INTRODUCTION

Many metals and alloys which used in different human activities are susceptible to different mechanisms of corrosion due to the their reaction chemically / electrochemically with corrosive medium to form a stable compound in which the loss of metal occurs. Among these, aluminium and tin are very important. Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular. Corrosion inhibitors are substances which when added in small concentrations to the corrosive media decrease or prevent the reaction of the metal with the media through retardation or completely stop the anodic or cathodic reactions or both.

Many studies revealed that organic or inorganic compounds specially those containing N, S and O showed significant inhibition efficiency. These studies reported that a number of these compounds successfully used as inhibitors for the corrosion of aluminium\(^1\)\(^{-11}\) and tin\(^12\)\(^{-17}\) in acidic solutions. But unfortunately most of these compounds are not only expensive but also toxic to living beings. However, plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors for corrosion of different metals and alloys.

The present work aims to find a naturally occurring cheap and environmentally safe substances that could be used for inhibiting the corrosion of aluminium and tin metals in acidic solutions. The use of such substances will establish simultaneously the economic and environmental goals. These compounds named carrageenans which are linear polymers of about 25000 glucose derivatives with regular and imprecise structure dependent on the source and extraction conditions. Three carrageenans were used in the present work; k-carrageenan, i-carrageenan and \(\lambda\)-carrageenan. Weight loss and thermometric techniques were used in this work for evaluation the inhibition efficiency of these compounds.

ABSTRACT

Some natural polymers (carrageenans) were tested as corrosion inhibitors for pure aluminium and pure tin in hydrochloric and nitric acid solutions, respectively, using the weight loss and thermometric techniques. It was found that the investigated compounds exhibited a very good performance as inhibitors for corrosion of these metals in all tested media. The degree of inhibition depends on the nature of the metal, nature of the inhibitor and type of the medium. The inhibition efficiency increases with increasing the concentration of the inhibitor in the order: \(k\)-carrageenan < \(i\)-carrageenan < \(\lambda\)-carrageenan. The inhibitive action of these natural polymers was discussed in view of adsorption of the molecules on the metal surface. This adsorption was found to follow Temkin adsorption isotherm in all tested media. Also, effect of temperature on the corrosion parameters was studied and discussed. Molecular orbital treatment was done to rationalize the electronic structure and the ground state properties of the studied carrageenan compounds.

Key words: Aluminium, tin, corrosion, weight loss, thermometry, carrageenan.
EXPERIMENTAL

Pure aluminium foil (99.999%) from Aldrich of 1.0 mm thick with an exposed area of 2cm$^2$ was used in weight loss measurements whereas in thermometric measurements aluminium pieces measuring 1×5 cm were cut from the specimen used. Also, pure tin foil (99.999%) of 1.0mm thick, BDH chemicals not containing more than 0.0025% arsenic was cut also to pieces measuring 2×2cm and 1×5cm for weight loss and thermometric measurements, respectively. All chemical used for preparing the test solutions were of analytical grade and the experiments were carried out at room temperature, 30±1°C.

Carrageenan compounds

Carrageenans are linear polymers of about 25000 galactose derivatives with regular but imprecise structures, dependent on the source and extraction conditions. Three carrageenans are used in the present work; k-carrageenan, i-carrageenan and k-carrageenan. The structural unit of these carrageenans are as follows:

Weight loss measurements

The reaction vessel used was graduate glass vessel having a total volume of 250ml. 10ml of the test solution were employed in each experiment. The test pieces of metal sheet (aluminium or tin) of 2×2cm were first polish with a fine grade emery paper in order to obtain a smooth surface then rinsed with double-distilled water, dried between two filter papers and weighed. The test pieces were suspended by suitable glass hooks and kept under the test solution by about 1cm. After specified period of time each piece was taken out of the test solution, rinsed with double-distilled water, dried carefully as before and weighed using a Metler balance. Each experiment was repeated three times and the average weight loss at certain time was taken in mg/cm$^2$. The rate of corrosion and the inhibition efficiency were determined after 5 minutes from the start up to 20 minutes for aluminium and 30 minutes for tin. The measurements were taken at time interal of 5 minutes. For each measurement, the sample is withdrawed from the acid bath, dried carefully and weighed.

