CORROSION INHIBITION OF Cu- Fe ALLOYS IN HCl SOLUTIONS BY AMPHOTERIC SURFACTANTS

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Submitted on July 2006 and accepted on December 2006

ABSTRACT

Amphoteric surfactants were tested as corrosion inhibitors for the Cu-Fe alloy corrosion in 1M HCl solutions. Weight – loss, electrochemical polarization, impedance measurements and atomic absorption spectroscopy were the techniques used. The surfactants were alkyl-N- (amino ethylene) – β – aspartamates of molecular formula:

H_2 N-$(CH_2)_2$ – HN-CH –COOH, (R=C_{10} – C_{14}).
|
CH_2 CONH-R

These surfactants behave as mixed – type inhibitors, i.e. they affect both the cathodic and anodic reactions without changing their mechanisms. The inhibition action of these surfactants may take place through blocking and hydrophobic effects. The inhibition effect increases with the increase of the alkyl group (-R) length. These surfactants were adsorbed in the alloy surface according to the Frumkin isotherm model. The presences of these surfactants in the aggressive media contribute to increases the values of the apparent activation energy.

Also, these surfactants refer the preferential dissolution of iron from the alloy.

Key words: *Cu- Fe Alloy, Inhibitors, Galvanostatic Polarization, Frumkin Isotherm, Amphoteric Surfactants*

INIBIÇÃO DA CORROSÃO DE LIGAS Cu-Fe EM SOLUÇÕES DE HCl ATRAVÉS DE SURFACTANTES ANFOTÉRICOS

RESUMO

Surfactantes anforéticos foram testados como inibidores de corrosão em ligas de Cu-Fe em soluções de 1M HCl. As técnicas usadas foram perda de peso, polarização electroquímica, medidas de impedância e espectroscopia de absorção atómica. Os surfactantes usados foram os β-aspartamatos de N-alquil-(amino etileno) de fórmula molecular:

H_2N-$(CH_2)_2$ – HN-CH –COOH, (R=C_{10} – C_{14}).
|
CH_2 CONH-R

Estes surfactantes comportam-se como inibidores tipo “hibrídos”, isto é, afectam as reacções catódicas e anódicas sem alterar os seus mecanismos. A acção inibidora destes surfactantes pode ocorrer por efeito hidrofóbico e de bloqueamento. O efeito inibidor aumenta com o aumento do comprimento do grupo alquídico (-R). Estes surfactantes serão adsorvidos na superfície da liga de acordo com o modelo isotérmico de Frumkin. A presença destes surfactantes em meio agressivo contribui para o aumento da energia de activação aparente. Ainda, estes surfactantes referem a dissolução preferencial do ferro da liga.

Palavras chave: *Liga Cu- Fe, Inibidores, Polarização Galvanostática, Isotérmica de Frumkin, Surfatantes Anfotéricos*

1. INTRODUÇÃO

Copper and its alloys have a long history of use in marine applications and continue to be widely used for many purposes despite the emergence in recent years of other materials that have technical or economic attraction [1]. These related to their corrosion resistance, mechanical workability, excellent electrical and thermal conductivies and resistance to microfouling [2] .

Copper alloys have gained increasing importance for applications sea water environments such as heat exchangers of power plants. Scale and corrosion products cause a decrease in the heating efficiency of the equipment, which is why periodic descaling and cleaning in acid-pickling solutions are necessary. In order to reduce the corrosion of the copper alloys during such Surface treatments, a corrosion inhibitor is typically added.

The corrosion resistance of copper alloys has been attributed to the formation of a protective films of cuprous oxide (Cu_2O) and to the doping of Cu_2O layer with ions such as iron [3-4]. This doping reduces the ionic or electronic conductivity of the film, improving the corrosion resistance.

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Since corrosion is one of the main concerns in the durability of materials and structures, many studies have been carried out to develop an effective means of corrosion control to prolong service life of existing structures and minimize corrosion damage in new structures. Even though corrosion inhibitors are the most effective and flexible means of corrosion control. The selection of an appropriate inhibitor for a particular system is actually complicated due to specificity of inhibitors and great variety of corrosion – related applications. In order to improve corrosion protection of copper and copper alloys, numerous advanced treatments, including organic inhibitors have been proposed. These corrosion inhibitors are heterocyclic organic compounds containing nitrogen, sulphur / or oxygen [5-12].

Hydrochloric acid has found wide applications in many fields, such as oil well acidizing, acid pickling, industrial acid cleaning, removal of oxide from metallic parts before applying coating, etc. The highly corrosive nature of this acid necessitates good corrosion control to preserve resources, reduce maintenance work and to ensure long service life. Of the various types of organic compounds available, some surface – active agents (surfactants) show good inhibition characteristics towards a number of metals, especially mild steel [13]. For this reason the present work aims to study the use of surfactants as corrosion inhibitors for the corrosion of copper – iron alloy in 1M HCl solutions. In this investigation the techniques used were: (i) weight loss, (ii) galvanostatic, (iii) linear polarization, (iv) electrochemical impedance spectroscopy (EIS) and (v) atomic absorption spectroscopy.

