

CORROSION INHIBITION OF CARBON STEEL IN HYDROCHLORIC ACID USING SODIUM DODECYL SULFONATE : THE SYNERGISTIC EFFECT OF NONIONIC CO-SURFACTANT AND SOME INORGANIC IONS

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In the present study, the corrosion inhibition characteristic of Sodium Dodecyl Sulfonate (SDSO), a surfactant on corrosion of carbon steel in hydrochloric acid was studied using weight loss method. The obtained results reveal that SDSO is good inhibitor and shows very good corrosion inhibition efficiency (IE) at relatively high SDSO concentration. The IE was found to vary with concentration of inhibitor and acidity.

The effect of Brij 58 nonionic co-surfactant addition on IE of SDSO was investigated. It was found that Brij 58 has synergistic influence on the corrosion inhibition efficiency of SDSO. This would be attributed to molecular association of SDSO-Brij 58 that would cause the enhancement of co-adsorption of the two surfactants on carbon steel surface and consequently increase the coverage of hydrophobic layer on Carbon Steel (CS) surface.

Special importance is attached to the effect of inorganic additives on the IE of SDSO. KCl and CaCl₂ were found to be good promoters to IE of the SDSO. This finding was explained on the basis of that K⁺ or Ca²⁺ ions would create active sites on the SC surface that would attract the negatively charged of SDSO ions and consequently hydrophobic layer (protective film) would be established on SC surface improving IE. However, the addition FeCl₃ deteriorates the Inhibitory action (anticorrosion performance) of SDSO. This can be inferred to the formation of ferric dodecyl sulfonate that have very low solubility product that would precipitate. This cause the deficiency of surfactant ions in the solution and consequently decreasing the adsorption of SDSO on SC surface.

KEYWORDS: *Corrosion Inhibition; Carbon Steel; Weight loss; Critical Micelle Concentration (CMC); Sodium Dodecylsulfonate (SDSO); Synergistic effect.*

1. INTRODUCTION

It is well documented that corrosion of metals generally takes place in the presence of oxygen and moisture and involves two electrochemical reactions. Oxidation occurs at anodic site and reduction occurs at cathodic site. In acidic medium hydrogen evolution reaction predominates. The cost of corrosion has been reported from many studies to be in the order of 1–5% of GNP for any country [1]. Corrosion never stops but its scope and severity can be lessened. Corrosion inhibitors are of great practical importance, being extensively employed in minimising metallic waste in engineering materials. Various scientific studies deal with the subject of corrosion inhibitors. The

inhibitors, which reduce corrosion on metallic materials, are inorganic inhibitors, organic inhibitors, surfactant inhibitors and mixed material inhibitors.

Inhibitors are generally used to control metal dissolution. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms through which they get adsorbed on the metal surface. However, unfortunately, most of these compounds are not only expensive but also toxic to living beings. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern.

The strict environmental regulations and the increasing of ecological awareness have resulted in the use of substitute nontoxic compounds, acceptable from the environmental point of view ‘‘green inhibitors’’ [2]. The use of surfactants, as ecologically-friendly corrosion inhibitors, has been studied and it was shown that the inhibition efficiency increases with the number of carbon atoms in the molecule. Surfactant molecules are amphiphilic in character, i.e., they possess hydrophilic and hydrophobic segments [3,4] having a long hydrocarbon tail and a relatively small ionic or polar head group. The high affinity of surfactant molecules to adsorb onto interfaces is responsible for their applications in several interfacial systems. For this reason, surfactants can be used as good corrosion inhibitors in metallic surfaces. In aqueous solution the inhibitory action of surfactant molecules may be due to the physical (electrostatic) adsorption or chemisorptions onto the metallic surface, depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface. Amphiphiles can be ionic (cationic, anionic), zwitterionic, or nonionic depending on the nature of their head groups.

Ionic and non-ionic surfactants have been reported to be corrosion inhibitors for metals like copper, carbon steel, cold rolled steel and mild steel [5–13]. Anionic surfactants are renowned as good corrosion inhibitors, in that they can adsorb onto positively charged metallic surfaces in a direct and more effective way than other types of compounds.

