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Microwave Assisted Economic Synthesis of 4-amino-3-alkyl-5-mercapto-1, 2, 4-triazole Derivatives as Green Corrosion Inhibitors for Copper in Hydrochloric Acid

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Abstract

We have investigated a microwave-assisted cost effective synthesis of 3-substituted-4 amino-5-mercapto-1, 2, 4-trizole derivatives by condensation of different alkanoic acids and thiocarbohydrazide. We found that the use of microwave irradiation allows a rapid (4-8 min) and high-yielding (90-93%) reaction. The effect of synthesized triazoles on corrosion of copper in hydrochloric acid solution has been investigated by potentiodynamic polarization method. Potentiodynamic polarization measurements indicate that all three (AMT, AMMT and AEMT) examined compounds are cathodic type inhibitors. All the compounds exhibited more than 90% anticorrosion activity and highest is 96.09% by AEMT.

Keywords: Microwave, Corrosion Inhibitors, 4-amino-3-alkyl-5-mercapto-1, 2, 4-triazole Derivatives, Green Synthesis

1. Introduction

Triazole and its derivatives are found to be associated with various biological Activities [1]. They possess wide spectrum of activities ranging from anti-bacterial, anti-inflammatory, anticonvulsant, anti-neoplastic, antimalarial, antiviral, anticancer [2-7]. The triazoles have also been reported as good corrosion inhibitors in different corrosive environment [8-11]. The corrosion inhibition of copper by the organic compounds in hydrochloric acid medium has received a considerable attention. Copper has an excellent thermal conductivity, good corrosion resistance and mechanical workability and is widely used in various industries. The copper undergoes corrosion in acidic medium. Organic compounds containing hetero atoms nitrogen-, sulfur- or oxygen, and heterocyclic compounds with polar functional groups [12-14] were found to be good corrosion inhibitors for copper in hydrochloric acid. It is of interest to note that mercapto triazoles contain sulfur atom and many organic compounds containing sulfur atom have been developed as copper corrosion inhibitors for different industrial application [15] owing to the ability of S atom to be strongly adsorbed on copper surface. Therefore, triazoles may be a potential nontoxic corrosion inhibitor for copper in hydrochloric acid solution. The adsorption of compounds on metal surface depends on the nature, surface charge of the metal, type of the electrolyte solution and by their electronic structure, steric factor, aromaticity, and molecular weight [16, 17].

Therefore, a number of methods have been reported for the preparation of triazoles derivatives [18, 19], most of them are associated with disadvantages such as longer reaction time, multi step procedure, lower yield and excess use of acid as solvent and reactant. As a part of our program aimed to develop new selective and environmental friendly methodology for the synthesis of industrially important heterocyclic compounds and in continuation of our work in the field of green chemistry and microwave chemistry [20, 21], We describe herein microwave assisted facile and economic synthesis of 3-substituted-4-amino-5mercapto-1, 2, 4-trizoles in higher yield (90-93%), shorter reaction time (4-8 min.) and their effect on corrosion of copper in hydrochloric solutions by using potentiodynamic polarization method.

2. Materials and methods

2.1 Chemicals and Material

All the chemicals used were of research grade and were used without further purification. The purity of compounds were checked on thin layers of silica gel in various non-aqueous solvent systems e.g. benzene: ethyl acetate (9:1), benzene: dichloromethane (8:2), and n-hexane: ethyl acetate (7:3). The microwave-assisted reactions were carried out in a MAS-II microwave oven (2450 MHz, Sineo Microwave Chemistry Technology Company, Shanghai, China) with a maximum power output of 1000W. This system is equipped with a power and temperature feedback control switch. The temperature is monitored by an infrared sensor. Melting points were recorded on a Toshniwal apparatus and are uncorrected. Melting points of our compounds are in agreement with literature data. Materials used for the study was copper (99.9%) coupons. The coupons were abraded by emery paper of 600-1200 grades rinsed with double distilled water, degreased with acetone and dried at room temperature [22]. These coupons were used for electrochemical studies. The working electrode (WE) for electrochemistry measurements were prepared of the size 1.0 × 1.0 cm (exposed) with a 7.0-cm long stem (isolated with epoxy resin). The aggressive environment used was 0.5 M HCl solution which was prepared from analytical reagent-grade HCl and doubled distilled water. Fig 1 shows molecular structure of triazoles used as corrosion inhibitors for copper.

