



ADS, ALS, AHDS and ADDBS Surfactants as Corrosion Inhibitors for Carbon Steel in acidic Solution

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Abstract

The role of some surfactants towards corrosion control of carbon steel in 1.0 M HCl has been investigated using weight loss and galvanostatic polarization techniques. Surfactants investigated are Ammonium decyl sulphate (ADS), ammonium lauryl sulphate (ALS), ammonium hexadecyl sulphate (AHDS) and ammonium dodecyl benzene sulfonate (ADDBS). Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The corrosion inhibition efficiency was found to increase with surfactant concentration and decreased with increasing temperature which is due to the fact, that the rate of corrosion of carbon steel is higher than the rate of adsorption of surfactant molecules. The inhibiting action of surfactants are considerably enhanced by the addition of KI, due to the increase of the surface coverage and therefore indicate the joint adsorption of surfactants and iodide ions. Thermodynamic parameters for adsorption and activation processes were also determined. Galvanostatic polarization data indicated that surfactants act as mixed-type inhibitors.

Keywords: Corrosion inhibitors, surfactant, carbon steel, HCl solution.

Introduction

Carbon steel has remarkable economic and attractive materials for engineering applications owing to its low cost, easy availability and high mechanical strength. The interest of the materials arises from their importance in recent civilization. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media¹. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of metal dissolution in acidic solutions²⁻⁶. Thus, many studies concerning the inhibition of carbon steel corrosion using organic substances are conducted in acidic and basic solutions⁷⁻¹⁰.

The present study aimed to investigate the efficiency of some surfactants as corrosion inhibitors for carbon steel in acidic media. An attempt was also made to clarify the effects of concentration and temperature on the corrosion inhibition efficiency of all the four investigated surfactant as corrosion inhibitors for carbon steel. The measurements of corrosion rate and percentage corrosion inhibition efficiency of different surfactant towards corrosion of carbon steel by weight loss and electrochemical polarization technique were performed in 1.0 M HCl without and with the presence of surfactants in the concentration range (10 to 100 ppm). The name and molecular

structures of all the four surfactants as corrosion inhibitor for carbon steel in acidic medium are given in scheme no. 1.

Material and Methods

Carbon steel used for the investigations was in the form of sheet (0.25 mm thick) and had the following composition (w/w): C = 0.14, Si = 0.03, Mn = 0.32, S = 0.05, P = 0.20, Ni = 0.01, Cu = 0.01, Cr = 0.01% and balance Fe.

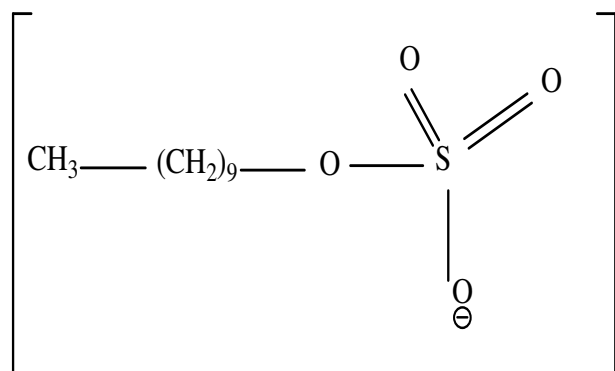
All the chemicals used were of AR grade and the solutions were prepared using triple distilled water. Duplicate or in some cases triplicate experiments have been performed to verify the reproducibility and consistency of the experimental data.

For weight loss measurements, carbon steel specimens of 3 × 1.5 cm² size were cut from the carbon steel sheet. All the metal specimens were mechanically polished successively with the help of emery papers of grades 100, 200, 300, 400 and 600 μ and then thoroughly cleaned with plenty of triple distilled water and then with acetone. The specimens were dried with hot air blower and stored in desiccators over silica gel¹¹⁻¹³.

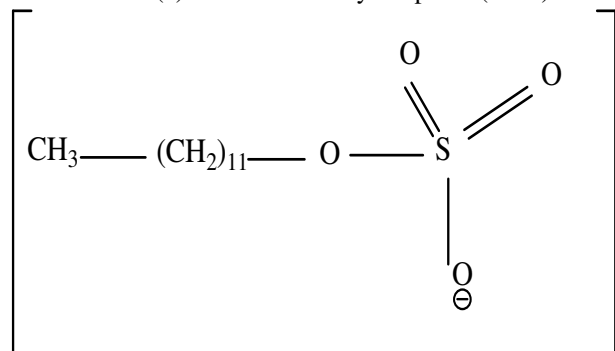
After recording the initial weights of carbon steel specimens on a Mettler Toledo, Japan AB 135-S/FACT, single pan analytical balance, (with a precision of 0.01mg), they were immersed in tilted position in 250 ml beakers each having 200 ml of acidic solution as corroding medium with or without the inhibitor. Experiments were carried out in an electronically controlled air thermostat maintained at a constant temperature of 30, 40 and

50°C with in an accuracy of $\pm 0.1^\circ\text{C}$. After exposing the specimens for 24 hours, the specimens were taken out from the beaker and washed initially under the running tap water.

