Corrosion Inhibition of Aluminum in Sodium Hydroxide Solutions by Some Thiazole Derivatives

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Abstract

Two organic inhibitors namely 2-amino[4-p-Bromophenyl]Thiazole (ABT) and 2-amino[4-p-Hydroxyphenyl]Thiazole (AHT) were synthesized. FT-IR and NMR studies were done in order to confirm the composition of the synthesized inhibitors. These compounds were evaluated as inhibitors for Aluminum in (0.02M) NaOH solutions by weight loss and potentiodynamic polarization techniques. Different concentrations of inhibitors, temperatures, and immersion time have been tested. Values of inhibition efficiency obtained from the two methods are in good agreement and are dependent upon the concentration of inhibitor. The results observed have been discussed in the light of the molecular structures of the compounds and their adsorption on the surface of the corroding metal.

Keywords: corrosion, inhibition, aluminum, Thiazole.

Introduction

Aluminum (Al) is one of the most essential metals owning its large industrial applications, such as electronics, because of their low density, pleasing appearance, and corrosion resistance in aqueous solution, due to the formation of passive film[1][2]. Corrosion behavior of aluminum in various mediums has been studies. Several inhibitors have been used to control corrosion of aluminum.

To prevent the corrosion of aluminum in acid medium, inhibitors such as imidazole derivatives[3], capparis deciduas[4], polyethylene glycol and polyvinyl alcohol[5], delonix regia extract[6], and sansevieria trifasciata extract[7], have been used. In alkaline medium, polyvinyl alcohol[8], gongronema latifolium extract[9], bismark brown dye[10], methyl orange[11] and onion extract[12] have been used as corrosion inhibitors to prevent corrosion of aluminum.

In neutral or weakly acidic solution, aluminum is quite resistance to corrosion [13].

One of the most important methods in the corrosion protection of metals is the use of organic inhibitors to protest the metal surface from the corrosion environment[14]. Inhibition of metal corrosion by organic compounds is a results of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer is reduces or prevents the 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 corrosive media [15][16].

A variety of organic compounds containing heteroatoms such as O, N, S, and multiple bonds [17] in their molecule are particular interest as they give better inhibition efficiency than those containing N or S alone [18][19], as lone pair of electrons present on heteroatoms are the important structural features that determine the adsorption of these molecules on the metal surface [20][21]. Thiazole derivatives molecules adsorb probably through the sulfur atom or through coordination with the surface, forming a protective layer [22].

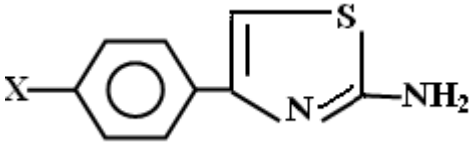
This work is devoted to test a some Thiazole derivatives as inhibitors for aluminum corrosion in 0.02M sodium hydroxide solution. Weight loss measurements and potentiodynamic polarization techniques were used in the study to evaluate the inhibition efficiency of the tested Thiazole derivatives. The effect of substituents groups on the inhibitors, their concentrations, solution temperatures & immersion times have been studies.

Experimental Procedure:

Synthesis of Inhibitors

The Thiazole derivative (ABT) was prepared by addition of resublimed iodine (2.54 gm) 0.01 mole to 2-Bromoacetophenone (1.99 gm)0.01 mole and thiourea (1.52 gm) 0.02 mole followed by heating of the mixture over night in an oil bath at (100ºC). After cooling, the reaction mixture was triturated with diethyl ether (50 ml) to remove any unheated iodine and 2-Bromoacetophenone. The solid residue was put in cooled distilled water (200 ml) and treated with (25%) aqueous ammonium hydroxide (to pH 9-10). The precipitated Thiazole was collected and purified by re- crystallization from hot ethanol (yield 85%).

* For prepared Thiazole derivative (AHT) was used 2-Hydroxyacetophe- none (1.36 gm) 0.01 mole instead 2-Bromoacetophenone.



Where X= Br, OH.

100ml stock solution (10^3 ppm) of two Thiazole derivatives were prepare-d by dissolving an accurately weighed quantity of each material in an appropriated volume of absolute ethanol, then the required concentrations (50 – 250 ppm) were prepared by dilution with bi-distilled water.

