Abstract

The influence of tetraethanol-β-octadecenyl succinylamide (TOSA) on the corrosion of steel in H₂SO₄ and HCl solutions of divers concentrations has been studied using gravimetrical, electrochemical and polarization corrosion test methods. It has been observed that the TOSA behaves as an inhibitor of molecular active cathodic type and has inhibition effect at the beginning stage of corrosion in both acids, but more effectively in H₂SO₄. It is shown that the inhibition effect of the TOSA increases with temperature increasing from 91 % at 20°C to 100 % at 80°C in 0.5 N H₂SO₄ solution and decreases with temperature increasing for higher concentrations of acid solutions. From obtained electrocapillary curves it is evidenced that the TOSA is a primarily additive of molecular type (insignificant shift of the maximum to the positive side on the curves). Moreover, it is surface active compound those superficial strength substantially decreases in H₂SO₄ (30 dyn/cm) and HCl (34.9 dyn/cm) solutions. It has been shown that the TOSA has a high protection effect and high formation rate of adsorption layer on the metal surface in H₂SO₄ (ψ = 96.4 % and τ = 8.0 min) and HCl (ψ = 91.5 % and τ = 4.0 min).

Introduction

The metal corrosion problem is getting the most urgent actuality due to the constant extending of industrial applications of metal articles and equipment in marine petrol mining, especially in the Caspian marine shelf.

It is known that the use of functional organic inhibitors is a very effective method for anticorrosive protection of metal surfaces contacting with corrosive acid solutions. Early the inhibitor properties of organic nitrogen-containing compounds in the solution of divers mineral acids were studied [1-4].

It was shown that some N-containing organic compounds such as pyridine and its derivatives [5], 4-phenyl thiosemicarbazide [6], alkylene di(tri or tetra)amines [7], aromatic and heterocyclic amines [8], pyrimidine derivatives [9], izomers ofaminobenzoic acid [10], and others [11-15] could be used as metal corrosion inhibitors in acid solutions.

The objective of this work is to study mechanism of inhibition effect of tetraethanol-P-octadecenyl succinylamide (TOSA), as corrosion inhibitor of low carbon steel in the mineral acid (HCl and H₂SO₄) solutions and to determine optimum conditions of their use including effects of temperature and concentrations of studied acids and inhibitor.

Experimental

Materials

The samples of Steel-3 containing 0.28 % C, 0.26 % Si, 0.42 % Mn, 0.024 % P and 0.03 % S before use were ground, refined by ethanol and dried in vacuum exsiccator. The 0.5-5.0 % solutions of chloride and sulfuric acids as a working environment were used. The initial N-containing functional organic compound of TOSA

\[ n-C_{15}H_{29}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}-\text{CON} (\text{CH}_2\text{CH}_2\text{OH})_2 \]

\[ \text{CH}_2-\text{CON} (\text{CH}_2\text{CH}_2\text{H})_2 \]

used as an inhibitor was synthesized by the known method [16].

Measurements

For quantitative assessment of studied inhibitor efficiency the gravimetrical, electrochemical and po-
lization corrosion test methods were used [17-21]. The gravimetry measurements were carried out at 20-
80°C by using planning experimental data method.

The polarization measurements were carried out in the galvanization conditions. The working surface of steel samples was 10 cm². The non-working surface was insulated with epoxide resin ED-5. The density of polarized electrodes was measured at 0.001-
6.0 mA/cm².

The adsorption rate of studied inhibitor on the steel surface was determined by electrochemical polarization method on the base values of measured polarization current in accordance with scheme of the plant presented in the Fig. 1. As a value ($\theta$, mA×h) identifying corrosion starting period in no-inhibitor and inhibitor conditions there was used the following equation:

$$\theta = \int_0^\tau I(\tau)d\tau$$

(1)

where $I$ is a value of polarization current (mA) at given difference of potentials ($V_\circ - V_a =$ const) and $\tau$ is a beginning inhibition time (min).