Recently non-ionic surfactants have been attracting much attention in various fields. A widely studied group of non-ionic surfactants is the polyoxyethylenic $[(\text{-OCH}_2\text{-CH}_2)_n]$ group, which has the advantage that its hydrophobic nature can be controlled not only by modifying the number of carbon atoms in its hydrophobic chain, but also by varying the oxyethylenic chain.. It is worth to mention that the introduction of ethylene oxides into surfactant molecule (ethoxylation) increases the inhibitive effect of surfactant [14]. The presence of these groups increases the solubility of surfactant and hence the extent of its adsorption on the metal surface increases and consequently its inhibitive action improves. In addition to these valuable properties, they are not expensive. They can be mixed with other types of surfactants, e.g., anionic or cationic, to enhance their properties and reduce surfactant precipitation [14,15].

Many studies on the inhibition of the corrosion of carbon steel by some polyoxyethylenic nonionic surfactants have been carried out in different corrosive environments [13,14]. Many nonionic surfactants have been widely used as corrosion inhibitors for iron in acidic media [4,7,11,13, 14].

The main objective of this work was to examine the anticorrosion ability of sodium dodecylsulfonate, anionic surfactant. The synergistic effect of Brij 58 non-ionic co-surfactant on anticorrosion performance of SDSO has been examined. Moreover, some light was shed on the influence of some inorganic additives on the

inhibitory action of the SDSO. It was found that Brij 58 has synergistic influence on the corrosion inhibition efficiency of SDSO. This would be attributed to molecular association of SDSO-Brij 58 that would cause the enhancement of co-adsorption of the two surfactants on carbon steel surface and consequently increase the hydrophobic layer. Special importance is attached to the effect of inorganic additives on the IE of SDSO. KCl and CaCl₂ were found to be good promoters to IE of the SDSO. This finding was explained on the basis of that K⁺ or Ca²⁺ ions would create active sites on the SC surface that would attract the negatively charged of SDSO ions and consequently hydrophobic layer (protective film) would be established on SC surface improving IE. However, the addition FeCl₃ deteriorates the Inhibitory action (anticorrosion performance) of SDSO. This can be inferred to the formation of ferric dodecyl sulfonate that have very low solubility product that would precipitate. This cause the deficiency of surfactant ions in the solution and consequently decreasing the adsorption of SDSO on SC surface.

2. EXPERIMENTAL WORK

2.1. Materials

Tests were performed on carbon steel (CS) of the following composition: 0.26 % C, 1.15 % Mn, 0.04% P, 0.05% S and the remainder is Fe Percentage inhibitor efficiency (IE) is given by :

$$IE = [(CR - CR_0)/CR] \times 100 \quad (1)$$

Where **CR** is the corrosion rate in uninhibited solution and **CR₀**, is the corrosion rate in inhibited solution.

2.2. Inhibitor

The anionic surfactant of sodium dodecyl sulfonate, NaC₁₂H₂₅SO₃, (SDSO) and cetyl ether polyoxyethylene (20) C₁₆H₃₃(OCH₂CH₂)₂₀OH (trade name Brij 58) were obtained from the Nacalai Tesque, Inc., Kyoto, Japan and used as received. All other chemical reagents were reagent grade in quality.

2.3. Solutions

The acidic solutions, 0.2–0.4 mole.dm⁻³ HCl, were prepared by dilution of analytical grade 35% HCl with distilled water. The concentration range of SDSO used was 1.33x10⁻⁵–6.67x10⁻⁵ mole.dm⁻³.

2.4. Weight Loss Measurements

The carbon steel (CS) sheets were abraded with a series of emery paper and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in 600 ml beaker, which contained 500 ml of predetermined concentration of hydrochloric acid with and without addition of different concentrations of the prepared inhibitors. All the acid solutions were open to air. After 24 h, the specimens were taken out, washed, dried, and weighted accurately. Experiments were carried out in triplicate. The average weight loss of three parallel CS sheets was obtained. The average weight loss of three parallel CS sheets could be

obtained. Then the tests were repeated at different HCl concentration. The corrosion rate (CR) was calculated from the following equation [16]:

$$CR = \Delta W / (S.t) \quad (2)$$

Where ΔW is the average weight loss of three parallel CS sheets, S the total area of the specimen, and t is immersion time. With the calculated corrosion rate, the inhibition efficiency (IE) of SDSO on CS surface in absence and presence of various additives was calculated using Equation 1.

