

Abstract

The synergistic effects of some ions such as KI, KCl and KBr on the corrosion inhibition of zinc in 0.4 M HCl by tetrahydrocarbazole derivatives compounds has been investigated using weight loss measurements. Potentiodynamic anodic polarization technique was used to measure the pitting corrosion potential and Quantum Chemical studies (Computational Study) were investigated. Results obtained show that these compounds are good inhibitors and their inhibition efficiencies (IE %) increase with the increase of inhibitor concentration. The presence of I, Br and Cl anions increase the inhibition efficiency of tetrahydrocarbazole compounds due to the synergistic effect. Halide ions are normally strongly adsorbed on the zinc surface and facilitate the adsorption of organic compounds by forming intermediate bridges between the positively charge metal surface and the positive end of the tetrahydrocarbazole molecule. Thus, the inhibitor is not adsorbed directly on the metal itself but rather by columbic attraction to the adsorbed halide ions on the metal surface. It is also found that these compounds inhibit the pitting corrosion of zinc in chloride containing solution by shifting the pitting corrosion potential into more positive/noble direction.

Introduction

Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous [1]. Looking at its increasing use, the study of corrosion inhibition is of paramount importance. The dissolution behavior of zinc in acidic and nearly neutral media is known to be inhibited by nitrogen and sulfur-containing organic compounds. Such compounds contain electron-donating groups that decrease the corrosion rate by increasing the hydrogen overvoltage on the corroding metal [2]. The use of inhibitors is one of metals and alloys, especially in acidic media. The increase in inhibition efficiency of organic compounds in the presence of some anions has been observed by investigators [3-5] and was ascribed to synergistic effect. Halide ions are normally strongly adsorbed on the surface of a corroding metal and facilitate the adsorption of organic compounds by forming intermediate bridges between the positively charge metal surface and the positive end of the organic molecule. Thus, the inhibitor is not adsorbed directly on the metal itself but rather by columbic attraction to the adsorbed halide ions on the metal surface. Studies of the effect of organic additives on the corrosion rate of zinc had been the subject of many investigators [6-12]. Most organic inhibitors are substances with at least one functional group that considered being a reaction center for the adsorption of the compound on the corroding surface, therefore forming Barrier Figure 1. Weight-loss versus immersion time for Zinc in the absence and presence different concentrations of compound(I) at 30±1°C.

Methods and Materials

Zinc strips (BDH grade) containing: 0.002% Fe, 0.001% Pb, 0.003% Cu, 0.001% Cd, and rest Zn were used in this investigation. All chemicals used were of AR grade. Specimens of zinc strips were abraded successively by emery papers of different grades, i.e. 150, 320, 400 and 600, and finally polished with a 4/0 emery paper to obtain mirror like finish. Then degreased ultrasonically with ethyl alcohol and rinsed with bi-distilled water several times and dried between two filter papers. AR grade hydrochloric acid (37 %) was used for preparing the corrosive solutions. Appropriate concentration of aggressive solutions used (0.4 M HCl) was prepared using bi-distilled water. The tetrahydrocarbazole derivatives were synthesized in the laboratory using standard procedure [14]. Stock solutions of NaCl, KI, KCl and KBr (1M) were prepared using bi-distilled water. From these stocks concentrated solutions exactly of 0.1 M NaCl and 1X10⁻² M of KI, KCl and KBr were prepared by dilution with bi-distilled water. It was purified and characterized by IR spectroscopy and other standard techniques before use. The following derivatives of tetrahydrocarbazole were studied; Tetrahydrocarbazole derivatives were used as corrosion inhibitors in this study are listed below

Compound	Structures	Names	M. FW. & M. Wt.
(I)		(Z)-2-(2-(4-methoxyphenyl)hydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₀ H ₂₀ N ₄ O ₂ Mol. Wt.: 372.42
(II)		(Z)-2-(2-(4-chlorophenyl)hydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₁ H ₁₇ ClN ₄ O Mol. Wt.: 376.84
(III)		(Z)-2-(2-phenyl)hydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₁ H ₁₈ N ₄ O Mol. Wt.: 342.39
(IV)		(Z)-2-(2-(4-nitrophenyl)hydrazono)-3-(5,6,7,8-tetrahydrocarbazol-9-yl)-3-oxopropanenitrile	C ₂₁ H ₁₇ N ₅ O ₃ Mol. Wt.: 387.39

Results

Weight – loss measurements

Fig. (1) shows the effect of increasing concentrations of compound (I) on the weight loss of Zn vs. time curves at 30 ±1°C. Similar curves (not shown) were obtained for the other three compounds. It is obvious that the weight loss of Zn in presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The calculated values of the percentage inhibition efficiency (I %) are listed in Table (1). Inspection of Table (1) reveals that, the inhibition efficiency increases with an increase in inhibitor concentration. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitors concentration, I % decreases in the following order: (I) > (II) > (III) > (IV).

