Applicability of Novel Anionic Surfactant as a Corrosion Inhibitor of Mild Steel and for Removing Thin Petroleum Films from Water Surface

V. M. Abbasov1,*, Hany M. Abd El-Lateef4,2, L. I. Aliyeva1, E. E. Qasimov1, I. T. Ismayilov1, Ahmed. H. Tantawy1,3, S. A. Mamedxanova1

1Mamedaliev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan
2Chemistry Department, Faculty of Science, Sohag University, Sohag, Egypt
3Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
*Corresponding author: Hany_shubra@yahoo.co.uk

Received December 31, 2012; Revised April 23, 2013; Accepted April 25, 2013

Abstract Sulfated fatty acid potassium salt (PS) as novel anionic surfactant was synthesized and then its corrosion inhibition for mild steel in CO2-saturated 1% NaCl solution was investigated using potentiodynamic polarization measurements. Results indicated that the PS compound acted as an anodic inhibitor by strong chemical interaction with the mild steel surface according to the Langmuir adsorption isotherm. The inhibition efficiency increases with increasing PS concentration, and the highest inhibition efficiencies are observed when the PS concentration reaches values close to its critical micelle concentration (CMC). This corrosion inhibition for mild steel in chloride solution can be attributed to the covering of adsorbed inhibitor molecules on the metal surface. Petroleum-collecting and petroleum-dispersing properties of the synthesized surfactant were studied using as an example thin films of Ramany crude oil on the surface of distilled, fresh and sea waters.

Keywords: anionic surfactant, corrosion inhibitor, mild steel, petroleum-collecting, dispersing agent.

1. Introduction

Mild steel is widely applied as the constructional material in many industries due to its excellent mechanical properties and low cost [1]. The majority of oil and gas pipelines failures result from CO2 corrosion of carbon and low alloy steels [2,3] and occurs at all stages of production from down hole to surface equipment and processing facilities [4]. The use of chemical inhibitors has been acknowledged as one, and a very practical and most economical, method of combating CO2 corrosion [5,6,7]. The inhibiting molecule retards the rate of corrosion by acting at the metal–corrosive medium interface.

Oil pollution is a significant hazard for the marine environment. Sources of such pollution include oil exploration and production operations, natural seeps, atmospheric input, tanker accidents, industrial discharge, and urban run-off [8]. Increasing demand for petrochemicals has led to increased levels of petroleum hydrocarbons in marine, coastal and estuarine environments.

Chemical dispersants and collectors are used as cleaning agents to alter the normal behaviour of petroleum hydrocarbons by increasing their functional water solubility, resulting in increased bioavailability and altered interactions between dispersant, oil, and biological membranes [9,10,11,12,13].

The use of chemical dispersants still are restricted by many governmental regulations and controlled by guidelines in field application [14,15,16]. Oil spill dispersants and collectors reduce the interfacial tension in the oil-water interface to very low values. It therefore takes only a small amount of mixing energy to increase the surface area and break the oil slick into droplets stabilized by oil spill surfactant [17,18,19,20,21].

In the present work, Sulfated fatty acid potassium salt (Figure 1) has been synthesized to investigate its inhibition effect on the corrosion of mild steel in CO2-saturated 1% NaCl solution by potentiodynamic (Tafel) polarization measurement. Petroleum-collecting and petroleum-dispersing properties of the PS (in the pure state and in the form of 5% wt. aq. solution) have been mainly studied on the example of Ramany crude oil.

![Figure 1. Molecular structure of Sulfated fatty acid potassium salt (PS)](image)

2. Materials and Experimental Methods

2.1. Chemical Composition of Carbon Steel Alloy

The rotating disk working electrodes for tests were made of carbon steel grade 080A15 and have an surface
area of 4.55cm² with a chemical composition (wt%) C 0.18%, Si 0.17%, Mn 0.70%, P 0.011%, S 0.03%, Ni 0.0%, Cr 0.01% and Fe balance. The data was provided by European Corrosion Supplies Ltd.