Thermometric measurements

The reaction vessel used in these measurements was described by Mylius.$^{18}$ The test piece of metal sheet (aluminium or tin) of 1×5cm was treated as before (weight loss measurements), then immersed in the test solution. The reaction vessel was immersed in a Dewar’s flask in order to minimize heat loss by radiation. The initial temperature was 30±0.2°C. The variation in temperature of the system was measured by using a thermometer, the lower end of which was fixed in a position at the middle of the sample. Each experimental was carried out with 15ml of the test solution using a new piece of metal.

The test solution in both cases (aluminium or tin) was the free acid solution (HCl or HNO$_3$) or the acid containing the additives (carrageenans). The latter solutions was prepared by mixing the appropriate volume of both the acid and the additive stock solutions then diluting with double-distilled water to obtain the required concentrations of the additives.

Microscopic examination

The microscopic examination of the metal surface has been carried out using a Meteological microscope model ZEISS KS300.
RESULTS AND DISCUSSION

Weight loss measurements

Aluminium

The corrosion of pure aluminium in hydrochloric acid solutions of different concentrations using weight loss method indicated that a molarity of 2M of the acid is the optimum for carrying out all corrosion tests in this study. Weight loss in mg was determined in an open system at various time intervals in absence and in presence of different concentrations of the used inhibitors (carrageenans). The weight loss-time curves denoted that 2M hydrochloric acid solution is characterized by an initial slow rate in weight loss due to the formed surface oxide film that is less soluble in the acid solution followed by a sharp rise Fig.1. Three natural polymers (I, II, III) were used as inhibitors; k-carrageenan, \( \lambda \)-carrageenan and \( \kappa \)-carrageenan which differ in the number of hydroxyl and sulphate groups within the polymer molecule. The data of weight loss are given in Table 1 and represented graphically in Fig. 1 for k-carrageenan as a typical example of these compounds. The corrosion rate \( r \) was found to be dependent on the nature and concentration of the inhibitor. The corrosion rate was determined using the relation\(^{19}\).

\[
\text{corrosion rate} = \frac{\text{weight loss (mg)}}{\text{electrode surface area (dm}^2\text{)} \times \text{time (day)}}
\]

The data given in Table 1 revealed that the corrosion rate decreases with increasing the concentration of the inhibitor. The decrease in corrosion rate follows the order:

\[ \text{III} > \text{II} > \text{I} \]

The inhibition efficiency (IE) is calculated using the relation

\[
\text{inhibition efficiency} = \frac{\text{weight loss}_{(\text{pass})} - \text{weight loss}_{(\text{inh.})}}{\text{weight loss}_{(\text{pass})}} \times 100
\]

The data given in Table 1 denoted that the IE increases with increasing the concentration of the additives. The increase in IE follows the order

\[ \text{III} > \text{II} > \text{I} \]

It was found that at higher concentration of the inhibitor (5×10\(^{-3}\)M), the time has less effect on the IE. This may be due to that in such solutions the inhibitor is sufficient to cover completely the metal surface and the rate of adsorption becomes slower comparing with that obtained at lower concentration of the additive. The plots of IE vs. log C of the carrageenan compounds have the character of S-shaped adsorption. Hence, one could expect a saturation point of adsorption at a critical concentration of the inhibitor above which the extent of adsorption is essentially independent of inhibitor concentration.

The degree of surface coverage (\( \theta \)) which represents the part of metal surface covered by inhibitor molecules was calculated using the relation\(^{20}\)

\[
\theta = 1 - \frac{\text{weight loss}_{(\text{inh.})}}{\text{weight loss}_{(\text{free})}}
\]