FT-IR Spectroscopy

FT-IR spectroscopy study was used to investigate the purity of the Thiazole derivatives synthesized. The results are show in Fig. (3).

NMR Spectroscopy

NMR spectral data for two Thiazole derivatives are listed below:

2-amino [4-p-Bromophenyl] Thiazole (ABT):

7.07 singlet (2H, NH_2 group)
7.01 singlet (1H, CH of Thiazole ring)
7.53 - 7.55 dd (2H, Benzene)
7.73 - 7.75 dd (2H, Benzene)
9.41 Singlet (1H, Br group)

2-amino [4-p-Hydroxyphenyl] Thiazole (AHT):

6.70 singlet (2H, NH_2 group)
6.75 - 6.77 dd (2H, Benzene)
6.98 singlet (1H, CH of Thiazole ring)
7.60 - 7.62 dd (2H, Benzene)
9.41 Singlet (1H, OH group)

Weight Loss Method

Coupons of aluminum with dimensions of 1×2×0.2 cm were used in weight loss experiments. All sheets containing 99.99% pure aluminum were polished to mirror finish with different grades emery paper, degreased with acetone and rinsed in distilled water.

All the weight loss experiments were carried out at various temperature ranging from (30 - 50ºC) and at various immersion times from 12– 60 hrs by immersing each of the aluminum sheets in an aqueous solution of (0.02M) NaOH containing different concentrations of inhibitor compounds.

The percentage inhibition efficiency (%IE) of the Thiazole derivatives was calculated by using the following equation:

$$\text{I.E.} = \left[1 - \frac{W_{add}}{W_{free}}\right] 100$$

Where, W_{add} and W_{free} are the weight loss of the metal in the presence and absence of the inhibitor.

Potentiodynamic polarization study

For potentiodynamic polarization studies of pure aluminum, a cylindrical rod embedded in araldite with an exposed surface area of (1.0 cm^2) was used and the experiments were carried out at temperature (30ºC).

potentiodynamic polarization studies were carried out using a PARSTAT 2273/Advanced Electrochemical System. Aluminum was used as working electrode, graphite as counter electrode, and saturated calomel electrode (SCE) as reference electrode. The corrosion parameters such as corrosion potential (E_{corr}), and corrosion current (I_{corr}) were measured. The values of (%IE) of the Thiazole derivatives was calculating using the following equation:

$$I.E. = \left[1 - \frac{I_{corr.,add}}{I_{corr.,free}}\right] 100$$

Results and discussion

Weight loss measurements

The losses weight of aluminum sheets due to their immersion in (0.02M) NaOH solution in the absence and presence different concentrations of Thiazole derivatives at various temperatures and immersion times were measured and given in table (1).

Table (1): Inhibition efficiency (%IE) of the inhibitors at their different concentrations for Al corrosion in (0.02M) NaOH solution for 12hrs from weight loss measurements.

Inhibitor conc.(ppm)	30ºC		40ºC		50ºC	
	Weight loss	%IE	Weight loss	%IE	Weight loss	%IE
0.02M NaOH	156.3	–	302.6	–	393.2	–
2-amino [4-p-Bromophenyl]Thiazole (ABT)						
50	119.1	50.13	156.6	45.50	307.3	43.25
100	85.3	57.72	94.1	51.54	224.5	46.33
150	55.2	63.91	63.4	60.93	157.3	58.67
200	30.6	75.23	38.1	65.13	93.6	62.05
250	15.4	80.52	19.3	76.20	27.5	70.05
2-amino [4-p-Hydroxyphenyl]Thiazole (AHT)						
50	105.6	69.73	123.7	65.51	255.4	60.90
100	73.0	78.30	84.6	70.20	120.0	69.32
150	44.5	82.51	56.4	78.35	64.2	75.45
200	29.2	91.21	31,5	86.01	40.5	81.11
250	9.6	93.55	12.3	88.22	20.4	84.02

It was found that addition of any of the used two Thiazole derivatives lowers the weight loss of the aluminum sheet than its value in the free base solution and the inhibition efficiency increases as the inhibitor concentration is increased. This result indicates that the two Thiazole derivatives act as inhibitors for aluminum corrosion in sodium hydroxide solution. The variation of inhibition efficiency with increase in inhibitor concentrations is shown in Fig. (1a).