3. RESULTS AND DISCUSSION

3.1. Effect of SDSO Concentration and Acidity on Inhibition Efficiency

The corrosion rate curves of carbon steel (CS) with the addition of SDS in various HCl concentration are shown in Fig. 1. The curves in Fig.1 show that the corrosion rate values (mdd) of CS in 0.2-0.4 mole.dm⁻³ HCl solution containing SDSO decrease as the concentrations of the inhibitor increase, i.e. the corrosion inhibition strengthens with the anionic surfactant concentration. It is noticed that optimum SDSO dosage to attain the lowest corrosion rate would be occurred at 5.33×10^{-5} mole.dm⁻³ SDSO in 0.2-0.4 mole.dm⁻³ HCl.

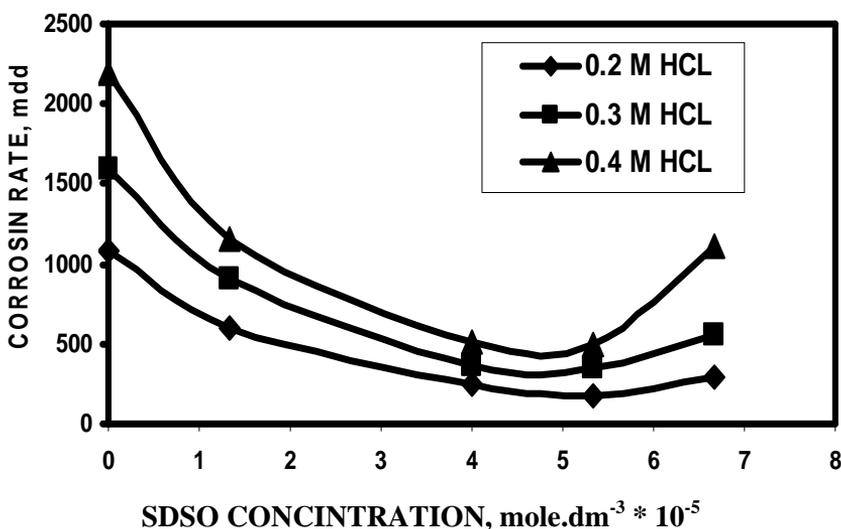


Fig. 1: Influence of SDSO additions on the corrosion rate on SC surface at various HCl concentration

The values of inhibition efficiencies obtained from the weight loss for different inhibitor concentrations in 0.2-0.4 mole.dm⁻³ HCl are given in Fig. 2. The results show that inhibition efficiency is increasing as the concentration of inhibitor increases. The inhibition mechanism of dodecyl sulfonate may also be interpreted as the adsorption of the sulfonate on an exposed metal atom through the oxygen atom of the sulfonate on the cathodic sites of CS, thus forming an adsorption layer which acts as a hindrance to the solution and enhances the protection of the metal surface [4].

It is also noticed that the inhibition efficiency drop to lower values after exceeding its maximum values at various HCl concentration. This would be attributed to the commencement of formation of the second layer of adsorbed surfactant in reverse direction. This supposed layer has its hydrophilic nature that suppress the inhibitory action of SDSA surfactant. It is worth mentioning that the inversion point corresponding to SDSA concentration ($5.33 \times 10^{-5} \text{ mole.dm}^{-3}$) at which the abrupt decreasing in inhibition efficiency occurred is at level well below its Critical Micelle Concentration ($9.3 \times 10^{-3} \text{ mole.dm}^{-3}$) [17].