2.2. Synthesis of Inhibitor

The inhibitor was synthesized in our laboratory based on cottonseed oil as in reference [22]. The sulfated fatty acid potassium salt (PS) as anionic surfactant was synthesized in high purity by the composition [R-CH-(OSO₃K)-COOK]. The structure of the synthesized surfactant is characterized by physical-chemical spectroscopic methods and FTIR.

2.3. Corrosion Inhibition Test

The aggressive solution, 1% NaCl, was prepared by dissolving of analytical grade NaCl in distilled water. The concentration range of the prepared inhibitor was from 10 to 150ppm used for corrosion measurements. All inhibitor solutions were prepared using a mixture from distilled water and isopropyl alcohol in a ratio 70:30.

2.4. Corrosion Measurements

The measurements were performed on the cylinder electrode (A=4.55cm²). This electrode was using for one time. The reference electrode was Ag/AgCl Electrode to which all potentials are referred.

Before beginning the experiment, the prepared solution of sodium chloride was stirred by a magnetic stirrer for 30min in 1000ml cell. Then this cell was placed on a heater at a temperature 50°C for 1 hour under a pressure of 0.9 bars. The solution was saturated with carbon dioxide. To remove any surface contamination and air formed oxide, the working electrode was kept at~1500mV (Ag/AgCl) for 5 min in the tested solution, disconnected shaken free of adsorbed hydrogen bubbles and then cathodic and anodic polarization was recorded. ACM GILL AC instrument connected with a personal computer was used for the measurements.

The extrapolation of cathodic and anodic Tafel lines was carried out in a potential range ± 100mV with respect to corrosion potential (E corr) at scan rate of 1mV s⁻¹.

2.5. Surface Tension Measurements

The surface tensions were determined by DuNouy Tensiometer, Kruss Type 8451 and the temperature was maintained precisely at 25 ± 1°C. A critical micelle concentration (CMC) value of surfactant was determined, according to the break points in the plots of the surface tension versus log molar concentration of investigated surfactant.


Petroleum-collecting properties of PS have been mainly studied on the example of Ramany crude oil (density and kinematic viscosity at 20°C are 0.86g/cm³ and 0.16cm²/s, respectively) from the oil field in the Absheron peninsula (Azerbaijan). The surfactant (0.02g) or its solution was added to a thin film (thickness 0.16–0.17mm) of this petroleum on the surface of distilled water, fresh water (Table 1) and the Caspian Sea water (Table 2) (separately) in Petri dishes. The maximum values of the petroleum collecting coefficient (K) are calculated using the formula K=S/S₀, where S₀ is an area of the surface of initial petroleum film and S is an area of the surface of accumulated petroleum (as a thickened spot). Since the moment of the surfactant application observations are carried out with measurement of the spot surface area and determination of the K values at fixed time intervals. When the crude oil film is dispersed, the percentage of the water surface cleaning (kₒ) is found at the appropriate times of measurements. Kₒ is calculated as the ratio of the surface area of the oil at the peripheral part of the dish and the surface area of the initial oil slick.

<table>
<thead>
<tr>
<th>Density</th>
<th>pH</th>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Calcium</td>
<td>Potassium</td>
<td>Magnesium</td>
</tr>
<tr>
<td>1.000 g/cm³</td>
<td>6.9</td>
<td>0.16 mg/l</td>
<td>0.8 mg/l</td>
</tr>
</tbody>
</table>

3. Experimental Results and Discussion

3.1. Confirmation Structure of the Synthesized Inhibitor

The chemical structure for the purified surfactant was recorded by FT-IR spectroscopy in the range 4000–500 cm⁻¹. The FT-IR absorption spectra showed an absorption band at the 2857 cm⁻¹ region was due mainly to the methyl asymmetric stretching vibration. In addition, there was a strong band at 871 cm⁻¹, indicating the presence of multiple (CH₂) groups. The sharp band at 2926 cm⁻¹ due to the stretching vibration of the symmetric methylene group. The strong band at 1723 cm⁻¹ indicating to the increasing C = O group of the carboxylic group, whereas the peak at 1377 cm⁻¹ is due to S=O stretching absorption bands. The FT-IR absorption spectra confirmed that the disappearance of OH band of acid (broad band), this confirmed that, the replacement of H atom in carboxylic group by K atom to form –COOK. FTIR spectra confirmed the expected functional groups in the synthesized anionic surfactant.