The inhibitive action of this inhibitors could be attributed to the adsorption of their molecules on the aluminum surface through π-electrons of aromatic ring and lone pair of electrons of N and S atoms, and as a protonated species like amines[17][22]. Thus forming a barrier between the bar metal and the corrosive environment and then increase of the metal surface area covered by the adsorbed inhibitor molecules with the increasing inhibitors concentration. Furthermore, data in table (1) show that the extent of inhibition of different Thiazole derivatives depends on their structure. The inhibition efficiency increase in the following order:- ABT < AHT

This sequence reflects the effect of type of the substituents in the ring.

The Thiazole derivatives have either electron-donating groups such as −OH group in compound (AHT), or electro with drawing groups such as −Br group in compound (ABT).

It is clear from the above sequence that compounds containing electron-donating groups are more efficient inhibitors than those containing electro with drawing groups. The electron-donating groups enhance adsorption with a consequent increase in IE [1].

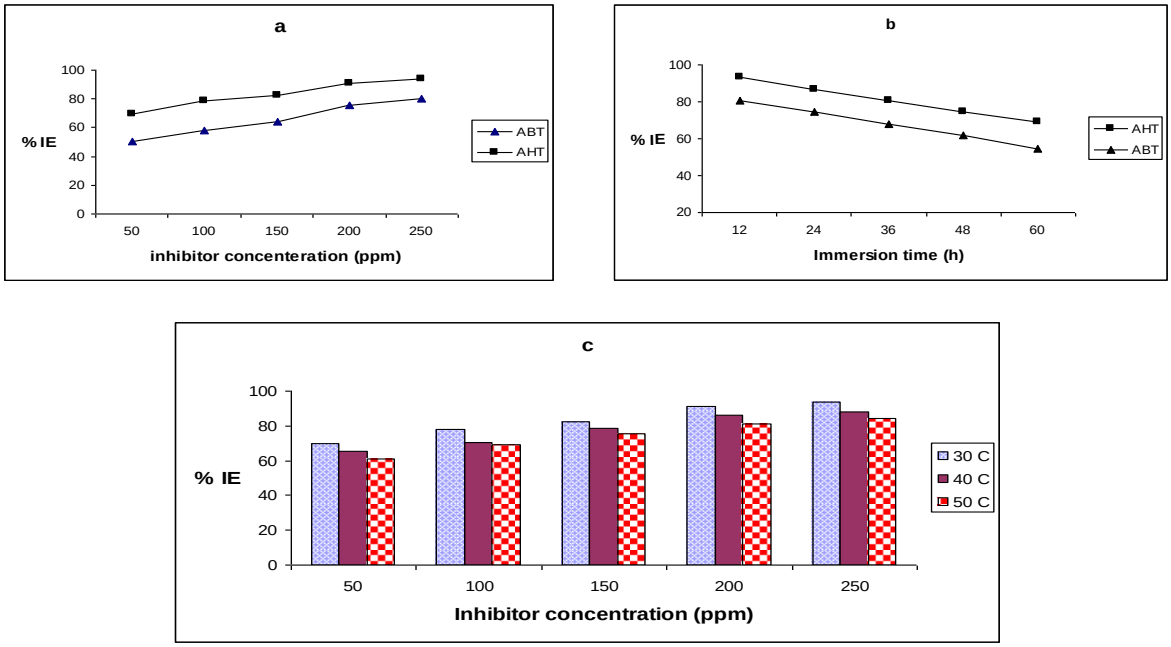


Fig. (1): Variation of inhibition efficiency with (a) inhibitor concentration (b) immersion time (c) solution temperature for Al corrosion in (0.02M) NaOH solution

The effect of immersion time on inhibition efficiency is shown in Fig.(1b). It is found that all the tested Thiazoles show decrease in the inhibition efficiency with the increase of immersion time from 12-60 hrs.