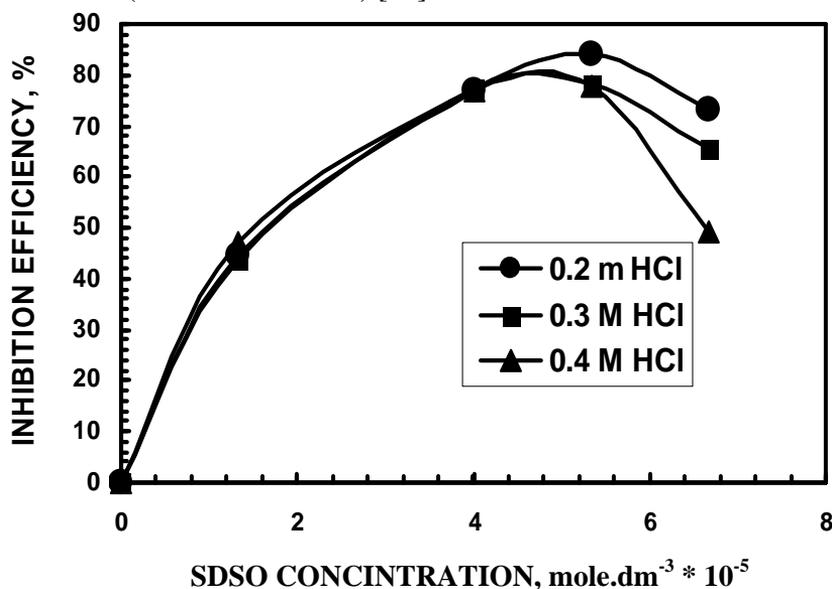


Fig. 2: Influence of SDSA additions on the inhibition efficiency at various HCl concentration

3.2. Effect of Electrolyte Additions on the Inhibition Efficiency

As seen from Fig. 3, corrosion rate is increasing as FeCl_3 addition increases leading to the deterioration of inhibitory action of SDSA. This antagonism between ferric and dodecyl sulfonate ions would be explained on the basis of the domination of ferric ions on CS i.e. the domination of active sites for oxidation reaction and consequently the increase the corrosion rate. The solubility product of ferric dodecyl benzene sulphonate ($\text{Fe}(\text{DBS})_3$) was calculated to be $K_s^0 = (1.23 \pm 0.80) \times 10^{-24}$ [18]. The corresponding value for ferric dodecyl sulphonate is not appear in the literature (to the best of our knowledge); its value could be little lower than that of $\text{Fe}(\text{DBSO})_3$. The formation of $\text{Fe}(\text{DSO})_3$ as insoluble phase would cause the depletion of surfactant available in aqueous solution and consequently in the interfacial zone of CS/liquid phase. The obtained results do indicate that Fe^{3+} ions functions as 'surfactant-robber'

Figure 3 illustrates also the effect of CaCl_2 and KCl addition on the inhibitory action of SDSA system. The results in Fig.4 display the inhibition efficiency of SDSA in the presence of CaCl_2 and KCl .

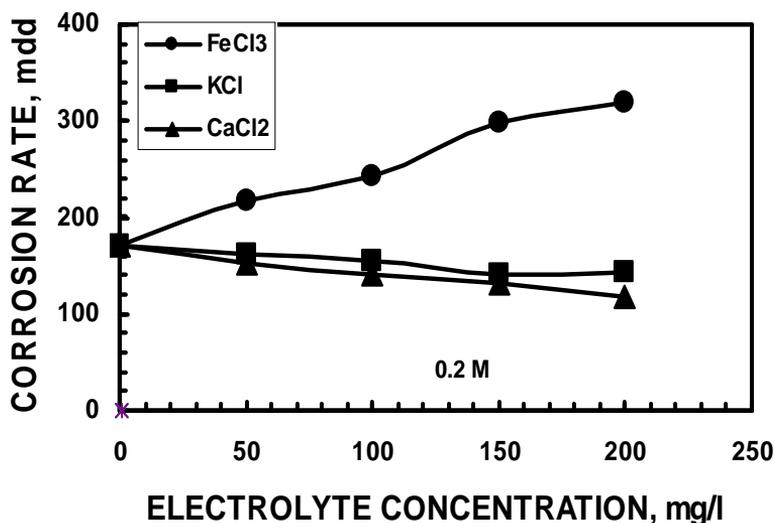


Fig. 3 : Influence of electrolyte additions on the corrosion rate on SC surface in the presence of 5.7×10^{-5} mole. dm^{-3} SDSO in 0.2 mole. dm^{-3} HCl solution.