Table 1. The General characterization of the fresh water

<table>
<thead>
<tr>
<th>Density</th>
<th>pH</th>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Calcium</td>
<td>Potassium</td>
<td>Magnesium</td>
</tr>
<tr>
<td>1.000 g/cm³</td>
<td>6.9</td>
<td>0.16 mg/l</td>
<td>0.8 mg/l</td>
</tr>
</tbody>
</table>

Table 2. The General characterization of the sea water [23]

<table>
<thead>
<tr>
<th>Density</th>
<th>pH</th>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Calcium</td>
<td>Potassium</td>
<td>Magnesium</td>
</tr>
<tr>
<td>1.0098 g/cm³</td>
<td>7.7</td>
<td>2.99 g/kg</td>
<td>0.34 g/kg</td>
</tr>
</tbody>
</table>
3.2. Potentiodynamic (Tafel) Polarization Measurement

In order to study the effect of PS concentrations as corrosion inhibitor on the corrosion behaviour of mild steel in CO$_2$-saturated 1% NaCl solution, cathodic as well as anodic polarization curves were carried out. Figure 2 shows the experimental results from the polarization curves for mild steel in CO$_2$-saturated 1% NaCl solution with and without different concentrations of PS at scan rate 1mV s$^{-1}$ and at 50°C. Corrosion parameters were calculated on the basis of cathodic and anodic potential vs. current density characteristics in the Tafel potential region [24, 25]. Steady state of open circuit corrosion potential ($E_{corr}$) for the investigated electrode in the absence and presence of the studied inhibitor was attained after 30–40 min from the moment of immersion. Corrosion current density ($I_{corr}$) of the investigated electrode was determined [26], by extrapolation of cathodic and anodic Tafel lines to corrosion potential ($E_{corr}$). The degree of surface coverage ($\theta$) and the percentage inhibition efficiency ($\eta$%) were calculated using the following Eqs. [26]:

$$\theta = 1 - \frac{I_{inh}}{I_{uninh}} \quad (1)$$  

$$\eta\% = \frac{I_{uninh} - I_{inh}}{I_{uninh}} \times 100 \quad (2)$$

Where $I_{uninh}$ and $I_{inh}$ are the uninhibited and inhibited corrosion currents. The inhibited corrosion currents are those determined in the presence of the studied surfactant used in this investigation. The uninhibited corrosion currents were determined in pure (inhibitor free) CO$_2$-saturated 1% NaCl solution at the same temperature. From Figure 2, it was found that, both anodic and cathodic reactions of mild steel electrode corrosion were inhibited with increasing concentration of the synthesized inhibitor. These results suggest that not only the addition of synthesized inhibitor reduce anodic dissolution but also retard the hydrogen evolution reaction. The results showed that the inhibiting action of this inhibitor on the both cathodic and anodic processes seems to approximately be equal. The inhibitor may decrease the corrosion through the reduction of carbon steel reactivity. Accordingly to this mechanism, a reduction of either the anodic or the cathodic reaction or both arises from the adsorption of the inhibitor on the corresponding active sites [27].

