Surfactants as Corrosion Inhibitors for Stainless Steel in HCl Solution

Diwan Singh Rajan[1,*] and Dr. Shiv Darshan Malik[2]
[1,*]Research Scholar, Department of Chemistry, JJT University, Jhunjhunu (Rajasthan) India
[2]Research Guide , Department of Chemistry, JJT University, Jhunjhunu (Rajasthan) India

The role of some surfactants in the corrosion of Stainless steel in 1.0 M HCl has been studied using weight loss and galvanostatic polarization techniques. Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The inhibition efficiency was found to increase with increasing inhibitor concentration and decreased with increasing temperature which is due to the fact, that the rate of corrosion of Stainless steel is higher than the rate of adsorption The inhibiting action of these compounds are considerably enhanced by the addition of KI, due to the increase of the surface coverage and therefore indicate the joint adsorption of these compounds and iodide ions. Thermodynamic parameters for adsorption and activation processes were determined. Galvanostatic polarization data indicated that these compounds act as mixed-type inhibitors. Results obtained from the two techniques are in good agreement.

1. INTRODUCTION

Stainless steel is a remarkable economic and attractive material for engineering applications owing to its low cost, easy availability and high mechanical strength. The interest of the material arises from its 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 media [1]. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of metal dissolution in such solutions. Thus, many studies concerning the inhibition of Stainless steel corrosion using organic substances are conducted in acidic and basic solutions [2-6].

The present study aimed to investigate the efficiency of some surfactants as corrosion inhibitors for stainless steel in acidic media. An attempt was also made to clarify the effects of concentration and temperature on the inhibition efficiency of the studied surfactant as corrosion inhibitors for stainless steel. The measurements of corrosion rate and percentage inhibition efficiency of different anionic surfactant towards corrosion of stainless steel by weight loss and electrochemical polarization technique were performed in 1.0 M HCl without and with the presence of the investigated surfactants in the
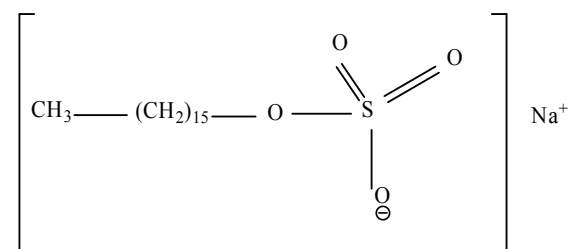
concentration range (10 to 100 ppm). The name and molecular structures of the anionic surfactants as corrosion inhibitor for stainless steel in acidic medium are:
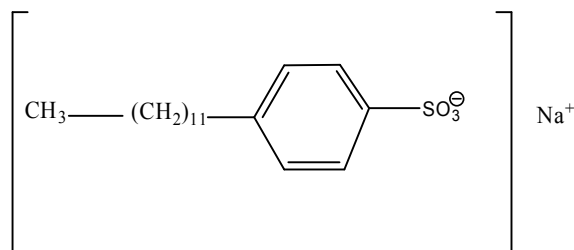
$$CH_3 - (CH_2)_9 - O - \overset{\displaystyle O}{\underset{\displaystyle O^{\ominus}}{S}} \hspace{-0.3em} \text{=O} \quad \Big]\ Na^+$$
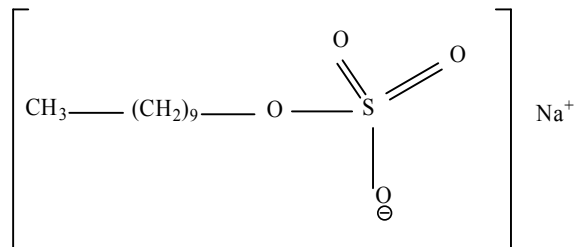
(a) Decyl sulphate sodium salt (SSDS)