2. EXPERIMENTAL

The investigated copper-iron alloy (70% Cu – 30% Fe) was prepared in non- ferrous laboratory at (MRDI), Egypt. The materials were melted using crucible furnace at temperature range 1100-1550 °C, and then casted into cylindrical rods 10 cm length and 1 cm diameter and also into sheets of thickness 0.4 cm in steel moulds. For the electrochemical measurements the electrodes were prepared from the casted rods. A Stout copper wire lead was fixed at one end of the cylindrical electrode by mechanical jamming. The electrode was then fitted into a Pyrex glass tubing of appropriate internal diameter and fixed with araldite (exposed area = 2 $cm^{2)}$. For weight loss measurements specimens of dimensions 3 x 2 x 0.4 cm were cut from the casted sheets (the exposed area = 10 cm^2). Just before being used the electrodes and specimens were abraded with emery papers of different grades. The abraded electrodes and specimens were then washed thoroughly with running distilled water and then degreased by acetone.

The surface – active agents (SAA) used as inhibitors in this study have the following structures:

$$H_2N - (CH_2)_2 - HN\text{-}\ CH\text{-}\ COOH$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad CH_2\ CONH\text{-}R$$

where – R = $C_{10}\ H_{21}$(I), $CH_{11}\ H_{23}$(II), $C_{12}\ H_{25}$(III), $C_{13}H_{27}$ (IV), $C_{14}\ H_{29}$ (V).

These surfactants are liquids with density values of: 1.10, 1.16, 1.20, 1.27, and 1.32 g cm^{-3} for the compounds I, II, III, IV and V, respectively. The molecular mass of these surfactants are: 280 294, 308, 322 and 336 for compounds I to V, are respectively. These surfactants are alkyl –N- (amino – ethylene) -β-aspartamates and were prepared by nucleophilic addition of ethylene – diamine to N – alkylmaleamic acid in presence of triethyl amine as a catalyst [13].

In electrochemical measurements, the current was derived from a constant current unit (LG precision Co. Ltd, Korea). The current and potential were measured by digital multimeters (model 1008 Kyoritsu, Japan). The potential was measured *versus* a saturated calomel electrode (SCE).

The impedance measurements were carried out using impedance measurement system (1M6 Zahner electrik Mebtechnik, Germany) The atomic absorption measurements are carried out using a flame – atomic absorption spectrophotometer (Perkin – Elmer Apparatus Model 23, Germany).

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

The values of inhibition efficiency, I%, are calculated from the corrosion rate R_w by using the equation:

$$I\% = \left[1 - \frac{(R_w)_{inh}}{(R_w)_{free}}\right] \times 100 \qquad (1)$$

where $(R_w)_{free}$ and $(R_w)_{inh}$ are the corrosion rates in absence and in presence of inhibitor, respectively.

Figure 1 represents the variation of the inhibition efficiency, I %, as a function of the concentration of the investigated surfactants (I-V). The inhibition efficiency increases with the increase of inhibitor concentration reaching a limiting value.

The results in figure 1 indicate that the investigated surfactants have high inhibiting action on the corrosion of the alloy in HCl solution. The inhibition efficiency, I%, of these surfactants increases following the order: I < II < III < IV < V.

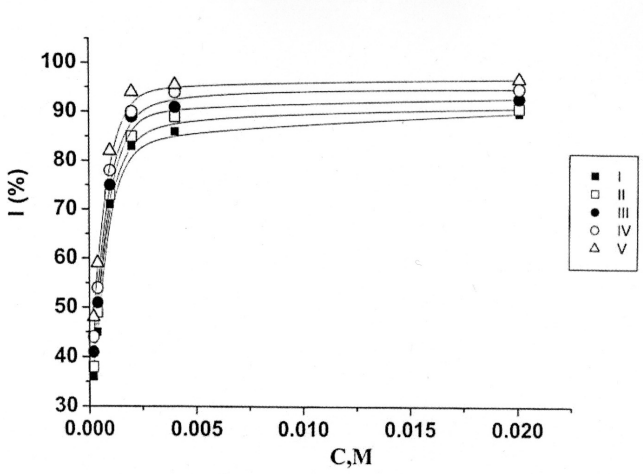


Fig. 1 – Inhibition efficiency, I %, of surfactants I to V as a function of their concentration.