The influence of solution temperature on inhibition efficiency is shown in Fig.(1c). It is observed that inhibition efficiency for all the derivatives decrease with the increase in solution temperature from 30-50ºC indicating that the adsorption phenomenon becomes less pronounced with the increase of temperature. This means that these compounds are adsorbed physically on aluminum surface [23].

Potentiodynamic polarization study

Fig. (2) represents the polarization curves of aluminum electrode in (0.02M) NaOH solutions containing different concentrations of Thiazole derivatives (AHT) at (30ºC). Similar curves were also obtained for the other Thiazole derivatives (ABT).

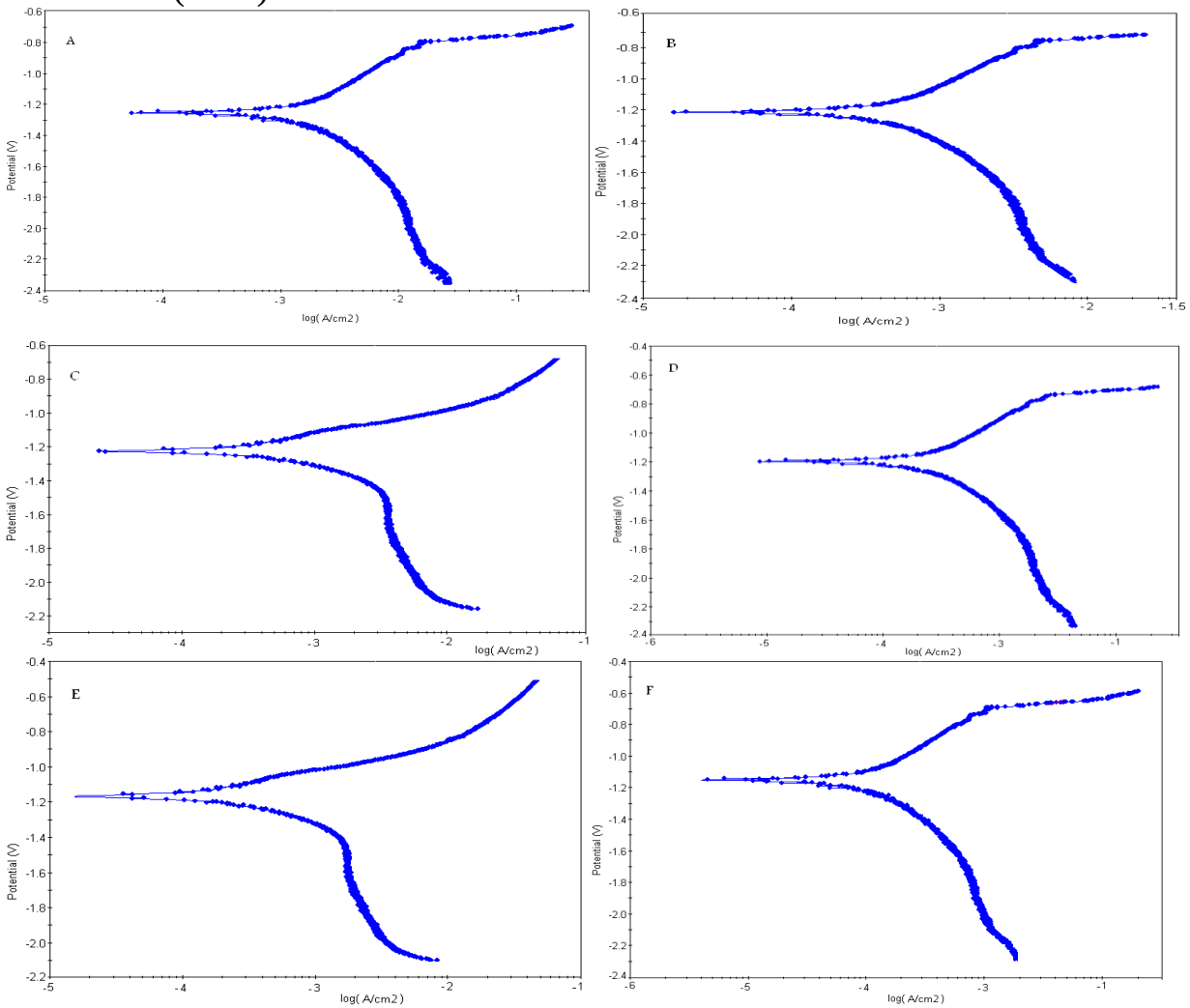


Fig. (??)