| [C], M  | \( r, \text{mg/dm}^2\text{d} \) | IE% | \( \theta \) |
|---------|-----------------|-----|-----|
| Compound I |     |     |     |     |
| 0.00    | 199.17          | 0.000 | 0.0000 |
| 5.0\times10^{-6} | 45.81          | 77.00 | 0.7700 |
| 2.5\times10^{-5} | 34.20          | 82.83 | 0.8283 |
| 5.0\times10^{-5} | 20.97          | 89.47 | 0.8947 |
| 5.0\times10^{-4} | 10.08          | 94.93 | 0.9493 |
| 5.0\times10^{-3} | 6.03           | 96.97 | 0.9697 |
| Compound II |     |     |     |     |
| 0.00    | 199.17          | 0.00  | 0.0000 |
| 5.0\times10^{-6} | 34.65          | 82.60 | 0.8260 |
| 2.5\times10^{-5} | 24.75          | 87.57 | 0.8757 |
| 5.0\times10^{-5} | 15.30          | 92.32 | 0.9232 |
| 5.0\times10^{-4} | 6.93           | 96.52 | 0.9652 |
| 5.0\times10^{-3} | 4.77           | 97.61 | 0.9761 |
| Compound III |     |     |     |     |
| 0.00    | 199.17          | 0.000 | 0.0000 |
| 5.0\times10^{-6} | 14.85          | 92.54 | 0.9254 |
| 2.5\times10^{-5} | 11.97          | 93.99 | 0.9399 |
| 5.0\times10^{-5} | 7.65           | 96.16 | 0.9616 |
| 5.0\times10^{-4} | 5.40           | 97.23 | 0.9723 |
| 5.0\times10^{-3} | 2.88           | 98.55 | 0.9855 |

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The data given in Table 1 revealed that the degree of surface coverage ($\theta$) increases with increasing the concentration of the additives in the same order as the inhibition efficiency.

**Tin**

The corrosion of pure tin in nitric acid solutions of different concentrations indicated that 0.5M of the acid is the optimum for carrying out all corrosion tests. The experimental work was done as described before in case of aluminium metal. The rate of corrosion ($r$) was found to be dependent on the time, the type and the concentration of the inhibitor used. The corrosion rate was determined in pure nitric acid and in presence of different concentrations of inhibitors I, II, III using equation\(^{19}\). The data given in Table 2 and represented graphically in Fig.2 for k-carrageenan

![Graph showing effect of k-carrogeenan concentration on weight loss curves for aluminium in 2M HCl.](image1)

![Graph showing effect of k-carrageenan concentration on weight loss curves for tin in 0.5M HNO$_3$.](image2)
as an example of these compounds revealed that the corrosion rate (r) increases with increasing time and decreases on increasing the concentration of the inhibitor. Also, the inhibition efficiency (IE) was determined and the results indicated that IE increases on increasing the concentration of the inhibitor in the order:

\[ \text{III} > \text{II} > \text{I} \]

The plots of IE vs. log C of the additive have the character of S-shaped adsorption (not shown) as indicated before in case of aluminium metal. The degree of surface coverage (\(\theta\)) was also calculated using equation\(^2\). The results given in Table 2 revealed that \(\theta\) found to increase with increasing the concentration of the additives in the same order as the inhibition efficiency.

### Adsorption isotherms

In this study, attempts were made to fit the surface coverage (\(\theta\)) values to various isotherms, including Frumkin, Freundlich, Langmiur and TemKin. By far, the best fit for Al in HCl and tin in HNO\(_3\) was obtained with TemKin isotherm applying the equation\(^2\)

\[ \theta = \text{constant} + (2.303/f) \log C \]

The relation between \(\theta\) and log C for aluminium gave S-shaped curves (Fig.3) suggesting that TemKin adsorption isotherm is obeyed for the adsorption of carrageenan compounds (I, II, III) on the surface of Al. Similar curves (not shown) were obtained for tin revealing that TemKin isotherm is also obeyed for adsorption of carrageenans on tin surface.

### Thermometric measurements

#### Aluminium

In this method the changes in temperature of the system involving aluminium in HCl solutions or tin in HNO\(_3\) solutions were followed in absence and in presence of different concentrations of the inhibitors (I, II, III). As the concentration of the additive increases the time required to reach the maximum temperature \(T_m\) increases and the rate of temperature rise decreases. The extent of corrosion inhibition by a certain concentration of the additive is evaluated from the percentage reduction in reaction number (%RRN) given by the relation

\[ \% \text{RRN} = \frac{R.N_{\text{pure}} - R.N_{\text{inh.}}}{R.N_{\text{pure}}} \times 100 \]

The reaction number (R.N) is evaluated using the relation

\[ R.N = \frac{T_m - T_i}{t} \text{ °C/min} \]

where \(T_i\) is the initial temperature, \(T_m\) is the maximum temperature and \(t\) is the time in minutes from the start of the experiment till the attainment of maximum temperature.