$$CH_3 - (CH_2)_{11} - O - \overset{\displaystyle O}{\underset{\displaystyle O^{\ominus}}{S}} \hspace{-0.3em} \text{=O} \quad \Big]\ Na^+$$
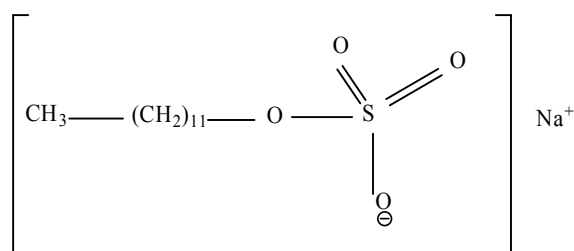
(b) Dodecyl sulphate sodium salt (SSDDS)

$$CH_3 - (CH_2)_{15} - O - \overset{\displaystyle O}{\underset{\displaystyle O^{\ominus}}{S}} \hspace{-0.3em} \text{=O} \quad \Big]\ Na^+$$

(c) Hexadecyl sulphate sodium salt (SSHDS)

$$CH_3 - (CH_2)_{11} - C_6H_4 - SO_3^{\ominus} \quad \Big]\ Na^+$$

(d) Dodecyl benzene sulfonate sodium salt (SSDDBS)

2. EXPERIMENTAL

Stainless steel used for the investigations was in the form of sheet (0.25 mm thick) and had the following composition.

Element	C	Si	Mn	S	P	Ni	Cu	Cr	Fe
Weight percentage (w/w)	1.08	0.08	0.58	0.07	0.51	0.05	0.03	0.04	Balance

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, stainless steel specimens of 3×1.5 cm^2 size were cut from the stainless steel sheet whereas for electrochemical polarization investigations, specimens of size 5×1.0 cm^2 were used. All the specimens were mechanically polished successively with the help of emery papers of grades 100, 200, 300, 400 and 600µ 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 gel.

After recording the initial weights of stainless 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 at 30, 40 and 50^{0}C with in an accuracy of ±0.1^{0}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 inhibition efficiency were calculated using the following equations.

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

where, W = Weight loss (mg), D = Density of stainless steel (gm/cm^3), 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:

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

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.

Electrochemical polarization studies were carried out in 500 ml glass cell having three electrodes system assembly. Potentiostatic polarization of the working electrode was carried out by using a Potentiostat / Galvanostat PGS 201 T (Tacussel, France).

The working electrode was stainless steel under study, platinum electrode was used as counter electrode or an auxiliary electrode. All the potentials were measured against a pencil type luggin capillary saturated calomel electrode as reference electrode. A Luggin capillary filled with the test solution was used to connect the reference electrode with the cell. The tip of the Luggin capillary was kept very close to the working area of the electrode but without touching it in order to minimize the IR drop and this distance was kept constant during the whole study. Only 1 cm^2 area of specimen was used as working area and the rest of the area of the specimen was covered with a lacquer except the other tip of specimen which was used for making electrical connection. The specimen was left in the test solution until a constant open circuit potential (OCP) was attained.

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 at 30, 40 and 50^{0}C. The resulting current is plotted against the potential and slope of the line is measured.

The corrosion current, I$_{corr}$ is related to the slope of the line by Stern-Geary equation.

$$\frac{\Delta E}{\Delta i} = \frac{\beta_a \times \beta_c}{2.303\, I_{corr}(\beta_a + \beta_c)} \qquad (3)$$

where $\frac{\Delta E}{\Delta i}$ is the slope which is linear polarization resistance (R$_p$), β_a and β_c are anodic and cathodic Tafel slopes respectively and I$_{corr}$ is the corrosion current density in μA/cm^2.

The anodic and cathodic Tafel slopes were measured after recording anodic and cathodic polarization curves of the specimen up to a maximum shift of ± 140 mV from OCP value in steps of 10 mV. Experiments were carried out in absence and presence of the inhibitor at their 10 to 100 ppm concentrations at 30, 40 and 50^{0}C.