3.2 Linear polarization measurements

Figure 2 represents the plot of the overpotential, ΔE, *versus* the current density, i, for the working electrode in 1M HCl solution in absence and in presence of different concentrations of compound (I), at temperature of 20 °C. Similar plots were obtained for the other surfactants, (II, III, IV, V), but not shown. The values of linear polarization resistance were evaluated from the slopes (ΔE/Δi) of the straight lines of figure 2 and similar ones and listed in table 1 . The values of the inhibition efficiency, I%, were calculated from R_p by using the following equation:

$$I\% = \left[1 - \frac{(R_p)_{free}}{(R_p)_{inh}}\right] \times 100 \qquad (2)$$

where $(R_p)_{free}$ and $(R_p)_{inh}$, are the linear polarization resistances in 1M HCl solution in absence and in presence of inhibitor, respectively. The values of I% are listed in table 1 for the different concentrations of the investigated surfactants (I-V). The results indicate that the inhibition efficiency of these surfactants is high and increases according to the order: I< II< III< IV< V. This order is the same as that obtained from the weight loss measurements.

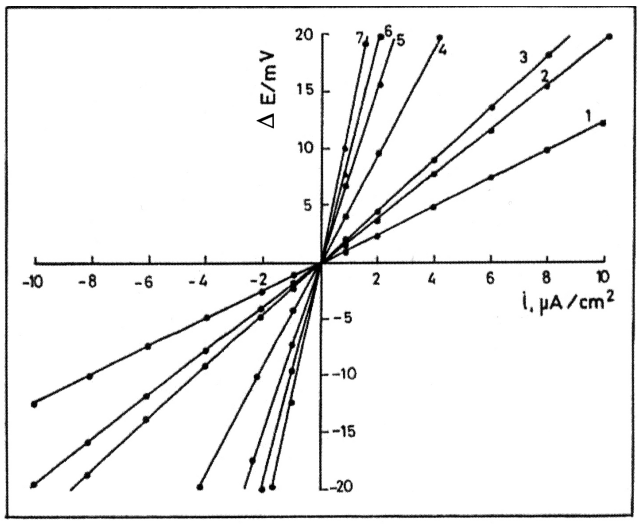


Fig. 2 – Potential – current plots for the alloy in 1M HCl in absence and in presence of different concentration of surfactant I, at 20 ºC: 1 – blank, 2 – $2x10^{-4}$, 3 – $4x10^{-4}$, 4 – $1x10^{-3}$, 5 – $2x10^{-3}$, 6 – $4x10^{-3}$, 7 – $1x10^{-2}$M.

3.3. Galvanostatic polarization measurements

Figure 3 represents the galvanostatic cathodic and anodic polarization of the working electrode (Cu- Fe alloy) in 1M HCl solution in absence and in presence of different concentrations of compound (I) at temperature of 20 °C. Similar polarization curves were obtained for the other compounds, but not shown. The corrosion potentials, E_{corr}, and corrosion current densities, I_{corr} for the working electrode immersed in 1M HCl in absence and in presence of inhibitors were determined by extrapolation of Tafel's lines of the corresponding cathodic and anodic polarization curves of Figure 3 and similar ones. The obtained values of I_{corr} are listed in table 2 for the investigated surfactants (I-V). The values of inhibition efficiency, I % were calculated from I_{corr} values by using the following equation.

$$I\% = \left[1 - \frac{(I_{corr})_{inh}}{(I_{corr})_{free}}\right] \times 100 \qquad (3)$$

where $(I_{corr})_{free}$ and $(I_{corr})_{inh}$, are the corrosion current densities in absence and in presence of inhibitor, respectively. The calculated values of I% are listed in table 2 for the different concentrations of the investigated surfactants. Also, the values of the cathodic Tafel's slopes, b_c and the anodic Tafel's slopes, b_a, deduced from the corresponding Tafel's lines of the polarization curves of Fig.3 and similar ones. It was found that $b_c \cong 118$mV/decade and $b_a \cong 40$ mV/ decade.

The results of Figure 3 and similar ones and table 2 indicate that the investigated surfactants present high inhibition effect on the corrosion of the working electrode in HCl solutions. The inhibition efficiency, I%, of these surfactants increases following the order: I<II<III<IV<V. This order is the same as that obtained from the weight loss and linear polarization measurements. Also, the presence of the investigated surfactants in the corrosive solution affects both the cathodic and anodic polarization curves, where both the cathodic and anodic polarization of the working electrode increase with increasing concentration of the surfactants. This means that these compounds behave as mixed inhibitors. The values of E_{corr} are slightly shifted to more positive values in the presence of increasing concentration of the inhibitors.