As seen in this figure 90% inhibition efficiency can be attained in CaCl₂-SDSO system. This figure reveals that both CaCl₂ and KCl have synergistic effect with SDSO on SC surfaces. The enhancement of the inhibitory action of SDSO in the presence of KCl is attributed to the function of K⁺ as counterion in the electrical double layer on SC surface. This would lead to increase zeta potential on CS surface and consequently increase the adsorption density of the negatively charged of dodecyl sulfonate. The higher IE produced in CaCl₂-SDSO system compared to that of KCl-SDSO system is attributed to that Ca²⁺ ions would be adsorbed in the stern plan in the electrical double layer (specifically adsorbed). This kind of adsorbed ions is strongly anchored on CS surface and resurfacing the charge on the metal surface [19]. While K⁺ the monovalent ions, would be adsorbed in the diffuse layer of the electrical double layer on SC surface. This type of adsorbed ions is weakly adsorbed and has little resurfacing action regarding surface charge and give limited additional active site to SDSO ions to be adsorbed. Moreover, Ca²⁺ ions and SDSO ions interact in solution to produce calcium salt of dodecylsulfonate that have low solubility product as compared with that of sodium salt of dodecylsulfonate i.e. high surface activity that would lead to improve the inhibitory action of SDSO.

3.3. Effect of Brij 58 Co-Surfactant Additions on the Inhibition Efficiency

Figure 5 illustrates the influence of Brij 58 additions on the corrosion rate on SC surface in the presence of 5.7×10^{-5} mole. dm^{-3} SDSO in 0.2 mole. dm^{-3} HCl solution. The same data in Fig.6 were replotted to display the Brij 58 concentration as a function inhibition efficiency of SDSO. Evident from the results displayed in Figs.5 and 6 is the synergistic effect of Brij 58 co-surfactant on the inhibitory action of SDSO. It is supposed that co-adsorption of both Brij 58 and dodecylsulfonate ions on CS surface. These figures reveal that the addition of Brij 58 causes drastic improvement of the inhibitory action of SDSO. 91% inhibition efficiency could be obtained in the

presence of 5.7×10^{-5} mole. dm^{-3} SDSO with 2×10^{-4} mole. dm^{-3} Brij 58 addition. It was found that the presence of nonionic surfactant induced the adsorption of ionic surfactant on mineral surface [15]. At such acidic solution the interaction through the hydrogen bonding, between oxygen atoms in polyethylene groups of Brij 58 molecules and surface iron hydroxyl groups on CS surface is predominant. Some of dodecyl sulfonate ions would be adsorbed through the preadsorbed Brij 58 molecules. Moreover, the role of hydrophobic interactions between the hydrocarbon tails of the two surfactant would contribute to the expected enhancement of the adsorption density and consequently the improvement of the inhibition efficiency of Brij 58-SDSO system.

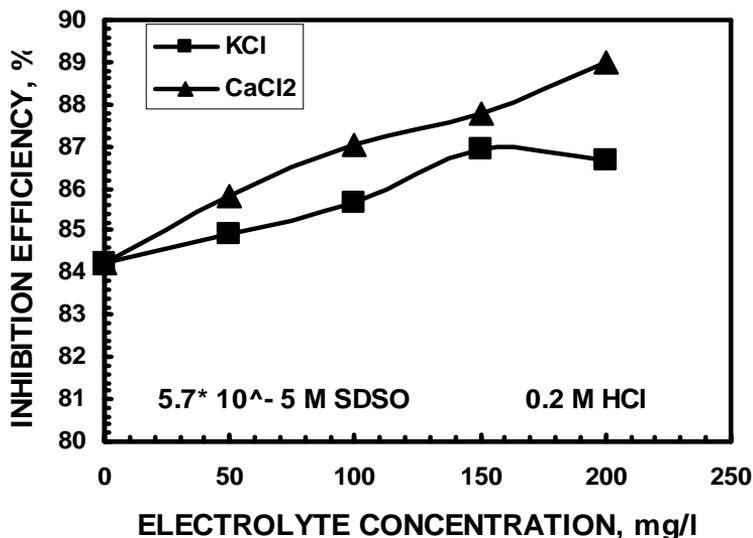


Fig. 4: Influence of electrolyte additions on the inhibition efficiency of SDSO in the presence of 5.7×10^{-5} mole. dm^{-3} SDSO in 0.2 mole. dm^{-3} HCl solution

