine, respectively, acting alone and η_{DH} is the experimentally observed inhibition efficiency for the mixture of 2DEAE and Hexamine (at the same separate concentrations). In this equation, if $s=1$, the inhibitors have no effect on another and adsorb at the metal/ solution separately. Alternatively, synergistic effects demonstrate themselves if $s>1$ and antagonistic effects if $s<1$. Combination of the equations 4 and 1 will result in the following equation:

(5)

$$S = \frac{V_D V_H}{V_{DH} V_0}$$

Where V_s is the corrosion rate in the presence of 2DEAE, V_H is the corrosion rate in the presence of hexamine and V_{DH} and V_0 are the corrosion rates with and without both inhibitors.

Figure 7 shows values of S as a function of the concentrations of both 2DEAE and hexamine, together. This curve was plotted by calculation of the best fit to the test results, based on a least square regression.

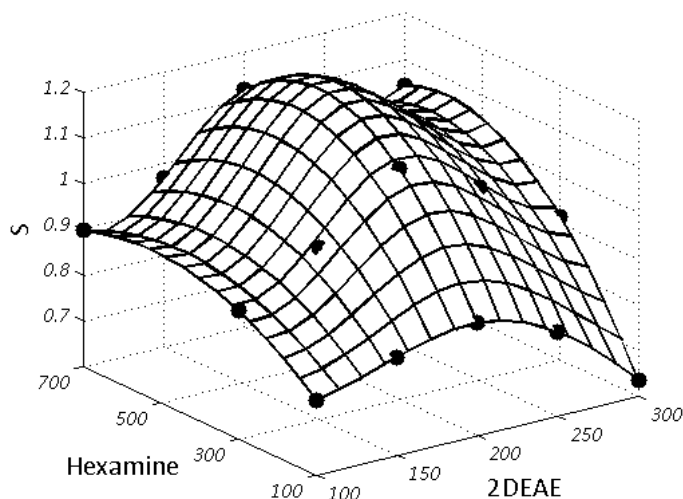


Fig. 7. Synergism parameter s for the combined effect of 2DEAE and HA on the corrosion of mild steel in 1M HCl

It is clear that in 150, 200 and 250 ppm of 2DEAE, in the presence of Hexamine, 2DEAE demonstrates improved inhibition and synergism effect could be observed in these situations. On the other hand, in 50 and 300 ppm amounts, synergism parameter is less than 1 and as mentioned, antagonism effect is appeared.

It is obvious from figure 7 that at high concentrations of both 2DEAE and Hexamine synergistic effect is observed. However, in low concentration of one each of them antagonistic effect is appeared.

Observed antagonistic effect in these concentrations is resulted from the overlay formation of the minor inhibitor. The oppositely charged ions aren't able co-adsorbed on the metal surface due to electrostatic interactions.

4. Conclusion:

When 2DEAE is used alone as corrosion inhibitor, the inhibition efficiency shows a maximum at a concentration of about 200ppm. The decrease of inhibition efficiency at higher

concentrations is ascribed to the formation of hemi-micellar aggregates that promote inhibitor desorption from the metal/solution interface. The 2DEAE molecule is found to affect both the anodic and cathodic processes by simple blocking of the active sites of the metal, i.e., 2DEAE is a mixed-type inhibitor. The results of EIS indicate that the value of CPE tends to decrease and both polarization resistance and inhibition efficiency tend to increase by increasing the inhibitor concentration to 200ppm. This result can be attributed to increase of the thickness of the electrical double layer. The results of electrochemical impedance spectroscopy and Tafel polarization measurements confirmed to each other. Upon mixing 2DEAE and hexamine inhibitor, a slight antagonistic effect was observed if one of the inhibitors was present in a concentration below 150ppm. For higher concentrations, this trend is reversed and a moderate synergism was found.

Reference

- [1]. Shengtao Zhang, Zhihua Tao, Weihua Li, Baorong Hou, Applied Surface Science 255 (2009) 6757–6763.
- [2]. X. Li, S. Deng, G. Mu, H. Fu, F. Yang, Corros. Sci. 50 (2008) 420.
- [3]. S.S. Abd El Rehim, Magdy A.M. Ibrahim, K.F. Khalid, Materials Chemistry and Physics 70 (2001) 268–273.
- [4]. O. Olivares , N.V. Likhanova, B. Go´mez, J. Navarrete, M.E. Llanos-Serrano, E. Arce, J.M. Hallen, Applied Surface Science 252 (2006) 2894–2909.
- [5]. R. Agrawal, T.K.G. Nambodhiri, J. Appl. Electrochem. 22 (1992) 383.
- [6]. G. Kear, B.D. Barker, K.R. Stokes, F.C. Walsh, Electrochim. Acta 52 (2007) 1889.
- [7]. S. Ramesh, S. Rajeswari, S. Maruthamuthu, Mater. Lett. 57 (2003) 4547.
- [8]. Emeka E. Oguzie, Corrosion Science 50 (2008) 2993–2998.
- [9]. H. Tavakoli, T. Shahrabi , M.G. Hosseini, Materials Chemistry and Physics 109 (2008) 281–286.
- [10]. Puja Singh, Kalpana Bhrara, Gurmeet Singh, Applied Surface Science 254 (2008) 5927–5935.
- [11]. M. Salasia, T. Shahrabia, E. Roayaeib and M. Aliofkhazraeia, Materials Chemistry and Physics 104 (2007) 183–190.
- [12]. Ying Ya, Weihua Li , Lankun Cai, Baorong Hou, Electrochimica Acta 53 (2008) 5953.
- [13]. Saliyan V. Ramesh, Airody Vasudeva Adhikari, Materials Chemistry and Physics 115 (2009) 618–627.
- [14]. J. Aljourani, K. Raeissi , M.A. Golozar, Corrosion Science 51 (2009) 1836–1843.
- [15]. K.F. Khaled, Corrosion Science 52 (2010) 2905–2916.
- [16]. D. D. N. SINGH, T. B. SINGH and B. GAUR, Corrosion Science, Vol. 37, No. 6, pp. 1005-1019, 1995.
- [17]. S. Gupta. M. Vajpeyi and S. N. Pandey, Corrosion Prev. and Contr. 33,47 (1986).
- [18]. M. Hosseini, Stijn F.L. Mertens, Mohammed R. Arshadi, Corrosion Science 45 (2003) 1473–1489.
- [19]. T. Murakawa, S. Nagaura, N. Hackerman, Corros. Sci. 7 (1967) 79.