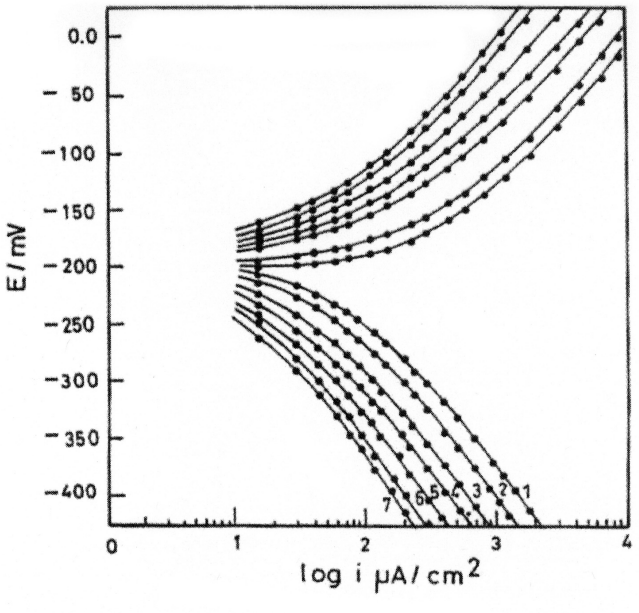


Fig. 3 – Cathodic and anodic polarization curves for the alloy in 1M HCl in absence and in presence of different concentration of surfactant I, at 20 ºC: 1 – blank, 2 – $2x10^{-4}$, 3 – $4x10^{-4}$, 4 – $1x10^{-3}$, 5 – $2x10^{-3}$, 6 – $4x10^{-3}$, 7 – $1x10^{-2}$M.

Table 1

Data from linear polarization measurements for the alloy in 1M HCl in a bsence and in presence of different concentrations of surfactants at 20 °C

Concentration (M)	I		II		III		IV		V	
	R_p Ω cm^{-2}	I %	R_p Ω cm^{-2}	I %	R_p Ω cm^{-2}	I %	R_p Ω cm^{-2}	I %	R_p Ω cm^{-2}	I %
0.000	1260.00	–	1260.00	–	1260.00	–	1260.00	–	1260.00	–
2 x 10^{-4}	2000.00	37	2065.60	39	2172.40	42	2333.33	46	2470.59	49
4 x 10^{-4}	2333.33	46	2520.00	50	2625.00	52	2800.00	55	3150.00	60
1 x 10^{-3}	4500.00	72	4846.15	74	5250.00	76	6000.00	79	7411.76	83
2 x 10^{-3}	7875.00	84	9000.00	86	12600.0	90	14000.0	91	25200.0	95
4 x 10^{-3}	9692.30	87	12600.0	90	15750.0	92	25200.0	95	42000.0	97
1 x 10^{-2}	12600.00	90	16800.0	92.5	22909.1	94.5	31500.0	96	126000	99

Table 2

Data from galvanostatic polarization measurements for the alloy in 1M HCl in absence and in presence of different concentrations of surfactants at 20 °C

Concentration (M)	I		II		III		IV		V	
	i_{corr} μ A cm^{-2}	I %	i_{corr} μ A cm^{-2}	I %	i_{corr} μ A cm^{-2}	I %	i_{corr} μ A cm^{-2}	I %	i_{corr} μ A cm^{-2}	I %
0.000	60.0	–	60.0	–	60.0	–	60.0	–	60.00	–
2 x 10^{-4}	37.5	37.5	36.3	39.5	34.5	42.5	33.3	44.5	31.5	47.5
4 x 10^{-4}	31.8	47.0	30.0	50.0	28.2	53.0	27.6	54.0	24.9	58.5
1 x 10^{-3}	16.5	72.5	15.3	74.5	14.1	76.5	12.0	80.0	10.8	82.0
2 x 10^{-3}	9.30	84.5	8.10	86.5	6.00	90.0	5.10	91.5	3.30	94.5
4 x 10^{-3}	9.50	87.5	6.00	90.0	4.80	92.0	3.30	94.5	2.40	96.0
1 x 10^{-2}	6.00	90.0	4.80	92.0	3.60	94.0	2.40	96.0	1.50	97.5

3.4 Impedance measurements

In principle, the method involves direct measurements of impedance of the electrochemical system in frequency domain 0.1 to 10^5 Hz and peak to peak AC amplitude of 5 mV. These experiments are carried out at steady state under open – circuit conditions.

Figures 4-8 represent the impedance diagrams (Nyquist plots) for the working electrode immersed in the corrosive solution in absence and in presence of increasing concentration of the investigated surfactants (I-V), respectively, at temperature of 20 °C. These impedance diagrams are not perfect semicircles which have been attributed to frequency dispersion [14-15]. The charge transfer resistances (R_t) were calculated from the difference in impedance at lower and higher frequencies, as suggested previously[16]. These R_t values have then been subtitled in the Stern – Geary equation:

$$I_{corr} = \frac{b_a b_c}{2.3(b_a + b_c)} \cdot \frac{1}{R_t} \qquad (4)$$

to obtain corrosion current density values, where b_a and b_c and the anodic and cathodic Tafel's slopes, respectively. The double layer capacitance, C_{dl}, was determined from the frequency, f, at which z_i was maximum, using the relationship:

$$f\,(-Z_{i,\,max}) = (2\pi\ C_{dl}\,R_t)^{-1} \qquad (5)$$

R_t and C_{dl} derived from the impedance measurements for the alloy are shown in table 3 as functions of concentrations of surfactants (I – V), respectively. The charge transfer resistance, R_t, which appeared to control the overall corrosion process, showed an increase with increasing inhibitor concentration. However, the double layer capacity decreased as inhibitor concentration increased.