![Figure 2: Potentiodynamic anodic and cathodic polarization curves of mild steel electrode in CO$_2$-saturated 1% NaCl solution in the absence and presence of various concentrations of PS at a scan rate of 1.0 mV s$^{-1}$ and at 50°C.](image)

The electrochemical parameters $E_{corr}$, $I_{corr}$, inhibition efficiency ($\eta$%), anodic and cathodic Tafel slopes ($\beta_c, \beta_a$) obtained from the polarization measurements were listed in Table 3. The data in exhibited that, the corrosion current density ($I_{corr}$) decreases, and the inhibition efficiency ($\eta$%) increases as the concentration of inhibitor is increased. These results suggest that retardation of the electrodes processes occurs, at both cathodic and anodic sites, as a result of coverage of these sites by surfactant molecule. The increase of inhibitor efficiency with increasing the concentration can be interpreted on the basis the adsorption amount and the coverage of surfactant molecule, increases with increasing concentration [28]. The $E_{corr}$ of carbon steel shifted to the positive side by addition of inhibitor and the shift increased with increasing concentration of inhibitor, indicating that the inhibitor reduces the anodic reaction. It was explained that this shift in $E_{corr}$ is due to active sites blocking effect that occurs when an inhibitor is added [29]. The fact that the slopes of the cathodic ($\beta_c$) and anodic ($\beta_a$) Tafel lines in Table 3 remain almost unchanged upon addition of the inhibitor. These results indicate that this inhibitor acts by simply blocking the available surface area. In other words, the inhibitor decreases the surface area for corrosion of the investigated metal, and only causes inactivation of a part of the surface with respect to corrosive medium.

![Table 3: Corrosion parameters obtained from polarization measurements of mild steel electrode in CO$_2$-saturated 1% NaCl solution in the absence and presence of different concentrations of the PS inhibitor at 50°C.](image)

<table>
<thead>
<tr>
<th>Conc. of inhibitor (ppm)</th>
<th>$E_{corr}$ (mV) (Ag/AgCl)</th>
<th>$I_{corr}$ (mAcm$^{-2}$)</th>
<th>$\beta_c$ (mVdec$^{-1}$)</th>
<th>$\beta_a$ (mVdec$^{-1}$)</th>
<th>$\theta$</th>
<th>$\eta$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-687</td>
<td>2.54</td>
<td>76</td>
<td>118</td>
<td>0.644</td>
<td>64.46</td>
</tr>
<tr>
<td>10</td>
<td>-678</td>
<td>0.897</td>
<td>75</td>
<td>118</td>
<td>0.765</td>
<td>76.57</td>
</tr>
<tr>
<td>25</td>
<td>-675</td>
<td>0.595</td>
<td>75</td>
<td>117</td>
<td>0.856</td>
<td>85.62</td>
</tr>
<tr>
<td>50</td>
<td>-670</td>
<td>0.365</td>
<td>74</td>
<td>116</td>
<td>0.933</td>
<td>93.30</td>
</tr>
<tr>
<td>75</td>
<td>-666</td>
<td>0.17</td>
<td>77</td>
<td>117</td>
<td>0.970</td>
<td>97.04</td>
</tr>
<tr>
<td>100</td>
<td>-661</td>
<td>0.075</td>
<td>74</td>
<td>115</td>
<td>0.972</td>
<td>97.24</td>
</tr>
<tr>
<td>150</td>
<td>-659</td>
<td>0.070</td>
<td>75</td>
<td>115</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

The effect of the inhibitor concentration on the corrosion of mild steel was examined; detailed experimental results were collected in Table 3 and graphically represented in Figure 3. At a studied temperature (50°C), the inhibition efficiency increases with increasing PS concentration, and the highest inhibition efficiencies are observed when the PS concentration reaches values close to its critical micelle
concentration (CMC). As the concentration of surfactant molecules approaches the CMC, micelles form in solution, and similar aggregate structures such as lamellar structures and rod-like micelles that can form in solution as well as analogous bilayers or multilayers that form at interfaces [30]. For concentration of 100ppm and higher, the inhibition efficiency did not show any significant decrease and remained approximately constant (Figure 3). The high θ value (Table 3) near unity indicates almost a full coverage of the investigated metal surface with adsorbed surfactant molecules. Conclusively, the surfactant inhibitor having θ near unity is considered as a good physical barrier shielding the corroding surface from corrosive medium and dumping the corrosion rate of carbon steel significantly.