The values of corrosion current density (I_{corr}), corrosion potential (E_{corr}), and the percentage inhibition efficiency (%IE), excluded from polarization curves are given in table (2). Inspection of table (2) reveals that the corrosion current density is greatly reduced upon addition of any of the two Thiazole derivatives.

Fig. (2): Potentiodynamic polarization curves for Al in(0.02M) NaOH solutions containing different concentrations of (AHT) at (30ºC), (A) (0.02M) NaOH, (B)50ppm, (C)100ppm, (D) 150ppm, (E) 200ppm, (F) 250 ppm .

Table (2): potentiodynamic polarization parameters for Al corrosion in (0.02M) NaOH solutions containing different concentrations of (ABT) & (AHT) at (30ºC).

Inhibitor conc.(ppm)	$-E_{corr}$ mV $_{SCE}$	I_{corr} $\mu A\ cm^{-2}$	%IE
0.02M NaOH	1250	732.04	–
2-amino [4-p-Bromophenyl]Thiazole (ABT)			
50	1044	379.86	48.11
100	1031	323.56	55.80
150	1029	308.12	57.91
200	1017	207.75	71.62
250	1003	91.87	87.45
2-amino [4-p-Hydroxyphenyl]Thiazole (AHT)			
50	1232	264.71	63.84
100	1222	187.92	74.33
150	1200	165.37	77.41
200	1184	73.79	89.92
250	1162	61.20	91.64

On the other hand, the corrosion potential is largely shift to less negative values upon addition of Thiazole derivatives. The magnitude of this shift increases with increasing of the additive concentration of Thiazole derivatives.

The data in table (2) reveal that the values of inhibition efficiency obtain- ned by polarization technique are comparable to those obtained by weight loss measurements. The inhibition efficiency depends on the type of Thiazole derivatives. It could be recognized in table (2) that the inhibiti-on efficiency of two Thiazole derivatives increases in the following order:- ABT < AHT

It is of interest to note that this sequence is the same like that obtained by weight loss measurements.

FT-IR Spectroscopy

The results of FT-IR spectroscopy of the 2-amino [4-p-Bromophenyl] Thiazole (ABT) and 2-amino [4-p-Hydroxyphenyl] Thiazole (AHT) are show in Fig. (3a, b) respectively .