The double layer between a charged metal surface and a solution behaves as an electrical capacitor and it is generally assumed that acid corrosion inhibitors adsorb on metal surface resulting in a structural change of the double layer and in a reduced rate of the electrochemical partial reaction.

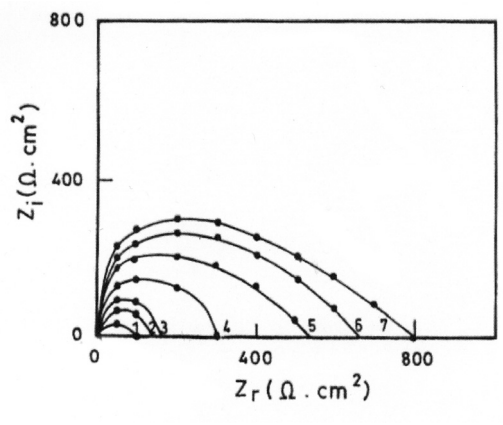


Fig. 4 – Nyquist plots for alloy in 1M HCl in absence and in presence of different concentration of surfactant I, at temperature of 20 °C: 1 – blank, 2 – 2 x 10^{-4} , 3 – 4 x 10^{-4}, 4 – 1 x 10^{-3}, 5 – 2 x 10^{-3} , 6 – 4 x 10^{-3} , 7 – 1 x10^{-2} M.

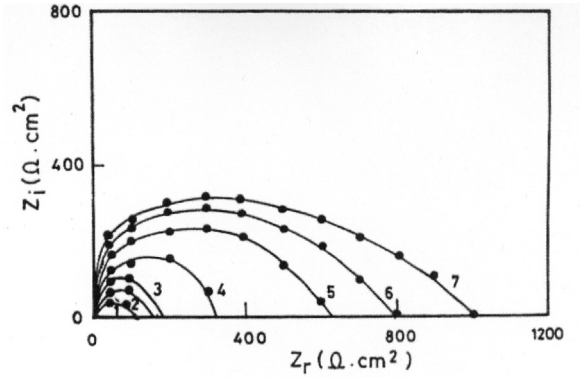


Fig. 5 – Nyquist plots for alloy in 1M HCl in absence and in presence of different concentration of surfactant II, at temperature of 20 °C: 1 – blank, 2 – 2 x 10^{-4}, 3 – 4 x 10^{-4}, 4 – 1 x 10^{-3} ,5 – 2 x 10^{-3}, 6 – 4 x 10^{-3}, 7 – 1 x10^{-2} M.

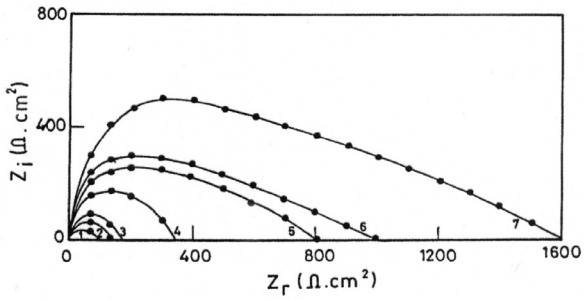


Fig. 6 – Nyquist plots in 1M HCl in absence and in presence of different concentration of surfactant III, at 20 ºC: I – blank, 2 – 2x10^{-4}, 3 – 4x10^{-4}, 4 – 1x10^{-3}, 5 – 2x10^{-3}, 6 – 4x10^{-3}, 7 – 1x10^{-2}M.

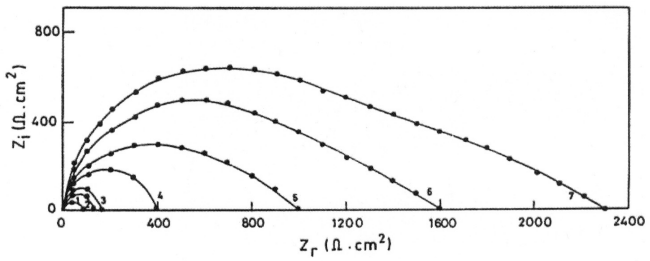


Fig. 7 – Nyquist plots in 1M HCl in absence and in presence of different concentration of surfactant IV, at 20 ºC: I – blank, 2 – 2x10^{-4}, 3 – 4x10^{-4}, 4 – 1x10^{-3}, 5 – 2x10^{-3}, 6 – 4x10^{-3}, 7 – 1x10^{-2}M.