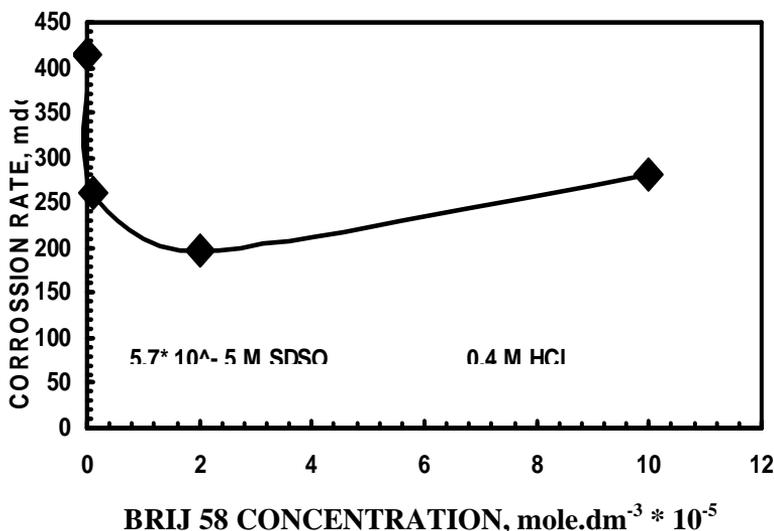


Fig.5 : Effect of Brij 58 co-surfactant on the inhibitory action of SDSO in the presence of 5.7×10^{-5} mole. dm^{-3} SDSO in 0.4 mole. dm^{-3} HCl

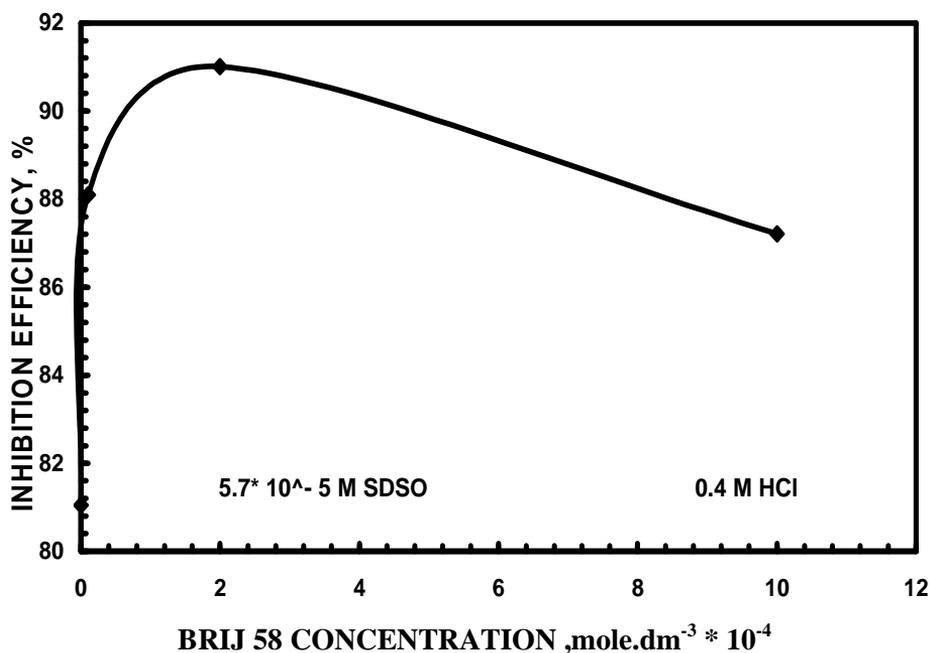


Fig.6 : Effect of Brij 58 co-surfactant on the inhibition efficiency of SDSO in the presence of 5.7×10^{-5} mole.dm⁻³ SDSO in 0.4 mole.dm⁻³ HCl.