As a criterion of inhibitor efficiency in the starting period of corrosion there was used protection effect values ($\psi$, %) determined by following equation:

$$\psi/100 = Q_0 - Q_i / Q_0$$

(2)

where $Q_0$ and $Q_i$ are amounts of electricity between electrodes at given value of potentials during $\tau$ time

To determine surface activity of studied inhibitor ($\sigma$) and state of its molecules on the electrode surface of electrolyte, the electrocapillary curves were recorded with capillary electrometer [22]. The $\sigma$ value was calculated by following equation:

$$\sigma = g \times \tau / 2 \left[ (h_1 - h_2) d_{Hg} - (h_2 - h_2) d_p \right]$$

(3)

where $h_1$ (30 cm) is a distance between the end of capillary and upper part of Hg (cm), $h_2$ is a distance between the end of capillary and lower part of Hg (cm), $h_p$ is a height of immersed part of capillary (cm), $d_{Hg}$ is a density of solution (g/cm³), $d_p$ is a density of Hg (g/cm³), $r$ is a radius of capillary (μm), $g$ is a gravitational acceleration.

The differential capacity of electrodes was measured with electrical resistor of alternating current (P-568) at 10 kHz frequency where any dispersion was appeared. To determine adsorption characteristics of studied inhibitor the adsorption isotherms were used. Assuming mono-molecular adsorption in calculation of saturation degree ($\varphi$) of metal surface with inhibitor, the values of electrode capacity were obtained and following known equation [23] was used:

$$\varphi = (C_0 - C_i) / (C_{sat} - C_{inhibitor})$$

(4)

where $C_0$, $C_i$ and $C_{inhibitor}$ are capacities of electrode in the blank solution, at given and breaking concentrations of inhibitor.

**Results and discussion**

The TOSA inhibitor efficiency was determined by study of the influence of following external factors on the surface properties of steel in acid solutions: (1) temperature, (2) concentration of corrosion solution, (3) concentration of inhibitor, and (4) type of corrosion solution, i.e., anionic composition of acid solution. The levels of these factors and the intervals of their variations for studied inhibitor are presented in Table 1.

At constant values of levels of $X_1$, $X_2$, and $X_4$ factors for all inhibitors the levels of $X_3$ factor were changed in the dependence on the following effective concentrations obtained for TOSA inhibitor: $1.8 \times 10^{-4} - 1.8 \times 10^{-3}$ mol/L. After statistical analysis of experimental results for given inhibitor accomplished, the following equation for inhibitor efficiency ($\psi$) was obtained:

$$\psi_{TOSA} = 68.6 - 3.6 X_1 - 13.5 X_2 - 13.9 X_3 + 5.7 X_4 - 8.0 X_4 X_5 + 6.0 X_4 X_5$$

(5)
As is evident from this equation the concentration of inhibitor \(X_3\) exerts essential influence on the protection properties of the TOSA inhibitor; the increase of its concentration in the electrolyte causes growth of its efficiency. The temperature of corrosion solution \(X_1\) also exerts essential influence on the inhibitor efficiency.

The increase of temperature exerts negative influence on the protection properties of the TOSA inhibitor. The essential changes for TOSA inhibitor were observed that could be explained by formation of monomolecular film layer of this inhibitor on the surface of steel which was kept on the surface due to the physical and chemical adsorption. The high value of effective energy of activation \(E_a\) found from the plots of corrosion rate vs. reverse value of temperature (Fig. 2) confirms this fact. The \(E_a\) values for studied inhibitor were determined in the various conditions. The obtained results are shown in Table 2.

Table 1
The levels of factors and their variation intervals for studied TOSA inhibitor

| Factors                  | Mark of Factors | Levels of Factors | Intervals of Variations |
|--------------------------|-----------------|-------------------|-------------------------|
| Temperature of corrosion media \(^\circ C\) | \(X_1\)          | -1 20 50 80       | 30                      |
| Concentration of acid (N) | \(X_2\)          | 0.5 2.75 5.0      | 2.25                    |
| Concentration of inhibitor (mg/L) | \(X_3\)          | 100 550 1000     | 450                     |
| Type of acid             | \(X_4\)          | HCl               | \(H_2SO_4\)             |