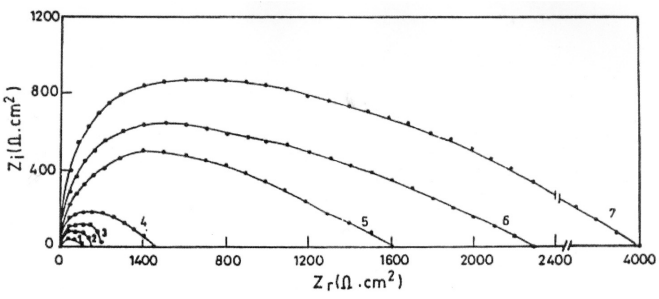


Fig. 8 – Nyquist plots in 1M HCl in absence and in presence of different concentration of surfactant V, at 20 ºC: I – blank, 2 – 2x10^{-4}, 3 – 4x10^{-4}, 4 – 1x10^{-3}, 5 – 2x10^{-3}, 6 – 4x10^{-3}, 7 – 1x10^{-2}M.

Table 3

Data from impedance measurements for the alloy in 1M HCl in absence and in presence of differente concentration of the surfactants under study, at 20 ºC

Concentration (M)	I (%)				
	Surfactant (I)	Surfactant (II)	Surfactant (III)	Surfactant (IV)	Surfactant (V)
0.000	–	–	–	–	–
2 x 10^{-4}	38	40	42	45.0	48.0
4 x 10^{-4}	47	50	53	55.0	59.0
1 x 10^{-3}	73	75	77	80.0	82.5
2 x 10^{-3}	85	87	90	92.0	95.0
4 x 10^{-3}	88	90	92	95.0	96.5
1 x 10^{-2}	90	92	95	96.5	98.0

The inhibition efficiency, I%, of Cu - Fe alloy was calculated from the charge transfer resistance, R_t, using the following equation:

$$I\% = \frac{R_{tcorr}^{-1} - R_{tcorr(inh)}^{-1}}{R_{tcorr}^{-1}} \times 100 \quad (6)$$

where R_{tcorr} and $R_{tcorr(inh)}$ are the charge transfer resistance values in absence and in presence of inhibitor respectively. The values of I% calculated from this investigation are listed in table 3 for the surfactants (I- V), respectively. It is clear from these results that, the inhibition efficiency, I%, of the surfactants increases following the order: I<II<III<IV< V. This order is the same as that obtained from weight loss, linear polarization and galvanostatic polarization measurements.

It can be proposed that the corrosion behavior of the investigated alloy (Cu- Fe) in HCl solution is similar to that of brass (Cu – Zn) , where the preferential dissolution of Fe occurs with simultaneous dissolution of Cu. The dissolution of Fe in HCl may occur according to the reaction:

$$Fe + 2\,HCl \rightarrow FeCl_2 + H_2 \quad (7)$$

The dissolution reaction of copper lead to the formation of Cu^+ ions which either form soluble complexes or precipitate, depending on their surface concentration [17].

$$Cu \rightarrow Cu^+ + e \quad (8)$$

$$Cu^+ + 2\,Cl^- \rightarrow CuCl_2^- \quad (9)$$

$$Cu^+ + 3\,Cl^- \rightarrow CuCl_3^{2-} \quad (10)$$

Air may oxidize Cu^+ to Cu^{2+}. When enough amount of Cu^{2+} accumulates in solution, the dissolution of copper is auto – catalyzed through the reaction [18].

$$Cu + Cu^{2+} \rightarrow 2\,Cu^+ \quad (11)$$

The relation between the surface coverage ($\theta = \frac{I\%}{100}$) and logarithim of the molar concentration of the inhibitors (C), shown in figure 9, had the characteristic S-shaped adsorption isotherm. This result showed that the investigated surfactants were adsorbed on the alloy surface according to the Frumkin isotherm [19].

$$\theta\,(1-\theta)^{-1} \exp(-fC) = kC \quad (12)$$

where k is the equilibrium constant of the adsorption reaction, f is a function of adsorption energy and θ is the surface coverage.

In this system, the chloride ions and inhibitor molecules compete with each other for the adsorption onto the electrode surface. The amount of adsorbed chloride ions decrease with the increase of inhibitor concentration. For higher concentrations of inhibitor the adsorption of the activating species, Cl^-, can be excluded completely.

The compounds under investigation are organic compounds containing bases, which protonize in acidic media in a similar manner to other nitrogen containing organic compounds [20-24]. That is, they could exist as cations in equilibrium with the corresponding molecular form. The following reaction shows the protonization process of the surfactants in acidic media.

$$H_2N\text{-}(CH_2)_2 - HN\text{-}CH\text{-}COOH + 3H^+ \rightarrow {}^+H_3N\text{-}(CH_2)_2\ {}^+H_2N\text{-}CH - COOH \quad (13)$$

$$\qquad\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\quad |$$

$$\qquad\qquad\quad CH_2\ CONH - R\qquad\qquad\quad CH_2\ CO\ N_+H_2\text{-}R$$

It has been suggested that certain determination of the inhibiting properties of the compounds investigated can be expected if they act as cations.