Rearranging the above equation:

$$I_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \,x\, \frac{1}{R_p} \qquad (4)$$

The corrosion current density I$_{corr.}$, is related to the corrosion rate by the equation,

$$\text{Corrosion rate (C.R.) (mpy)} = \frac{0.1288 \times I_{Corr.} \times Eq.Wt.}{D} \qquad (5)$$

where, Eq. Wt. = Gram equivalent weight of metal/alloy, D = Density of metal (gm/cm^3), I$_{corr}$ = Corrosion current density (μA/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. Aramiki and Hackerman [7] calculated the synergism parameter, S_θ, using the following equation.

$$S_\theta = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \qquad (6)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, $\theta_1 =$ surface coverage by anion, $\theta_2 =$ surface coverage by cation and $\theta'_{1+2} =$ measured surface coverage by both the anion and the cation, which may be attributed to competitive adsorption as can be seen from Table 3, S_θ values nearly equal to unity which suggests that the enhanced inhibition efficiencies caused by the addition of these anions to surfactants is due to mainly to the synergistic effect.

3. RESULTS AND DISCUSSIONS

Table 1 gives the values of percentage corrosion inhibition efficiency for different concentrations of investigated surfactant compounds at 30 ^{0}C. Figure 1 shows percentage corrosion inhibition efficiency of all the four organic surfactants for stainless steel at 30^{0}C in presence of 1.0 M hydrochloric acid solution. It is observed from the Table 1 and Figure 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. Thus, the metal surface is efficiently separated from the corroding medium [8-9]. 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 Table 1 that percentage corrosion inhibition efficiency increases with increase in concentration of different surfactant as corrosion inhibitor. The percentage corrosion inhibition efficiency for different investigated anionic surfactants as corrosion inhibitor increases in the following order d > c > b > a.

Diwan Singh Rajan[1,*] and Dr. Shiv Darshan Malik

Table 1: Percentage corrosion inhibition efficiency at different concentrations of anionic surfactant for the corrosion of stainless steel after immersion in 1.0 M HCl at 30 ^{0}C.

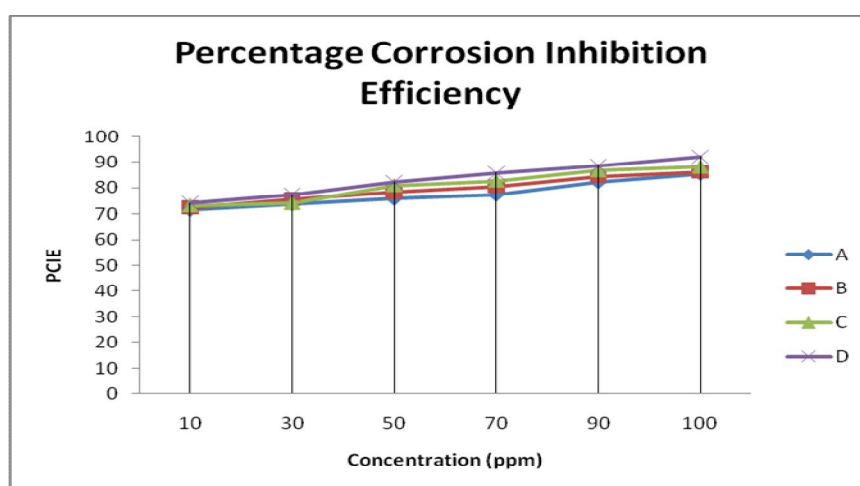| Concentration of Surfactant (ppm)	Percentage Corrosion Inhibition Efficiency of Surfactants			
	(a)	(b)	(c)	(d)
10	71.6	72.5	73.2	74.1
30	73.7	75.6	74.1	77.3
50	75.8	78.3	80.9	82.3
70	77.3	80.6	82.6	85.8
90	82.2	84.5	86.7	88.6
100	85.4	86.2	88.1	92.1

Figure 1: Percentage corroison inhibition efficiency of all the four organic surfactants for Stainless steel at 30^{0}C in presence of 1.0 M hydrochloric acid solution.