Fig. 4 shows the thermometric curves of Al in 2M HCl devoid of and containing increasing additions of k-carrageenan (I) as a typical example of these compounds. Similar curves having the same
Fig. 3: Temkin adsorption isotherm of polymers I, II and III for aluminium in 2M HCl solution after 20 min.

Fig. 4: Variation of temperature with time at different concentrations of k-carrageenan for aluminium in 2M HCl solution.
features (not shown) were obtained for i-carrageenan (II) and \( \lambda \)-carrageenan (III). The features of all curves are the depression of \( T_m \), elongation of the time (t) necessary to reach \( T_m \), as the additive concentration is increased and diminution of the slope of the rising parts of the curves.

All these features are characteristics for strongly adsorbed the additives molecules on the anodic sites of the metal surface \(^{21,22} \). The results of R.N and %RRN are given in Table 3. These results denoted that the R.N decreases with increasing the concentration of the additives and consequently the %RRN increases. The decrease in R.N follows the order:

\[ \text{III} > \text{II} > \text{I} \]

Tin

Fig. 5 shows the thermometric curves of tin in 0.5M HNO\(_3\) in absence and in presence of different concentrations of the k-carrageenan. Similar curves having the same features (not shown) were obtained for i-carrageenan and \( \lambda \)-carrageenan. The feature of all curves are similar to those of aluminium in which \( T_m \) decreases on increasing the concentration of the additives. The results of R.N and %RRN are given in Table 3. The decrease in R.N and the increase in %RRN follows the same order as in case of aluminium.

**Thermodynamic studies**

Effect of temperature on the corrosion of aluminium in 2M HCl and tin in 0.5M HNO\(_3\) solutions in absence and in presence of 5×10\(^{-3}\)M of the three carrageenans (k-, i-, \( \lambda \)-) was studied at temperature 313, 323 and 333K using weight loss measurements. It was found that the weight loss and consequently the corrosion rate (r) increase on increasing the temperature in the free and inhibited acid solutions. The plots of \( \log r \) vs. \( 1/T \) using Arrheinus equation\(^{23} \) gave straight lines as represented in Fig. 6, for aluminium as a typical example.

\[ r = A \exp \left( -E_a / RT \right) \]

in which \( r \) is the corrosion rate and \( E_a \) is the apparent activation energy, \( T \) is the absolute temperature, \( R \) is the gas constant and \( A \) is the constant frequency factor. Similar plots (not shown) were obtained for tin in nitric acid solutions.
From the slopes of these plots, values of $E_a$ of corrosion of aluminium and tin in the free and inhibited acid solutions were calculated and given in Table 4. The results showed that $E_a$ decreases in presence of the compounds I, II and III comparing with the free acid solutions. This behavior indicates that these compounds acts as inhibitors for dissolution of the metals due to their adsorption on the metal-solution interface making a barrier of mass and charge transfer. The sequence of adsorption of these compounds on the metal surface according to the magnitude of activation energy increases in the order:

$$III > II > I$$

The activation thermodynamic parameters of the corrosion process such as the activation enthalpy change $\Delta H^*$, the activation free energy change $\Delta G^*$ and the activation entropy change $\Delta S^*$ were calculated in the free and inhibited acid solutions using the transition state theory relations $^{24}$

$$\Delta H^* = E_a - RT$$

$$\Delta G^* = RT \left( \ln K_T/h - \ln k \right)$$

where $K$ is the Boltzmann constant ($38 \times 10^{-23}$), $h$ is the Plank’s constant and $k$ is the specific rate constant, and the relation $^{24}$

$$\Delta S^* = (\Delta H^* - \Delta G^*) / T$$

The values of $\Delta H^*$, $\Delta G^*$ and $\Delta S^*$ for aluminium and tin in the free and inhibited acid solutions were calculated and represented in Table 4. The results of activation thermodynamic parameters revealed that $\Delta H^*$ decreases slightly with increasing temperature, whereas $\Delta G^*$ is increased. For a given temperature $\Delta H^*$ and $\Delta G^*$ increases on going from compound I to compound III. This means that the rate of dissolution reaction decreases in the same order. At the same time the negative sign and increase of $\Delta S^*$ values with increasing temperature denoting an increase of disorder accompanied the dissolution process. In presence of the inhibitors at a given temperature, the negative increase in $\Delta S^*$ on going from compound I to compound III revealed that the dissolution process decreases and consequently the disorder decrease in the same direction.