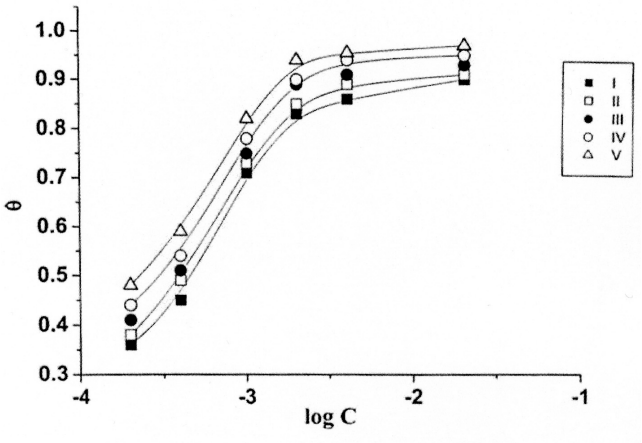


Fig. 9 – Frumkin adsorption isotherm for the surfactants (I-V) on the surface of alloy in 1M HCl at 20 ºC.

The effect of temperature on the corrosion behavior of Cu- Fe alloy in the absence and in presence of 0.05% of each surfactant was studied by weight loss measurements. Fig. (10) Shows Arrhenius plots for the corrosion rates R_w in pure 1M HCl and in presence of inhibitors. The apparent activation energies, E_a, could be determined form equation (15).

$$R_w = K \exp\left(\frac{-E_a}{RT}\right) \quad (14)$$

From the plots of figure 10 it was found that E_a = 21.6, 40, 48, 55, 60 and 70 KJ mol^{-1} in absence and in presence of surfactants I, II, III, IV and V, respectively. Results indicate that the corrosion rate of the alloy increases with the increase of temperature and the inhibition efficiency, I%, of surfactants decreases. Also, the addition of surfactants to the aggressive solution increases the activation energy to an extent, which is proportional to the inhibition efficiency of the inhibitor i.e. the order of increase of E_a is I<II<III<IV<V. This indicates that the corrosion of alloy occurs at uncovered part of the surface. The presence of inhibitor, which results in blocking the active sites on the alloy surface, must be associated with an increase in activation energy, E_a, of alloy.

Figure 11 represents the variation of, I%, as a function of the alkyl group length (-R) at different concentrations. These plots indicate that the inhibition efficiency increases with the length increase of the alkyl group (-R). This alkyl group has electron reapeling properties, which increase with the increase of the number of CH_2 groups in R. This state increases the electron density on the adsorption centers of the surfactant molecules.

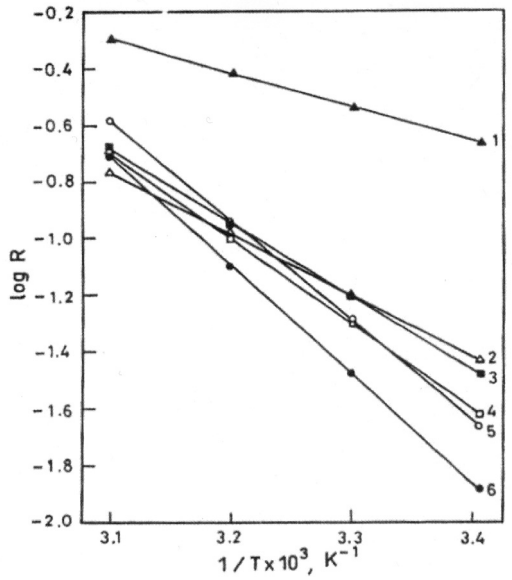


Fig. 10 – Arrhenius plots for the corrosion rates (Rw) of the alloy 1 – 1M HCl, 2 – (1M HCl + 2x10^{-3}M surfactant I), 3 – (1M HCl + 2x10^{-3}M surfactant II), 4 – (1M HCl + 2x10^{-3}M surfactant III), 5 – (1M HCl + 2x10^{-3}M surfactant IV), 6 – (1M HCl + 2x10^{-3}M surfactant V).

The inhibition of corrosion process by addition of surfactants may take place through blocking and hydrophobic effects. The former effect occurs when the metal surface becomes covered through the adsorption centers in the molecules (which are mainly N-atoms). This adsorption (physical or chemical) takes place on active sites on the electrode surface. The higher the concentration of adsorbed species, the more surface sites are blocked. The second effect of inhibitors is hydrophobing the interface by surfactants to inhibit charge and mass transfer. Surfactants have a characteristic structure, consisting of a structural group that has very little attraction for the solvent, known as a hydrophobic group, together with a polar head. When the surfactant is dissolved in water, the presence of the hydrophobic group in the interior of the solvent causes a distortion of the solvent liquid structure, increasing the free energy of the system. As comprise, the surfactant concentrates at the interface because the thermodynamically best arrangement is possible. At the metal solution interface the surfactant molecules orientate their polar heads towards the metal and are adsorbed on its surface. The hydrophobic part is oriented away into the solution, repelling the solvent molecules. Under such conditions a diffusion barrier to chemical and / or electrochemical attack of the solution on the metal surface is established. It is worthy mentioned that the hydrophobic interaction increases with R length increase, state of which increases the inhibition efficiency of the surfactant.