The values of the degree of surface coverage (θ) obtained from polarization measurements for the investigated inhibitor PS have been applied to different adsorption isotherms. Since adsorption isotherms can provide important clues to the nature of metal–inhibitor interaction it was established isotherms that describe the adsorptive behavior of the studied corrosion inhibitor. The best correlation among the experimental results was found to fit the Langmuir adsorption isotherm as shown in Figure 5. Plotting $C_{inh}/\theta$ versus $C_{inh}$ yielded a straight line with a correlation coefficient ($R^2$) higher than 0.9999 and a slope close to 1 according to the following equation [31]:

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}}$$

(3)

Where, $C_{inh}$ is the inhibitor concentration and $K_{ads}$ is the adsorption equilibrium constant of the inhibitor on mild steel surface.

This indicates that, the adsorption of this inhibitor can be fitted to a Langmuir adsorption isotherm. The strong correlation of the Langmuir adsorption isotherm may confirm the validity of this approach. The equilibrium constant ($K_{ads}$) for the adsorption–desorption process of these compounds can be calculated from reciprocal of the intercept. It is clear that, the large value of the equilibrium constant ($K_{ads}$; $5.95 \times 10^5$ M$^{-1}$) indicate a strong adsorption of the synthesized inhibitor on the surface of mild steel in CO$_2$-saturated 1% NaCl solution. This may be due to the formation of coordinated bonds between the oxygen or sulfur groups in inhibitor molecule and vacant d-orbitals of steel surface atoms. Immediately afterwards, as the corrosion reaction starts, ferrous ion is surrounded by two oxygen atoms at Fe–O (COO$^-$) and Fe–O (OSO$_3^-$) and form Fe–PS complex on the metal surface.

The adsorption of surfactant inhibitor molecule from the aqueous solution can be regarded as a quasisubstitution process between the surfactant compound in the aqueous phase [Surf.$(sol)$] and water molecules at the electrode surface [H$_2$O$_{ads}$].

$$\text{Surf.} + n \text{H}_2\text{O}_{(ads)} \rightarrow \text{Surf.} _{ad} + n \text{H}_2\text{O}_{(sol)}$$

(4)

Where, n is the size ratio, that is, the number of water molecules replaced by one surfactant inhibitor. In this situation, the adsorption of the synthesized surfactant inhibitor is accompanied by desorption of water molecules from the surface.
The free energy of adsorption (ΔG^o_{ads}) of the inhibitor on carbon steel surface was calculated as follows [32]:

\[ K_{ads} = \frac{1}{55.5} \exp(-\frac{\Delta G^o_{ads}}{RT}) \]  

(5)

The value of ΔG^o_{ads} were calculated. The negative values of ΔG^o_{ads} indicate the spontaneous adsorption of the prepared inhibitor on metal surface [33]. Generally, values of ΔG^o_{ads} up to -20kJ mol⁻¹ are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40kJ mol⁻¹ involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [33]. The obtained value of the adsorption free energy, ΔG^o_{ads}, was 38.65kJ mol⁻¹ is indicative of chemisorption [34].