**Molecular orbital treatment**

The chemical and physical properties of the studied polymers were understood and rationalized through knowledge of their electronic structure and their ground state properties. The empirical method (AM1)(Austin Model 1) was used for such study$^{26}$. The dimmer form is considered as a simple model for these polymers. Some ground state properties of the best energetically structure
Table 4: Thermodynamic activation parameters of corrosion of Al in 2M HCl and tin in 0.5M HNO₃ solutions, containing 5.0×10⁻³ of carrageenan compound (I-III)

| Compound  | Temp. | Metal | Ea*(kJ) | ΔH*(kJ) | ΔG*(kJ) | ΔS*(kJ) |
|-----------|-------|-------|---------|---------|---------|---------|
| Free acid | 313   | Al    | 56.64   | 54.04   | 74.83   | -66.00  |
|           |       | Sn    | 37.51   | 34.91   | 75.09   | -128.37 |
|           | 323   | Al    | 53.96   | 74.24   | -63.00  |
|           |       | Sn    | 34.83   | 77.00   | -130.56 |
|           | 333   | Al    | 53.87   | 75.21   | -64.00  |
|           |       | Sn    | 34.74   | 77.76   | -129.19 |
| Inhib. I  | 313   | Al    | 89.86   | 67.26   | 75.33   | -26.00  |
|           |       | Sn    | 43.44   | 40.84   | 75.95   | -112.17 |
|           | 323   | Al    | 67.81   | 74.95   | -24     |
|           |       | Sn    | 40.76   | 77.01   | -112.23 |
|           | 333   | Al    | 67.09   | 76.18   | -27.00  |
|           |       | Sn    | 40.67   | 78.23   | -112.74 |
| Inhib. II | 313   | Al    | 88.61   | 86.01   | 76.94   | 29.00   |
|           |       | Sn    | 50.53   | 47.73   | 76.44   | -91.73  |
|           | 323   | Al    | 85.93   | 75.88   | 31.00   |
|           |       | Sn    | 47.65   | 77.65   | -92.88  |
|           | 333   | Al    | 85.84   | 77.07   | 26.00   |
|           |       | Sn    | 47.56   | 78.67   | -93.42  |
| Inhib. III | 313  | Al    | 101.81  | 99.21   | 78.26   | 67.00   |
|           |       | Sn    | 55.50   | 52.90   | 77.41   | -78.31  |
|           | 323   | Al    | 99.31   | 76.61   | 70.00   |
|           |       | Sn    | 52.82   | 78.65   | -79.29  |
|           | 333   | Al    | 99.04   | 77.62   | 64.00   |
|           |       | Sn    | 52.73   | 78.67   | -79.91  |

Fig. 6: Arrhenius plots of the corrosion rate of aluminium in 2M HCl solutions in absence and in presence of inhibitors I, II and III.
of these polymers were calculated and collected in Table 5. The boat shape of pyran moiety was used through these calculations. It was found that the optimized forms of the three compounds have nearly the same bond length, bond angles and atomic charges. In case of compound II, the two sulphate groups have nearly opposite direction with respect to basic skeleton, while for compound III, the three sulphate groups have the same direction. Small differences of ground state properties of the three compounds except of dipole moments which depends mainly on the orientation of the substituents and their charge density can be explained through the weak interactions between different subsystems of each molecule due to existence of only single bonds and lack of conjugation and weak substituent interaction. Also, it is clear from the data given in Table (5) that a small difference between the $E_{\text{LUMO}}$, the $E_{\text{HOMO}}$ and $\Delta E_g$ for the three compounds. This small difference may be attributed to the negligible effect of the sulphate and hydroxyl groups on the geometry and thus the ground state properties and low accuracy of the Hamiltonian used in this calculation.