![Fig. 2. Arrhenius plots of corrosion rate log \(R_c\) vs. \(1/T\) to determine effective activation energy \(E_a\) at divers concentrations of acid solutions: (-o-) 0.5 N, (-•-) 1.0 N, (-Δ-) 2.0 N, (-∇-) 3.0 N, (-|-) 4.0 N and (-×-) 5.0 N;](image-url)
The influence of temperature factor is correlated with the following experimental data: Inhibition effect increases with temperature increasing from 91% at 20°C to 100% at 80°C in the 0.5 N H₂SO₄ solution. The inhibition effect decreases with temperature increasing for higher concentrations of acid solution (Table 3). It is shown that the inhibitor efficiency decreases with solution corrosiveness increasing. The TOSA inhibitor is more efficient in sulfuric acid solutions in comparison with chloride acid, and shows more stable protection properties at 20°C.

### Table 3
Dependence of the efficiency of TOSA inhibitor (ψ) on temperature and concentrations of inhibitor, H₂SO₄, and HCl acid solutions

| Acid concentration (N) | Concentration of inhibitor [TOSA] x 10⁻³ (mol/L) | 20°C | 40°C | 60°C | 80°C |
|------------------------|-----------------------------------------------|------|------|------|------|
| (H₂SO₄) | 0.18 | 0.92 | 1.8 | 0.18 | 0.92 | 1.8 | 0.18 | 0.92 | 1.8 |
| 0.5 | 75.5 | 82.6 | 91.3 | 78.5 | 85.5 | 94.3 | 81.3 | 88.4 | 69.7 | 77.0 | 58.3 | 100 |
| 1.0 | 73.2 | 81.4 | 91.4 | 75.1 | 82.8 | 93.3 | 76.9 | 97.1 | 85.8 | 85.7 | 74.4 | 97.0 |
| 2.0 | 67.8 | 78.5 | 91.7 | 67.2 | 77.9 | 91.0 | 66.6 | 84.3 | 53.8 | 72.9 | 42.4 | 89.8 |
| 3.0 | 62.7 | 78.5 | 91.7 | 67.2 | 72.7 | 88.9 | 56.7 | 91.4 | 66.8 | 80.0 | 55.4 | 82.9 |
| 4.0 | 57.7 | 73.0 | 92.1 | 52.5 | 67.8 | 86.9 | 46.9 | 84.6 | 62.2 | 73.2 | 50.8 | 76.1 |
| 5.0 | 52.5 | 70.2 | 92.3 | 44.7 | 62.5 | 84.5 | 37.1 | 95.1 | 81.3 | 83.7 | 69.9 | 69.1 |
| (HCl) | 0.5 | 64.1 | 71.1 | 79.9 | 67.1 | 74.1 | 82.9 | 69.9 | 78.8 | 41.7 | 67.4 | 30.3 | 88.7 |
| 1.0 | 61.8 | 70.0 | 80.0 | 63.7 | 71.4 | 81.9 | 65.5 | 86.5 | 57.0 | 75.1 | 45.6 | 85.6 |
| 2.0 | 56.4 | 67.1 | 80.3 | 55.8 | 66.5 | 79.6 | 55.2 | 77.2 | 54.8 | 65.8 | 43.4 | 78.4 |
| 3.0 | 51.3 | 64.3 | 80.4 | 48.3 | 61.4 | 77.5 | 45.3 | 90.4 | 76.9 | 79.0 | 65.5 | 71.5 |
| 4.0 | 46.3 | 61.6 | 80.8 | 41.1 | 56.4 | 75.5 | 35.5 | 65.9 | 29.3 | 54.5 | 17.9 | 64.7 |
| 5.0 | 41.1 | 58.8 | 80.9 | 33.3 | 51.1 | 73.1 | 25.7 | 76.6 | 47.0 | 65.2 | 35.6 | 57.7 |

Afterwards, the surface activity of the inhibitor and the state of its molecules in electrolyte at electrode layer were studied. For this purpose the electrocapillary curves were recorded, those results of which are given in Fig. 3. The comparative analysis of these curves and curves of initial solutions shows that the studied inhibitor is a surface active compound those superficial strength substantially decreases a in H₂SO₄ and HCl solutions. The difference of superficial strength (Δσ) for the TOSA close to the corrosion potentials of Fe has following values: 30 and 34.9 dyn/cm in 0.5 N H₂SO₄ and HCl solutions. The inhibition effect decreases with temperature increasing for higher concentrations of compounds as well as with additives of ionic type [24]. The analogous specific adsorption of some N-containing compounds noted for Fe corrosion in acid solutions was observed by Hackerman and Hurd [25].