Table 2 gives the values of percentage corrosion inhibition efficiency for different concentrations of investigated surfactant compounds in presence of 10^{-2} M KI. Figure 2 shows synergistic effect of KI on the percentage corroison inhibition efficiency of all the four organic surfactants for stainless steel at 30^{0}C in 1.0 M hydrochloric acid solution. It is observed from the Table 2 and Figure 2 that the addition of KI improves the percentage corrosion inhibition efficiency of the investigated surfactant molecules significantly. The synergistic effect between investigated surfactant molecules and KI is due to interactions between chemisorbed I- and organic compounds. The stabilization of adsorbed organic cations on the surface of stainless steel, which may be exhibited by electrostatic interactions of surfactants molecules with I- ions, leads to higher surface coverage of metal surface and hence provides greater corrosion protection to metal.

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 stainless steel after 24 hours of immersion in 1.0 M HCl at 30 ^{0}C.

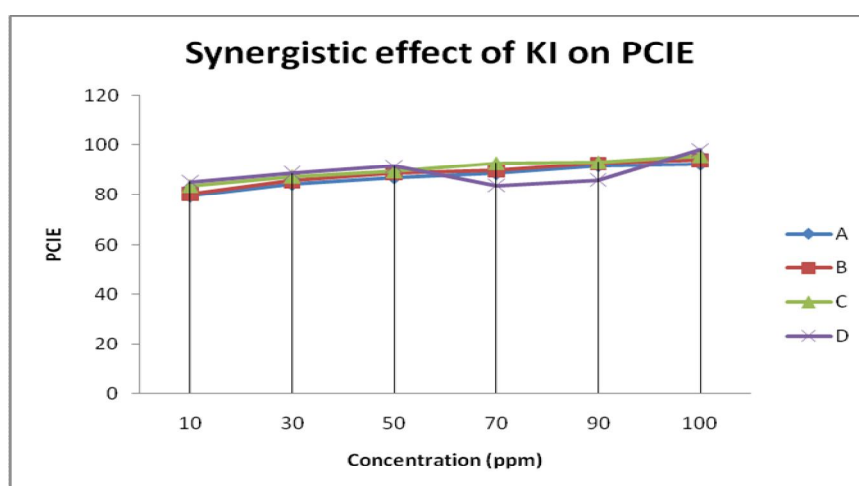| Conc. of Surfactant (ppm)	Percentage Corrosion Inhibition Efficiency of Surfactants			
	(a)	(b)	(c)	(d)
10	79.5	80.3	83.6	85.2
30	84.3	85.5	87.4	88.6
50	86.9	88.6	89.4	91.4
70	88.5	89.7	92.7	83.7
90	91.6	92.5	93.1	85.8
100	92.2	93.9	95.7	97.9

Figure 2: Synergistic effect of KI on the percentage corroison inhibition efficiency of all the four organic surfactants for stainless steel at 30^{0}C in 1.0 M hydrochloric acid solution.

Table 3 shows 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 stainless steel metal alloy after 24 hours of immersion in1.0 M HCl at 30^{0}C.

Diwan Singh Rajan[1,*] and Dr. Shiv Darshan Malik

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 stainless steel after 24 hours of immersion in 1.0 M HCl at 30 ^{0}C.

Conc. of Surfactant (ppm)	Synergism Parameter (S_θ)			
	(a)	(b)	(c)	(d)
10	1.001	1.025	1.102	1.149
30	1.004	1.034	1.111	1.156
50	1.008	1.041	1.123	1.166
70	1.012	1.047	1.132	1.173
90	1.017	1.058	1.141	1.191
100	1.021	1.068	1.148	1.203

Table 4 shows typical current-potential electrochemical polarization study of stainless steel metal alloys in 1.0 M HCl in the absence and presence of various concentrations of organic 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 given in Table 4. It is evident from the Table 4 that the Tafel constants did not change significantly. It observed from the Tafel curves that the inhibitor was mixed type because they enhance the anodic and cathodic polarization to an equal extent but the anode is more polarized when the magnitude of external current was increased. Addition of surfactant compounds increased both cathodic and anodic over voltage and caused mainly parallel displacement to the more negative and positive side, respectively.