As expected, the adsorption properties of the carrageenans molecules takes place through the interaction of oxygen atoms of the sulphate with the surface metal atoms. The molecular orbital calculation showed that the atomic charges do not differ appreciably through the three compounds, thus the atomic charge does not play a significant role on adsorption process. However, it was found that the dipole moment values of the three carrageenan compounds Table 5 differ appreciably as a result of different orientations of the substituent sulphate groups and thus different interaction of their dipole victor. The dipole moment of these polymers was found to increase going from I to III. The results obtained from weight loss measurement were found to be in agreement with the result of the dipole moment calculations, i.e., the inhibition efficiency of these compounds increases on increasing the dipole moment in the order:

$$III > II > I$$

**Microscopic examination**

The morphology of the pure and corroded metals (Al and Sn) in free acids (HCl and HNO$_3$) and in presence of carrageenans inhibitors was studied in order to investigate the changes which appeared on the surface of corroded metals. The surface morphology of a specimen of pure tin prior to exposing to HNO$_3$ acid solution shows a lamellar form of a lustrous in order arrangement Fig.7a. Immersing this specimen in 0.5M HNO$_3$ acid solution for 30 minutes indicates the disappearance of the lamellar structure and exposed instead a corrosive tendency composed of pitting areas. That pitting was found to be composed of irregular circular structural distributed allover taken image Fig.7b.

When immersing the tin specimen in the same acid solution in presence of 5×10$^{-3}$M of inhibitor I, a much less change surface has been observed Fig.7c probably due to the formation of a protective film as a result of adsorption of the inhibitor molecules at the metal surface. The specimen exposes some patches of pitting corrosion that less bright comparing with that image taken in the absence of the inhibitor. The image obtained in presence of 5×10$^{-3}$M of inhibitor II Fig.7d showed a better protective film when compared with that showed in presence of inhibitor I. However, the image obtained after the treatment with 5×10$^{-3}$M of inhibitor III provided the best protection between all carrageenan family in the sense that the surface of tin was very smooth comparatively Fig.7e, i.e., the surface of this specimen exposes very small pitting pores with very small dimension confirming that inhibitor III provided the highest percentage inhibition.

**Table 5: Ground state properties calculated for the most stable conformer of the carrageenan compounds I-III using AM1 method**

| Compound | I (kJ) | II (kJ) | III (kJ) |
|----------|-------|--------|---------|
| DH$_f$   | -606.45 | -728.09 | -900.23 |
| $E_t$, ev| -6202.92 | -7358.85 | -8835.66 |
| I.P      | 10.82  | 10.86  | 10.72   |
| $E_{\text{HOMO}}$| -10.82 | -10.86 | -10.72 |
| $E_{\text{LUMO}}$| -0.701 | -1.07  | 0.88    |
| $\Delta E_g$| 10.12  | 9.79   | 9.84    |
| Dipole moment | 3.69  | 3.81   | 4.16    |

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efficiency. Similar results (not shown) were obtained for aluminium in HCl acid solutions.

**CONCLUSION**

Carrageenan compounds which classified as natural polymers effectively reduced the rate of corrosion of Al and Sn in HCl and HNO₃ solutions with markedly different efficiencies. Corrosion rate increases on increasing temperature and decreases with increasing inhibitor concentration. The inhibition action of these compounds is attributed to their adsorption on the metal surface. The inhibition efficiency was found to be dependent on the number

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**Fig. 7:** Microscopic examination of tin in 0.5M HNO₃ solution in absence and in presence of 5×10⁻³M k-carrageenan.

(a) Pure tin
(b) in 0.5M HNO₃
(c) in 5×10⁻³M of compound I.
(d) in 5×10⁻³M of compound II.
(e) in 5×10⁻³M of compound III.
of sulphate groups in carrageenan molecule. The adsorption of the inhibitor molecules on the metal surface obeys TemKin's adsorption isotherm.

ACKNOWLEDGMENTS

The authors would like to thank to Dr. Adel Ahmed Mohammed for his generous support while performing the theoretical part of this manuscript.

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