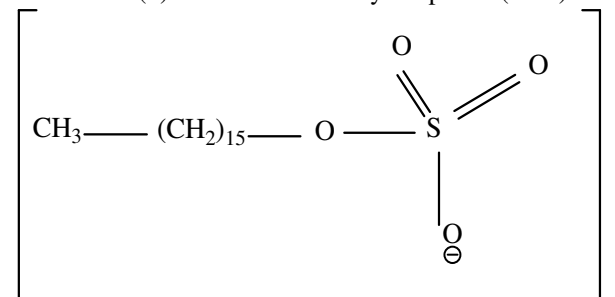
Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with triple distilled water and dried with hot air blower and then weighed again. Corrosion rate in mils per year (mpy) and percentage corrosion inhibition efficiency were calculated using the following equations¹⁴⁻¹⁵.



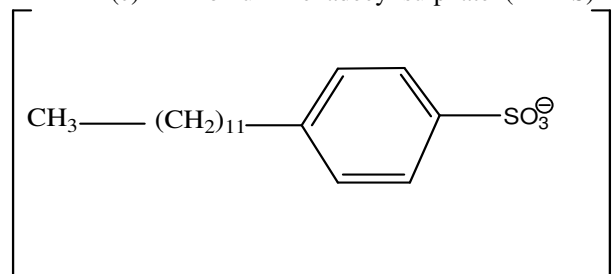
(a) Ammonium Decyl sulphate (ADS)



(b) Ammonium Laruryl sulphate (ALS)



(c) Ammonium Hexadecyl sulphate (AHDS)



(d) Ammonium Dodecyl benzene sulfonate (ADDBS)

Scheme-1
Molecular formula and structure of four surfactants

NH₄⁺

NH₄⁺

NH₄⁺

NH₄⁺

Corrosion rate in mils per year (mpy) and percentage corrosion inhibition efficiency were calculated by weight loss technique using the following equations.

$$\text{Corrosion rate (mpy)} = \frac{534 \times W}{DAT} \quad (1)$$

Where W = weight loss (mg), D = density of carbon steel (gm/cm³), A = area of specimen (sq. inch), T = exposure time (hours).

The degree of surface coverage (θ) of the investigated surfactant compounds were calculated from the following equation:

$$\theta = \left[1 - \left(\frac{\Delta W_{Inh}}{\Delta W_{Free}} \right) \right] \quad (2)$$

Where, ΔW_{Free} and ΔW_{Inh} are weight losses of metal per unit area in absence and presence of inhibitor at given time period and temperature, respectively.

Linear polarization resistance measurements were carried out potentiostatically by scanning through a potential range of 14 mV above and below the OCP value in steps of 2 mV. Experiments were carried out in absence and presence of inhibitors at their different concentrations and at a constant temperature of 30, 40 and 50°C. The resulting current is plotted against the potential and slope of the line is measured.

The corrosion current density i_{Corr} , is related to the corrosion rate by the equation,

$$\text{Corrosion rate (C.R.) (mpy)} = \frac{0.1288 \times i_{Corr} \times Eq. Wt.}{D} \quad (3)$$

Where Equation Wt. = Gram equivalent weight of metal/alloy, D = Density of metal (gm/cm³), i_{Corr} = Corrosion current density ($\mu\text{A}/\text{cm}^2$).

The interaction of inhibitor molecules can be described by introducing of an parameter, S_θ , obtained from the surface coverage values (q) of the anion, cation and both. Synergism parameter, S_θ , was calculated using the following equation.

$$S_\theta = \frac{1 - \theta_{1+2}}{1 - \theta_{1+2}} \quad (4)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, θ_1 , surface coverage by anion, θ_2 , surface coverage by cation and θ_{1+2} , surface coverage by both i.e. anion and the cation.