The corrosion current density (i_{corr}) decreases with increasing the concentration of surfactant compounds from 10 to 100 ppm, which indicates that the presence of these surfactant molecules retards the dissolution of stainless steel in 1.0M HCl and the degree of corrosion inhibition depends on the concentration of surfactant molecules.

The values of corrosion potential (E_{corr}) values shifted to less negative values by increasing the concentration of surfactant molecules from 10 to 100 ppm.

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 & β_c), %age corrosion inhibition efficiency (%age CIE) and degree of surface coverage (q) for the corrosion of stainless steel in 1.0 M HCl at 30 ^{0}C.

Conc. of Surfactant 'd' (ppm)	$-E_{corr}$, (mV)	i_{corr}, ($\mu A/cm^2$)	$-\beta_c$ (mV/dec)	β_a (mV/dec)	q	Percentage CIE
Blank	745	71.1	245	78	-	-
10	738	42.0	227	102	0.782	77.7
30	737	39.8	219	109	0.807	79.9
50	736	36.1	215	107	0.815	83.2
70	735	34.2	213	106	0.839	84.4
90	734	32.3	211	104	0.848	87.2
100	733	29.6	210	103	0.881	92.8

The effect of temperature on the corrosion behavior of stainless steel was studied by weight loss methods at various temperatures in the range 30-50^{0}C in the absence and presence of different concentrations of surfactant (d) in 1.0 M HCl media. Percentage corrosion inhibition efficiency of surfactant molecule (d) is shown in Table 5. It is obvious from Table 5 that percentage corrosion inhibition efficiency increases with increasing the concentration of surfactant molecule (d) and decreases with increasing the temperature. This indicates the fact that the augmentation of temperature led to the reduction of the inhibitor adsorption and then the acceleration of the metal dissolution process [9-13].

Table 5: The effect of temperature on the percentage corrosion inhibition efficiency of organic surfactant (d) for stainless steel at different concentrations and temperatures.

Concentration of Surfactant (d) (ppm)	30^{0}C	40^{0}C	50^{0}C
10	74.1	52.3	30.1
30	77.3	56.4	38.7
50	82.3	61.5	47.2
70	85.8	66.2	52.3
90	88.6	71.8	57.5
100	92.1	73.9	62.7

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 corrosion inhibitors to the corroding medium modified the values of E_a^*. This may be attributed to the adsorption of inhibitors on stainless steel surface., and this adsorption makes an energy barrier and this energy barrier of corrosion reaction increases as the concentration of the inhibitor is increased., and hence percentage corrosion inhibition efficiency increases. This suggested that the process is activation controlled. Since, the activation energy value of 71.26 kJ mol^{-1} (Table 6) for HCl–inhibitor systems support the fact that the inhibitors are physically adsorbed on stainless steel surface. This is in agreement with reports of Abiiola et. al [14], Ebenso et al. [15], Ebenso [16] and Barrow [17]. 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 inhibitors 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 present inhibitor. The entropy of activation (ΔS^*) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step [18-20].

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

Conc. of Surfactant (d) (ppm)	$E_a^* \left(kJmol^{-1} \right)$	$\Delta H^* \left(kJmol^{-1} \right)$	$-\Delta S^* \left(Jmol^{-1}K^{-1} \right)$
10	61.23	58.42	166.53
30	63.54	61.34	161.24
50	64.75	63.43	158.32
70	66.42	63.04	156.21
90	68.71	65.83	153.25
100	71.26	66.11	151.88