The ϕ - scale potentials allow to use surface activity data obtained on the Hg for interpretation of adsorption properties on the Fe. The obtained adsorption characteristics of surface activity (σ) and inhibition rates of corrosion (γ) for the TOSA inhibitor in acid solutions are: σ = 396 dyn/cm, Δσ = 30.0 dyn/cm and γ = 11.6 in 0.5 N H₂SO₄ solution (ϕ_Hg = -0.1 V), σ = 392 dyn/cm, Δσ = 34.9 dyn/cm and γ = 5.0 in 0.5 N HCl solution (ϕ_Hg = -0.2 V).

As is evidenced from these data there is a parallelism between adsorption of the TOSA inhibitor on the Hg and its protection effect on Fe in H₂SO₄ (γ = 11.6) and in HCl (γ = 5.0).

Then, the inhibition effect of the TOSA at the beginning stage of steel corrosion was studied. The necessity of this study is conditioned by known fact
that the most extent of corrosion destruction processes is noted exactly at the beginning stage of contact between metal surface and corrosive media.

The obtained experimental results are presented in Table 4. It is shown that the TOSA inhibitor have the most protection effects and higher formation rate of adsorption layer on the metal surface in H₂SO₄ (ψ = 96.4 % and τ = 8.0 min) and in HCl (ψ = 91.5 % and τ = 4.0 min). As is obvious from the data of Table 5 the low concentration of TOSA inhibitor in 0.5 N H₂SO₄ does not provide stable inhibition at the beginning stage of corrosion. However, increase in TOSA concentration (9.2 × 10⁻⁴ mol/L) provide 91.8 % protection during 20 min. Further increase in concentration (to 3.7 × 10⁻³ mol/L) causes a substantial decreases in formation time of the adsorption layer (to 8 min) and increases in the protection effect (95.4 %). The transfer from sulfuric acid to HCl also considerably decreases the formation time of the adsorption layer. The high adsorption of surface active organic compound on the steel electrode surface can be explained by specific adsorption power of Cl⁻ anions with negative charge increasing of electrode surface.

The increase in H₂SO₄ concentration from 1.0 N to

**Table 4**

| [TOSA] × 10⁻¹ (mol/L) | 0.5N H₂SO₄ solution | 0.5N HCl solution |
|-----------------------|---------------------|------------------|
|                       | θ (max) | ψ (%) | τ (min) | θ (max) | ψ (%) | τ (min) |
| 0.55                  | 221.3   | 75.2  | -       | 50.4    | 70.2  | 6.0    |
| 0.92                  | 114.9   | 87.1  | 20      | 28.6    | 83.0  | 6.0    |
| 1.80                  | 77.0    | 91.4  | 13      | 18.2    | 89.2  | 4.0    |
| 3.70                  | 40.9    | 95.4  | 8       | 14.4    | 91.5  | 4.0    |
| 9.20                  | 36.6    | 95.9  | 8       | -       | -     | -      |
| 0.00                  | 893.2   | -     | -       | 169.2   | -     | -      |

Fig. 3. Electrocapillary curves of the TOSA inhibitor in (a) 0.5 N H₂SO₄ and (b) 0.5 N HCl solutions at [TOSA] = 0.0 (-•-) and 3.7 × 10⁻³ mol/L (-○-).
2.0 N does not change protection efficiency of inhibitor and has rather high value (Table 5). The protection properties of inhibitor change no either in the high concentration of HCl and the electrochemical corrosion rate has a tendency to decrease. However, the protection efficiency of its molecules on the metal-electrolyte interface, the field of adsorption potentials of the inhibitors and the interfacial interactions with metal surface excite interest to further thorough investigation.