Results and Discussion

Percentage corrosion inhibition efficiency of all the four surfactant at different concentrations for the corrosion study of carbon steel after exposure to 1.0 M HCl at 30°C have been tabulated in table 1. It is observed from the table 1 that the weight loss decreased, percentage corrosion inhibition efficiency increased and therefore the corrosion inhibition strengthened with increase in inhibitor concentration from 10 to 100 ppm. This trend may result from the fact that adsorption and surface coverage increases with the increase in concentration of surfactant molecules. The linear variation of weight loss with time in uninhibited and inhibited 1.0 M HCl indicates the absence of insoluble surface films during corrosion. It is clear from the tables 1 that percentage corrosion inhibition efficiency increases with increase in inhibitor concentration. The percentage corrosion inhibition efficiency for different investigated anionic surfactants as corrosion inhibitor increases in the following order $d > c > b > a$.

Table 2 gives the values of percentage corrosion inhibition efficiency for different concentrations of all the four surfactant molecules and 1.0×10^{-2} M KI. The addition of KI improves the percentage corrosion inhibition efficiency of the investigated surfactants molecules significantly. The synergistic effect between surfactants molecules and KI is due to interactions between chemisorbed I⁻ ions and surfactants molecules. The stabilization of adsorbed organic cations on the surface, which may be exhibited by electrostatic interactions with I⁻ ions, leads to higher surface coverage and greater corrosion inhibition.

Table 3 shows synergism parameters for different concentrations of all the four investigated surfactant (a to d) with addition of 1.0×10^{-2} M KI for the corrosion of carbon steel after 24 hours of immersion in 1.0 M HCl at 30°C. It is observed from the table 3 that synergism parameters for all the four investigated surfactant increase with increase in concentration of surfactant molecules from 10 to 100 ppm. Among the four investigated surfactants molecules, order of synergism parameters is $a < b < c < d$.

Table 4 shows typical current-potential polarization curves of carbon steel in 1.0 M HCl in the absence and presence of different concentrations of surfactant molecules. Values of associated electrochemical parameters such as current density (i_{Corr}), corrosion potential (E_{Corr}), Tafel slopes, and corrosion inhibition efficiency (per cent) as function of surfactant d concentrations in 1.0 M HCl are shown in table 4. It is evident from table 4 that the Tafel constants did not change significantly. It is clear from the Tafel plots that the surfactant d was mixed type because it enhances both the anodic and cathodic polarization but the anode is more polarized when an external current was applied. Addition of surfactant compounds increased both cathodic and anodic over voltage and caused mainly parallel displacement to the more negative and positive respectively.

The corrosion current density (i_{Corr}) decreases with increase in the concentration of surfactant compounds, which indicates that the presence of these surfactant molecule retards the dissolution of carbon steel in 1.0 M HCl and the degree of inhibition depends on the concentration of surfactant molecule. The values of corrosion potential (E_{Corr}) values shifted to less negative values on increasing the concentration of surfactant molecule from 10 to 100 ppm.

The effect of temperature on the corrosion behavior of carbon steel was studied by weight loss methods at different temperatures in the range 30-50 °C in the absence and presence of different concentrations of compound (d) in 1.0 M HCl media and percentage corrosion inhibition efficiency of compound (d) is shown in table 5. It is obvious from the table 5 that percentage corrosion inhibition efficiency increases with increase in the concentration of compound (d) and decreases with increase of temperature.

The calculated values of the apparent activation energy, E_a^* , activation enthalpies, ΔH^* and activation entropies, ΔS^* are shown in table 6. These values indicate that the presence of the additives increases the activation energy, E_a^* and the activation enthalpy ΔH^* , and decreases the activation entropy, ΔS^* for the corrosion process. The addition of inhibitors modified the values of E_a^* . This may be attributed to the adsorption of inhibitors on carbon steel surface and this adsorption make an energy barrier and this energy barrier of corrosion reaction increases with increase in concentration of the surfactant molecule, and hence percentage corrosion inhibition efficiency increases. This suggested that the process is activation controlled¹⁶⁻¹⁷. Since, the activation energy value of 62.36 kJ mol⁻¹ (table 6) for HCl-inhibitor systems support the fact that the surfactants are physically adsorbed on carbon steel surface. According to these reports, E_a^* due to chemical adsorption (>80 kJ mol⁻¹) is considerably larger than due to physical adsorption (< 80 kJ mol⁻¹) the increase in the activation enthalpy (ΔH^*) in presence of the inhibitors implies that the addition of the surfactants to the acid solution, increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the surfactant molecules.

Mechanism of corrosion inhibition of all the four investigated surfactants molecules can be explained on the basis of the molecular size and the number of adsorption centers. Organic surfactant compound (d) should be the most effective inhibitors, inspite of it has two active adsorption centers. The highest inhibition efficiency of the compound (d) may be due to: i. higher molecular size and ii. benzene ring contributes p electrons to the adsorption centers and hence increases the electron density on the adsorption centers. Compounds $a < b < c$ in percentage corrosion inhibition efficiency and this is agrees with their molecular size.