Mechanism of corrosion inhibition of all the four investigated organic 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 agrees with their molecular size.
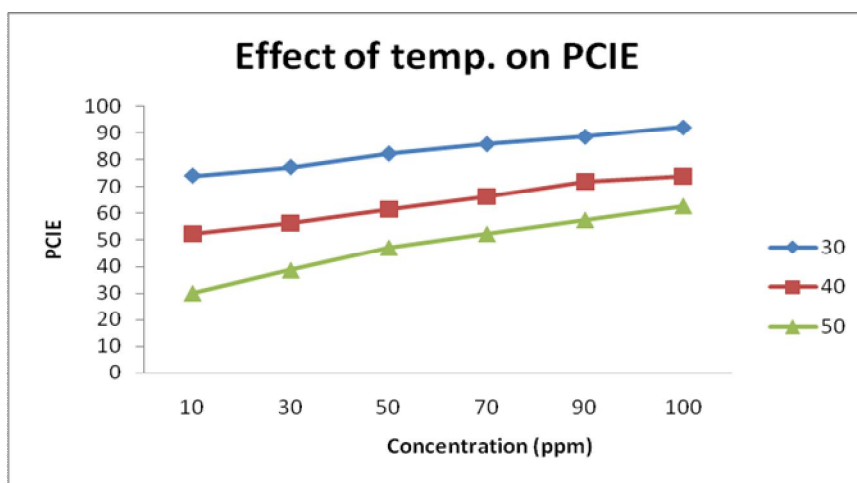
Figure 3: Effect of increasing temperature i.e. 30 to 50 ^{0}C on percentage corrosion inhibition efficiency of surfactant D in case of stainless steel.
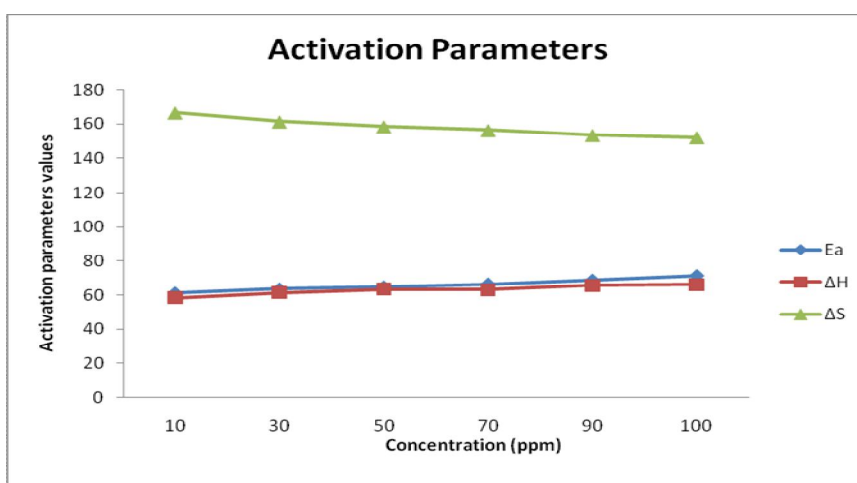

Figure 4: Activation parameters i.e. activation energy, change in enthalpy and change in entropy for stainless steel in case of surfactant D at different concentrations.

4. CONCLUSIONS

i. The investigated surfactant compounds act as corrosion inhibitors for the stainless steel in hydrochloric acid solution.

ii. Surfactant compounds adsorb on stainless steel surface according to the Freundlich adsorption isotherm.

iii. The inhibitors increase the value of activation energy of corrosion and consequently, decrease the rate of dissolution of stainless steel in HCl solution.

iv. Polarization data showed that these investigated surfactant compounds acted as mixed-type inhibitors.

v. The inhibition efficiencies obtained from polarization and weight loss measurements are in good agreement with each other.

vi. Increase of temperature leads to the decrease in corrosion rate of stainless steel in HCl solution.

vii. Addition of KI to inhibitor formulation shows synergistic effect on corrosion inhibition efficiency of organic surfactant towards stainless steel.

REFERENCES

[1] Mazhar, A.A., Badaway, W.A. and Abou-Romia. M.M.; "Impedance studies of corrosion resistance of aluminium in chloride media", Surf. Coat. Techol., Vol. 29, pp. 335-345, 1986.

[2] Stern, M. and Geary, A.I.J.; "Efficiency of xylenol orange as corrosion inhibitor for aluminium in acidic medium", J. Electrochem. Soc., Vol. 104, pp. 56, 1957.