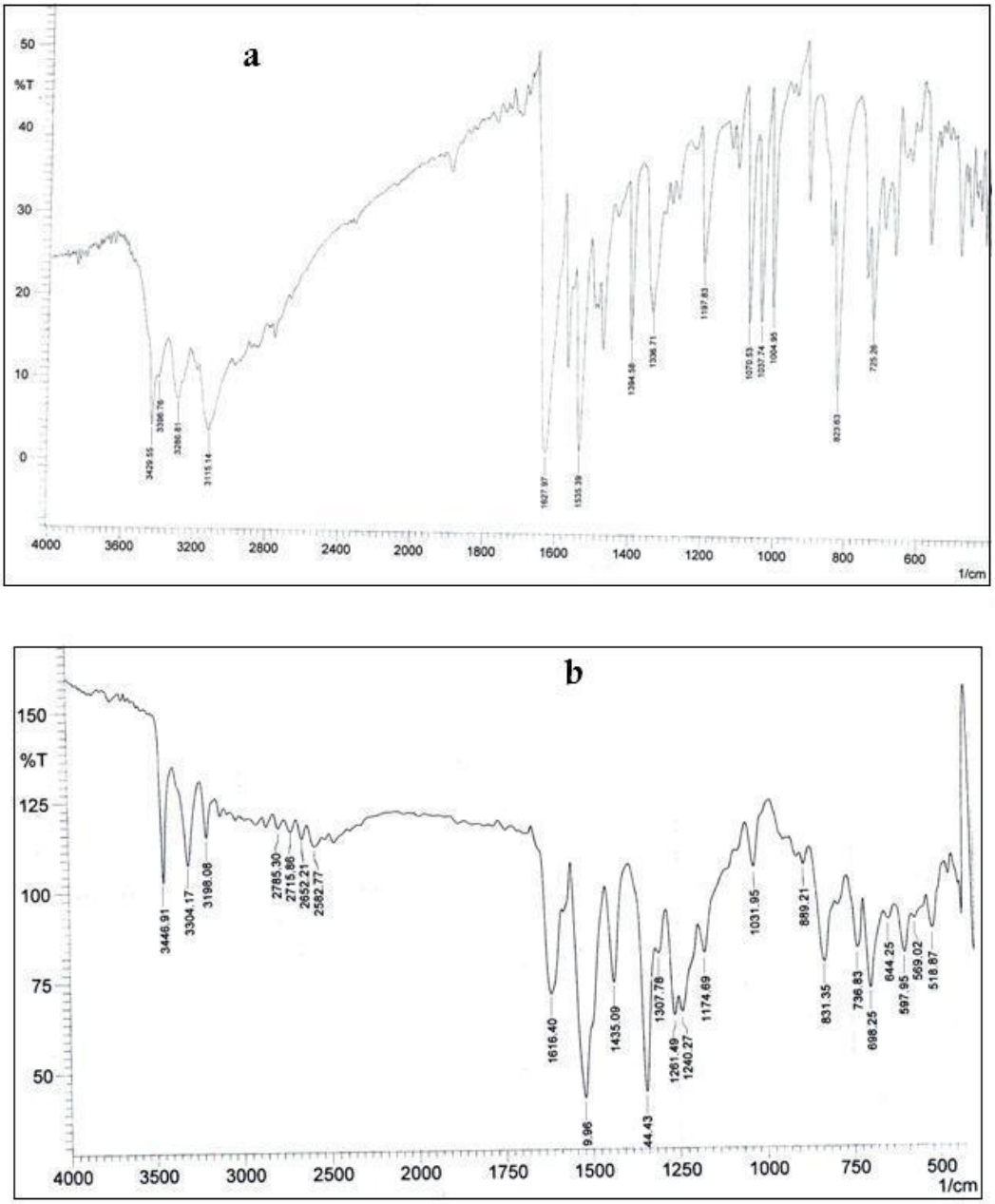


Fig. (3): FT-IR spectroscopy of the –a- (ABT) & -b-(AHT)compounds.

Conclusion

1) The tested Thiazole derivatives establish a very good inhibition for aluminum corrosion in NaOH solution.
2) Thiazole derivatives inhibit the aluminum corrosion by adsorption on its surface.
3) The inhibition efficiency of the tested Thiazole derivatives increase with increasing of their concentrations, but decreases with an increase in temperatures and immersion times.

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الخلاصة

تم دراسة تآكل الألمنيوم النقي في محاليل قاعدية هي NaOH بتركيز (0.02M) وتثبيطها باستخدام مثبطات عضوية محضرة هي (٢- امينو [٤-بارا- برومو فينيل] ثايوزول) (ABT) و (٢- امينو[٤-بارا- هيدروكسي فينيل] ثايوزول) (AHT)، وشخصت نقاوة هذه المركبات بواسطة مطيافية الأشعة تحت الحمراء FT-IR وتقنية الرنين النووي المغناطيسي NMR. واجريت دراسة التآكل باستخدام قياسات فقدان الوزن وتقنية الاستقطاب البوتنشيوديناميكي. تم كذلك دراسة بعض ظروف التآكل في درجات حرارية وفترات غمر مختلفة مع تراكيز مختلفة من المثبطات وتأثيرها على تآكل الألمنيوم وتثبيطه وبالتالي معرفة كفاءة التثبيط Inhibition Efficiency لهذه المثبطات. تبين من نتائج كفاءة التثبيط المستحصلة من قياسات فقدان الوزن وتقنية الاستقطاب البوتنشيوديناميكي إن هناك توافق جيد في النتائج بين الطريقتين وان كفاءة التثبيط تزداد بزيادة تركيز المثبط. كما قورنت تأثير المجاميع المعوضة في المركب العضوي على مقدار التثبيط وبالتالي على كفاءة التثبيط.