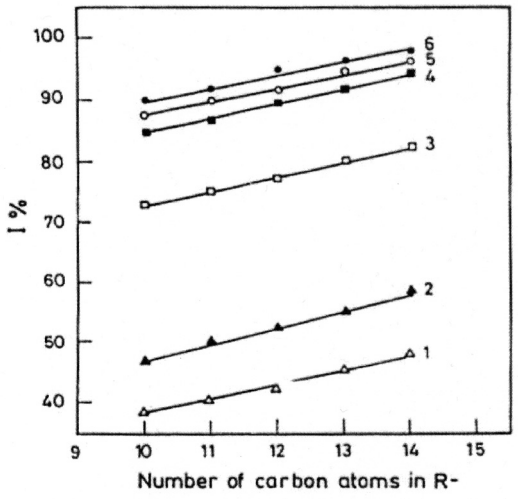


Fig. 11 – Variation of, I% with the number of carbon atoms in the alkyl group (-R) for the alloy, 1 – (1.0 M HCl + 2x10^{-4}M surfactant), 2 – (1.0 M HCl + 4x10^{-4} M surfactant), 3 – (1.0 M HCl + 1x10^{-4} M surfactant), 4 – (1.0 M HCl + 2x10^{-3} M surfactant), 5 – (1.0 M HCl + 4x10^{-3} M surfactant), 6 – (1.0 M HCl + 1x10^{-2} M surfactant).

According to Hajjaji *et al.* [22] the inhibiting effect increases with an increase of surfactant concentration, where the adsorption takes place by horizontal binding to hydrophobic region. This adsorption is a competitive one because the inhibitor displaces progressively the water molecules and other adsorbed ions when the surfactant concentration increases, a perpendicular adsorption takes place as a result of an inter – hydrophobic chain interaction [26]. DeBerry *et al.* [27] proposed hemimicellar coverage of the metallic surface over a wide inhibitor concentration, which plays a key role in the inhibition mechanism. At higher inhibitor concentrations, an efficiency plateau appears which corresponds to the formation of a bimolecular layer at the electrode solution interface. In this case the adsorption increases by the binding of the second layer of the surfactant through hydrophobic interactions.

Table 4
Results of atomic absorption analysis solution after exposure time of five hours in absence and in presence of 2 x 10^{-3} M of each of surfactants

Aggressive solution	*Fe*	*Cu*
	Wt. loss (mg)	*Wt. loss(mg)*
1.0 M HCl	8.8	2.2
1.0 M HCl + I	1.216	0.654
1.0 M HCl + II	1.04	0.61
1.0 M HCl + III	0.726	0.484
1.0 M HCl + IV	0.616	0.484
1.0 M HCl + V	0.3432	0.3168

The investigated surfactants also, retard the dissolution of iron and copper from the alloy in HCl solution. This was indicated by the results of atomic absorption analysis of the solution after an exposure of 5 hours in absence and in presence of $2x10^{-3}$ M of each surfactant, as shown in table 4.

4. CONCLUSIONS

From the results of the present investigation the following conclusions can be drawn:

1 – The corrosion of Cu-Fe alloy in HCl solution occurs on the account of the preferential dissolution of Fe with simultaneous dissolution of Cu.

2 – The investigated surfactants have shown high inhibiting effect on the corrosion of Cu-Fe alloy in 1M HCl.

3 – The inhibition efficiency of the surfactants depends on their concentration and molecular structure, where it increases with increase of concentration and with the increase of the length of the alkyl group (-R) of the surfactant.

4 – These surfactants acted as mixed – type inhibitors. The cathodic and anodic processes were affected by their presence in the aggressive media.

5 – The impedance measurements revealed the occurrence of adsorption of these surfactants onto the reactive sites on the metallic surface preventing supply of the aggressive ions to the surface and / or transport of reaction products away from the surface.

6 – The relation between the surface coverage, θ, and log C (molar concentration) had a characteristic S- shaped adsorption isotherm. This means that the adsorption obeys to the Frumkin's isotherm.

7 – The inhibition effect of these surfactants may take place by blocking the active sites on the electrode surface and by hydrophobic effects.

8 – In HCl solutions the protonization of the molecules of the surfactants may occur forming cations. These cations may adsorb electrostatically on the electrode surface.

9 – The inhibition efficiency decreases with increasing temperature.

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