4. CONCLUSIONS

Based on the obtained results the following conclusions can be drawn from the present study:

- The results obtained from corrosion rates curves by weight loss method indicate that SDSO has a good inhibition efficiency for carbon steel in HCl solution.
- The inhibition efficiency was found to be increased with increasing SDSO concentration and decreased with increasing the concentration of HCl. The IE% up to 84 was obtained.
- The inhibition effect of SDSO is explained to be due to its adsorption on the cathodic sites on the carbon steel surface. The obtained results indicate also the optimum dosage of SDSO is very lower than CMC of SDSO.
- The effect of adding some inorganic ions e.g K⁺, Ca²⁺ and Fe³⁺ on the inhibitory action of SDSO have been used to investigate, which indicating that some of these ions have a synergistic role with SDSO on the inhibiting the corrosion of carbon steel. While Fe³⁺ ions retard the inhibitory action of SDSO.
- Brij 58 polyoxyethylene nonionic co-surfactant improves the anticorrosion property of SDSO. The synergistic action was explained in terms of molecular association and coadsorption of the two surfactants on SC surface.

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تنشيط التآكل الكيميائي لسبيكة الصلب الكربوني في وسط حمضي الهيدروكلوريكي باستخدام محفز السطوح سلفونات الصويوم: التأثير التآزري لمحفز السطوح المصاحب الغير متآين وبعض الأيونات الغير عضوية

تم في هذا البحث دراسة خاصة تنشيط التآكل باستخدام محفز السطوح سلفونات الصويوم الهيدروكلوريكي (عدد ذرات الكربون 12) على تآكل الصلب الكربوني في حمض الهيدروكلوريك باستخدام طريقة الفقد في الوزن . وقد أوضحت النتائج أن هذا المحفز السطحي يعتبر مثبطاً جيداً للتآكل ولقد أعطى كفاءة جيدة جداً للتنشيط خاصة عند التركيزات المرتفعة نسبياً من محفز السطوح ولقد تبين أن كفاءة التنشيط تتوقف على تركيز كل من محفز السطوح و الحامض. كما تم دراسة تأثير إضافة محفز سطوح مساعد غير متآين (Brij 85) على كفاءة التنشيط لمحفز السطوح (SDSO) حيث وجد أن هناك تجانس بينهما في العمل على زيادة كفاءة التنشيط . وقد يعزى ذلك إلى أن الجزيء المصاحب من كلا المحفزين يزيد من قدرة إمتزاجيهما على سطح المعدن وبالتالي إلى زيادة سمك الطبقة التي تغطي سطح المعدن من الجزء الطارد للماء .

وفي هذا البحث أيضاً كان هناك اهتمام خاص بدراسة تأثير إضافة بعض من الأملاح غير العضوية على كفاءة التنشيط لمحفز السطوح (SDSO) . فبالنسبة إلى كل من كلوريد البوتاسيوم وكلوريد الكالسيوم فقد وجد أنهما يساعدان على رفع كفاءة التنشيط لمحفز السطوح (SDSO) ويمكن تفسير ذلك على أساس أن أيونات البوتاسيوم والكالسيوم الموجبة تؤدي إلى تكون مواقع نشطة على سطح المعدن يجذب الشحنات السالبة لمحفز السطوح وبالتالي تنشأ طبقة أخرى من الجزء الطارد للماء على سطح المعدن مما يؤدي إلى زيادة كفاءة التنشيط .

أما إضافة كلوريد الحديد فإنها يسبب انخفاض كفاءة التنشيط لمحفز السطوح (SDSO) وقد يكون ذلك بسبب تكوين مركب ملحي من أيون الحديد الموجب وأيون محفز السطوح السلب والتي لها درجة ذوبان منخفضة جداً مما قد يسبب لها ترسيب في المحلول ينتج عنه انخفاض التركيز الفعال لمحفز السطوح ودرجة امتزاجه على سطح المعدن .