3.3. Petroleum-Collecting and Dispersing Properties of PS

Petroleum-collecting and petroleum-dispersing properties of the synthesized surfactant were studied by using thin films of Ramany crude oil on the surface of distilled, fresh and sea waters, the surfactant being taken in undiluted form and as 5-15% wt. water solutions. Table 3 showed that, the results studies of petroleum-collecting and petroleum-dispersing abilities of the synthesized surfactant. Figures 6a, b and c show shapes of petroleum-collecting and petroleum-dispersing abilities of the synthesized surfactant. Figure 6a shows the shape of petroleum oil slick before addition of reagent and Figure 6c represents the shape of petroleum-collecting after addition of reagent. While Figure 6b shows the shape of petroleum-dispersing after addition of reagent. From Table 3, it can be noted that PS in undiluted form exhibits a good petroleum-collecting action in distilled water (K_{max} = 7.60, τ=2-50h) and a good effect in fresh water (K_{max} = 12.15, τ=0-2h). But in sea water gave a week effect (K_{max}= 2.64, τ=0-50h). In the concentration of 5% wt. aq. solution PS exhibits highest petroleum-collecting properties in distilled water (K_{max}=13.50, τ=2-50h) and a week petroleum-collecting effect in fresh and sea waters. Also in the form of 10% wt. aq. solution PS gave a better petroleum-collecting properties in sea water (K_{max}=15.19, τ=0-2h) and in distilled and fresh waters (K_{max}=12.16, τ=0-2h). In the form of 15% wt. aq. solution PS gave highest petroleum-collecting effect in distilled water (K_{max}=17.37, τ=0-2h) and a good effect in fresh (K_{max}=13.50, τ=0-2h) and sea (K_{max}=11.05, τ=0-2h) waters. Finally, it was noted that PS gave a good petroleum-collecting properties in diluted form and as the concentration of the synthesized compound increases the petroleum-collecting effect increases and as well as the effect in the initial hours is better than the effect in the last hours.

![Figure 6](image_url)

Figure 6. Represents the shape of petroleum film at water surface before addition of reagent (a); petroleum-dispersing shape after addition of reagent (b); petroleum-collection shape after addition of reagent (c)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Media</th>
<th>Distilled water</th>
<th>Fresh water</th>
<th>Sea water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>t (h)</td>
<td>k(%)</td>
<td>δ (h)</td>
</tr>
<tr>
<td>Undiluted product</td>
<td></td>
<td>0</td>
<td>6.32</td>
<td>0-2</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>7.60</td>
<td>5-50</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>60-100</td>
<td>7.50</td>
<td>60-100</td>
<td>6.08</td>
</tr>
<tr>
<td>5% wt. aq. solution</td>
<td></td>
<td>0</td>
<td>11.05</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>13.50</td>
<td>1.50</td>
<td>4.67</td>
</tr>
<tr>
<td></td>
<td>60-100</td>
<td>7.60</td>
<td>60-100</td>
<td>3.19</td>
</tr>
<tr>
<td>10% wt. aq. solution</td>
<td></td>
<td>0-2</td>
<td>12.16</td>
<td>0-2</td>
</tr>
<tr>
<td></td>
<td>5-70</td>
<td>9.35</td>
<td>5-100</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>spilling</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>15% wt. aq. solution</td>
<td></td>
<td>0-2</td>
<td>17.37</td>
<td>0-2</td>
</tr>
<tr>
<td></td>
<td>5-70</td>
<td>10.13</td>
<td>5-50</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>spilling</td>
<td>60-100</td>
<td>6.08</td>
</tr>
</tbody>
</table>

K is collecting coefficient; k₄ is water surface cleaning percentage; τ is fixed time interval

4. Conclusions

1. The inhibition efficiency of mild steel in 1% NaCl saturated with CO₂ increase with increasing concentrations of PS inhibitor, and the highest inhibition efficiencies was observed when the PS concentration reaches values close to its critical micelle concentration (97.04% at 100 ppm).

2. The compound acts as an anodic inhibitor through the forming of an adsorption protective film on the mild steel surface, which can sufficiently hinder the access of chloride ion to the metal surface.

3. The adsorption of the PS inhibitor obeys the Langmuir adsorption isotherm via a strong chemical interaction with the mild steel surface.

4. PS surfactant gave a good petroleum-collecting properties in diluted form and as the concentration of the compound increases the petroleum-collecting effect increases, as well as the effect in the initial hours is better than the effect in the last hours.
References