Table-1
Percentage corrosion inhibition efficiency at different concentrations of surfactant for the corrosion of carbon steel after exposure to 1.0 M HCl at 30°C

Conc. of Surfactant (ppm)	Percentage corrosion inhibition efficiency of Surfactants			
	(a)	(b)	(c)	(d)
10	70.3	73.5	79.7	81.3
30	74.5	78.6	82.4	85.4
50	80.2	81.7	86.6	88.3
70	86.7	89.2	90.6	94.6
90	88.2	92.5	96.7	96.5
100	90.3	95.6	96.1	97.4

Table-2
Percentage corrosion inhibition efficiency at different concentrations of the four investigated surfactants (a to d) with addition of 1.0×10^{-2} M KI for the corrosion of carbon steel after 24 hours of immersion in 1.0 M HCl at 30°C

Conc. of Surfactant (ppm)	Percentage corrosion inhibition efficiency of Surfactants			
	(a)	(b)	(c)	(d)
10	77.7	80.3	83.6	85.2
30	83.2	84.5	86.4	88.3
50	86.8	88.4	88.4	91.4
70	89.7	92.3	93.7	96.7
90	92.6	95.1	96.1	97.8
100	95.2	96.9	97.7	98.9

Table-3
Synergism parameter (S_{θ}) for different concentrations of investigated surfactant (a to d) with addition of 1.0×10^{-2} M KI for the corrosion of carbon steel after 24 hours of immersion in 1.0 M HCl at 30°C

Conc. of surfactant (ppm)	Synergism parameter (S_{θ})			
	(a)	(b)	(c)	(d)
10	1.011	1.082	1.128	1.161
30	1.023	1.088	1.134	1.179
50	1.032	1.094	1.147	1.199
70	1.038	1.098	1.156	1.223
90	1.047	1.107	1.158	1.242
100	1.068	1.115	1.168	1.283

Table-4
The effect of concentrations of compound (d) on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a and β_c), Percentage corrosion inhibition efficiency (%age CIE) and degree of surface coverage (θ) for the corrosion of carbon steel in 1.0 M HCl at 30°C

Conc. of surfactant (d) (ppm)	$-E_{corr}$, mV	i_{corr} , ($\mu A/cm^2$)	$-\beta_c$ (mV/dec)	β_a (mV/dec)	θ	%age CIE
Blank	942	62.0	217	89	-	-
10	930	34.0	204	108	0.788	82.2
30	926	30.8	211	110	0.817	87.7
50	920	27.1	216	116	0.823	91.5
70	915	24.2	220	120	0.845	93.9
90	908	20.3	224	123	0.857	94.8
100	903	18.6	227	126	0.894	98.1

Table-5
The effect of temperature on the percentage corrosion inhibition efficiency of surfactant (d) at different concentrations and temperatures

Conc. of surfactant (d) (ppm)	30 ^o C	40 ^o C	50 ^o C
10	81.3	75.3	68.5
30	85.4	78.6	72.4
50	88.3	85.1	76.8
70	94.6	88.4	80.1
90	96.5	90.1	83.4
100	97.4	92.3	84.8

Table-6
Activation parameters of the corrosion of carbon steel in 1.0M HCl in absence and presence of different concentrations of compound (d)

Conc. of surfactant (d) (ppm)	E_a^* (kJmol ⁻¹)	ΔH^* (kJmol ⁻¹)	$-\Delta S^*$ (Jmol ⁻¹ K ⁻¹)
10	54.28	46.12	112.42
30	57.14	48.24	107.23
50	60.05	52.29	103.15
70	61.12	55.24	101.05
90	61.05	55.12	98.35
100	62.36	56.06	96.30

Conclusion

All the four investigated surfactant molecules act as corrosion inhibitors for the carbon steel in hydrochloric acid solution. Surfactant molecules adsorb on carbon steel surface according to the Freundlich adsorption isotherm. The surfactants molecules increase the value of activation energy of corrosion and consequently decrease the rate of dissolution of carbon steel in HCl solution. Polarization data showed that all the four investigated surfactant molecules acts as mixed-type inhibitors. The inhibition efficiencies obtained from polarization and weight loss measurements are in good agreement with each other. Increase of temperature leads to the increase in corrosion rate of carbon steel in HCl solution. Addition of KI to surfactant molecules shows synergistic effect on corrosion inhibition efficiency of organic surfactant towards carbon steel.

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