[3] Maayta, A.K. and Al-Rawashdeh N.A.F.; "Inhibition of acidic corrosion of pure aluminum by some or- ganic compounds", Corros. Sci., Vol. 46, pp. 1129, 2004.

[4] Ebenso, E.E., Okafor, P.C. and Ekpe, U.J.; "Anionic Surfactants as Corrosion Inhibitors for Carbon Steel in HCl Solution", Anti-Corrosion Methods and Materials, Vol. 37, pp. 381, 2003.

[5] Bereket, G., Pinarbasi, A. and Ogretir,C.; "Benzimidazole-2-tione and benzoxazole-2-tione derivatives as corrosion inhibitors for aluminium in hydrochloric acid", Anti-Corrosion Methods and Materials, Vol. 51, pp. 282, 2004.

[6] Fouda, A.S., Moussa, M.N., Taha, F.I. and Elneanaa, A.I.; "The role of some thiosemicarbazide derivatives in the corrosion inhibition of aluminium in hydrochloric acid", Corros. Sci., Vol. 26, pp. 719, 1986.

[7] Kazaraji, A., Keertit, S., Aride, Bougrin. K. and Soufiaoui, M.; "Corrosion inhibition of aluminum metal by some organic substance", Bull. Electrochem., Vol.16 (3), pp. 97, 2000.

[8] Zhao, T. and Corros, Mu. G.; "Influence of some surfactants in the corrosion inhibition of aluminium in hydrochloric acid", Corros. Sci. 41, pp. 1999, 1937.

[9] Al-Andis, N., Khamis, E., Al-Mayouf, A. and Aboul-Enein, H.; "The kinetics of steel dissolution in the presence of some thiouracil derivatives", Corros. Prev. Cont., Vol. 42, pp. 13, 1995.

[10] Oguzie, E.E.; "Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract", Corros. Sci., Vol. 49, pp. 1527, 2007.

[11] Kliskic, M., Radosevic, J., Gudic, S. and Katalinik, V.; "Aqueous extract of Rosmarinus officinalis L. as inhibitor of Al-Mg alloy corrosion in chloride solution", J. Appl. Electrochem., Vol. 30, pp. 823, 2000.

[12] Yurt, A., Ulutas, S. and Dal, H.; "Electrochemical and theoretical investigation on the corrosion of aluminium in acidic solution containing some Schiff bases", Appl. Surf. Sci., Vol. 253, pp. 919, 2006.

[13] Abd E L-Maksoud, S.A. and Fouda, A.S.,"Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium", Mater. Chem. Phys., Vol. 93, pp.84, 2005.

[14] Abiiola, O.K. and Oforka, N.C.; "Studies on the inhibition of mild steel corrosion by 1-phenyl-3-methylpyrazol-5-one in hydrochloric acid (HCl) solution", Corros. Sci. & Eng., Vol. 3, pp. 21, 2002.

[15] Ebenso, E.E.;" Inhibition of acid corrosion of mild steel by Telfaria occidentalis", Nig. Corros. J., Vol. 1(1), pp. 29, 1998).

[16] Damaskin, B.B.; "Adsorption of organic compounds on electrodes", Plenum press, N.Y., pp. 221, 1971.

[17] Ebenso, E.E.; "AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives", Mater. Chem. Phys., Vol. 79, pp. 58, 2003.

[18] Gomma, G.K. and Wahdan, M.H.; "New telechelic compounds as corrosion inhibitors for steel in 1M HCl", Mater. Chem. Phys., Vol. 30, pp. 209, 1995.

[19] Marsh, J.; "Advanced Organic Chemistry" 3rd ed., Wiley Eastern New Delhi, 1988.

[20] Soliman, M.S.; "The use of rotating cylinder electrode to study the effect of 1,3-dihydroxypropane on copper electrorefining ", Ph. D. Thesis, Alex. Univ., Egypt, 1995.