The plots of differential capacity vs. adsorption potential for divers TOSA inhibitor concentrations in H2SO4 and HCl solutions are presented in Fig. 4. As is evident from Fig. 4 data the capacity is approximately up to 24.0 mKf/cm² in the blank solution (0.5 N H2SO4 and 0.5 N HCl) while this parameter is substantially decreased by addition of inhibitor to the studied system. The minimum value of capacity in H2SO4 solution is somewhat lower than in HCl solution and adsorption potential field is shifted to the negative side. The field of inhibitor adsorption in HCl solution is extended in the anode field and the desorption come at -0.05 V potential against -0.2 V for H2SO4 solution. This fact can be explained by the well known additional specific adsorption effect of surface active chlor-anions [27,28].

The adsorption parameters of inhibitor layer were calculated on the base of capacity measurements. The values of adsorption properties of studied inhibitor, such as adsorption equilibrium constant (Ka) and attraction constant (A), were calculated by following known equation [24]:

\[
K_a I = \varphi/(1- \varphi) \exp[-2A\varphi]
\]  

(6)

where I is a concentration of TOSA initiator (mol/L) and \(\varphi\) is a saturation degree of electrode surface (%) which is determined by following equation:

\[
\varphi = (1/f) \ln[(1 + K_{a(max)}I)/(1 + K_{a(min)}I)]
\]  

(7)

where f is a factor associated with a heterogeneous surface, \(K_{a(max)}\) and \(K_{a(min)}\) are adsorption equilibrium constants corresponding to the maximum and minimum values of adsorption energy respectively.

The obtained TOSA adsorption parameters have the following values: \(K_a = 13.6\) and \(A = 4.4\) in 0.5 N H2SO4 solution and \(K_a = 3384\) and \(A = 0.36\) in 0.5 N HCl solution. As is evidenced from these values, the attraction constant A has positive values in both acid solutions that is associated with intermolecular attraction force of adsorption molecules of the inhibitor. The TOSA inhibitor forms more compact (\(\varphi = 98\%) \) and dense (\(A = 4.4\)) surface film in H2SO4 and ensures high inhibition effect on corrosion intensity of the steel with temperature increase.

The TOSA adsorption ability conforms to its effi-

### Table 5

| Concentration of acids | [TOSA]×10³ (3.7 mol/L) |
|------------------------|-------------------------|
|                        | \(\theta\) (mA×s⁻¹) | \(\psi\) (%) | \(\tau\) (min) |
| H2SO4                  |                         |             |             |
| 1.0                    | 920                     | 49.3        | 94.6        | 13          |
| 2.0                    | 1572                    | 92.4        | 94.1        | 17          |
| 3.0                    | 1774                    | 140.0       | 92.1        | 9-30        |
| 4.0                    | 1977                    | 201.0       | 89.9        | 12-21       |
| 5.0                    | 1959                    | 261.0       | 86.7        | -           |
| HCl                    |                         |             |             |
| 1.0                    | 283                     | 39.9        | 86.0        | 12          |
| 2.0                    | 315                     | 45.4        | 85.5        | 15          |
| 3.0                    | 406                     | 42.6        | 89.5        | 18          |
| 4.0                    | 523                     | 55.5        | 89.4        | 21          |
| 5.0                    | 594                     | 82.3        | 86.1        | 16          |
The TOSA as a molecular additive showing higher effects of protection considerably reduce the capacity of double layer on the steel surface.

**Conclusion**

Surface active functional N-containing compound of TOSA is effective cathodic inhibitor of carbonized steel corrosion in H$_2$SO$_4$ and HCl solutions, being more efficient in H$_2$SO$_4$.

TOSA inhibitor shows the most protection effects and higher formation rate of adsorption layer on the metal surface in H$_2$SO$_4$ ($\psi = 96.4\%$ and $\tau = 8.0$ min) and in HCl ($\psi = 91.5\%$ and $\tau = 4.0$ min).

TOSA inhibitor enhances protection properties of adsorption layer with increase in the concentrations of both acids and inhibitors in corrosive solution.

TOSA inhibitor forms more compact ($\varphi = 98\%$) and dense ($A = 4.4$) surface film in H$_2$SO$_4$ and ensures higher inhibition effect on steel corrosion with temperature increasing; the protective effect of the TOSA inhibitor increases with temperature increasing that is correlated with chemical nature of its adsorption ability on the steel surface.

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