Synergistic effect

Figures.(2) represent the weight loss time curves for zinc dissolution in 0.4M HCl in the presence of 10⁻² M of I, Br, Cl and also in the presence of different concentrations of organic additives. The strong chemisorption of these anions on the metal surface is responsible for the synergistic effect of these ions in combination with cation of the inhibitor. Stabilization of these adsorbed anions with cations leads to greater surface coverage and therefore, greater inhibition, as shown in Table(2).

Pitting corrosion of zinc

Effect of NaCl concentration

Pitting corrosion is an electrochemical process in which the pit act as a fixed anode. This process is similar to so-called phenomenon of anion induced adsorption. The formation of a pit depends on number of factors including type and concentration of attacking (depassivating) anions, type of material present and relative concentration of other anions as well as temperature. For pitting corrosion by halogen ion to effect the solution that should contain an oxidizing agent. The interesting feature of pitting corrosion of Zn electrode by halide ions in aqueous solution is that, it does not start directly after the presence of the metal in the corrosive medium but that, a certain time, so called induction period elapses before dissolution starts.

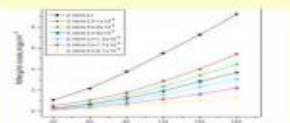


Fig. 1 : Weight-loss versus immersion time for Zn in 0.4 M HCl solution at 30 ± 1°C in the presence of different concentrations of compound (I) at 30°C.

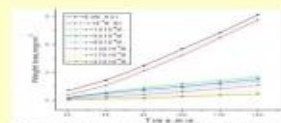


Fig. 2 : Weight-loss versus immersion time for Zn in 0.4 M HCl solution at 30 ± 1°C in the presence of different concentrations of compound (I) at 30°C and different concentrations of chloride ions (10⁻² M, 10⁻³ M and 10⁻⁴ M) at 30°C.

Table (1): Effect of inhibitors concentrations on the percentage inhibition efficiency (I %) of zinc in 0.4 M HCl solution from weight – loss method at 30 °C ±1C

[Inhibitor], M	% IE			
	(I)	(II)	(III)	(IV)
1x10 ⁻⁴	53.4	38.1	30.0	28.2
5x10 ⁻⁴	61.4	51.2	46.2	44.4
9x10 ⁻⁴	68.0	58.8	56.1	55.7
1.3x10 ⁻³	76.0	68.5	66.8	64.1
1.7x10 ⁻³	80.8	79.4	78.6	74.1
2.1x10 ⁻³	88.4	84.3	82.8	77.5

Table (2) : Inhibition efficiency of all inhibitors at different concentrations of tetrahydrocarbazole derivatives in presence of 1X10⁻² M KI after 90 min. immersion at 30±1°C.

Conc. (M)	% IE			
	(I)	(II)	(III)	(IV)
1x10 ⁻⁴	61.1	58.4	56.0	53.9
5x10 ⁻⁴	68.5	64.9	62.2	60.5
9x10 ⁻⁴	73.8	71.2	70.6	69.5
1.3x10 ⁻³	81.9	80.5	78.1	75.7
1.7x10 ⁻³	88.0	86.1	85.2	83.2
2.1x10 ⁻³	94.1	93.2	91.6	90.1

Conclusions

- 1-The tetrahydrocarbazole derivatives are considered as corrosion inhibitors for zinc in 0.4 M HCl act as efficient inhibitor.
- 2-The addition of KI, KCl and KBr to these compounds improve the values of inhibition efficiency due to synergistic effect
- 3-The adsorption process follows Langmuir isotherm.
- 4- Tetrahydrocarbazole derivatives provide protection against pitting corrosion of zinc in presence of chloride ions by shifting the pitting potential into positive direction.
- 5-The values of inhibition efficiencies calculated using weight loss, potentiodynamic anodic polarization and quantum chemical calculation were in good agreement.

References

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