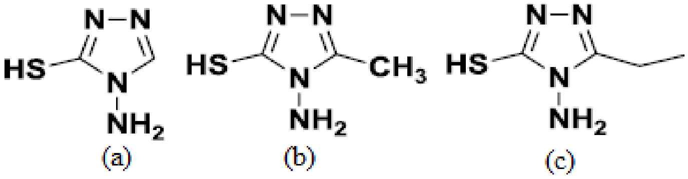
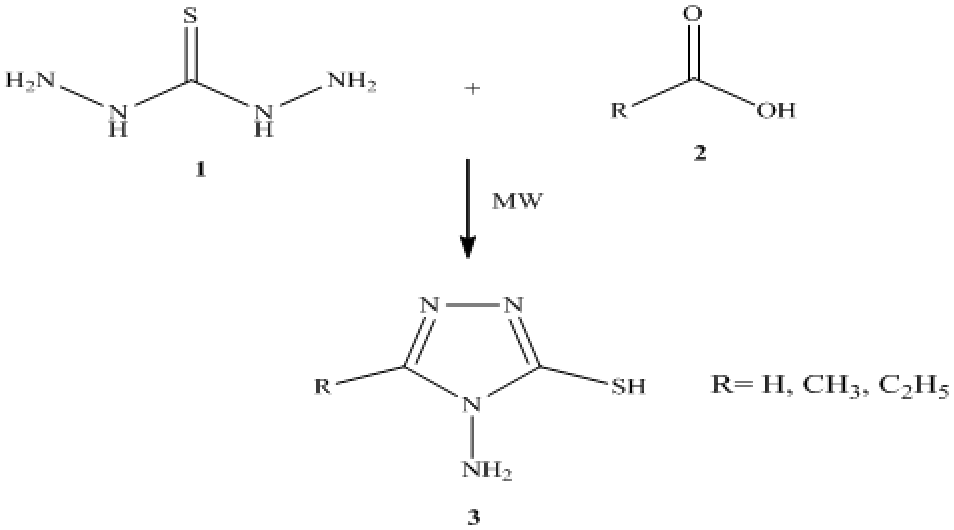


Figure 1: Moleular structure of triazoles (a) 4-amino-5-mercapto-1, 2, 4-triazole (AMT), (b) 4-amino-3-methyl-5-mercapto-1, 2, 4-triazole (AMMT), (c) 4-amino-3-ethyl-5-mercapto-1, 2, 4-triazole (AEMT).

2.2 General procedure

A mixture of thiocarbohydrazide (10mmol) and acetic acid (15mmol) was irradiated under microwave radiations at 400 W for appropriate time. Completion of the reaction was monitored by TLC. All the reactions were invariably completed with in 5-10 min. After completion of the reaction, solution was poured into crushed ice. The obtained solid was filtered, washed well with cold water and crystallized from ethanol. All inhibitors (AMT, AMMT and AEMT) were synthesized according to Scheme 1. The electrochemical studies carry through using three electrodes cell assembly at room temperature. A three-electrode cell, employing a copper coupons as working electrode (WE), platinum foil as counter electrode, and saturated calomel electrode as reference electrode (SCE) for measurements. All potentials were measured versus SCE. The electrochemical measurements were accomplished by using a Gamry Potentiostat/Galvanostat with a Gamry framework system based on ESA400. Gamry applications include software DC105 for corrosion.

The Tafel polarization was carried out from anodic and cathodic potential at a scan rate of 1 mV s^{-1} to study the effect of inhibitor on copper corrosion. Measurements were performed by changing the electrode potential automatically from -250 to +250mV vs. corrosion potential. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion current densities (I_{corr}). Prior to the potentiodynamic measurements, the working electrode was immersed in the 0.5 M HCl with and without addition of inhibitor for 2 h for stabilization of the OCP wrt SCE.



Scheme 1: Synthesis route of triazoles derivatives.

3. Results and discussion

3.1 Synthesis of triazoles derivatives

To achieve suitable conditions for the synthesis of 4 amino-3-substituted--5-mercapto-1, 2, 4-trizole derivatives, we tested the reaction of thiocarbohydrazide **1** and acetic acid **2b** as a simple model substrate. While investigating the effect of the molar ratios of reactants on the reaction, it was found that the 1 equiv each of thiocarbohydrazide (1**)** and acetic acid (**2b**) resulted in the desired triazole derivative **3b** with lower yields (Table 1; Entry 2). When we conducted the above reaction by changing the ratio of reactants (**1:1.5**), the desired triazole derivative **3b** was generated with good yield (Table 2; Entry 2). Further increase in the molar ratio of acid (**2b**) did not cause any change in the product yield. Next we investigated the effect of power on the yields of product. We found that an initial increase in power from 300 watt to 400 watt resulted in decrease of reaction time with increase in yield (Table 2; Entry 2) but further increment in power from 400 watt to 500 watt does not seem to affect the reaction time, in fact the yield of product was slightly decreased. So it can be conclude that **1:1.5** molar ratio of reactant and 400 watt power is best suitable condition for reaction. All spectral data of triazoles derivatives are shown in Table 3. After optimizing the molar ratio and output power of microwave synthesizer system, we shifted our attention upon the comparison between conventional and microwave heating. To our expectation, a strong specific microwaves effect [23] was visualized in the comparative study. The best results obtained under MW irradiation were compared to conventional heating. The reaction, in the case of compound 3b, was carried out using a preheated oil bath, under similar reaction conditions as under MW (time and temperature). It has been found that reactions proceed with considerable lower yields under similar thermal conditions demonstrating that the effect of MW is evidently not purely thermal [24].

Table 1:-(1:1 molar ratio of thiocarbohydrazide and acid)

Entry	Comp	R	Time and Yield at different power						Temp (^{0}C)	Mp (^{0}C)	Lit.Mp (^{0}C)
			300 watt		**400 watt**		**500 watt**				
			Time (min.)	Yield* (%)	Time (min.)	Yield* (%)	Time (min.)	Yield* (%)			
1	3a	H	14	62	8	67	10	66	98	168-169	166-167[18a]
2	3b	CH_3	10	65	6	74	7	72	115	201-203	204[18c]
3	3c	C_2H_5	9	71	4	77	6	76	139	141-143	140-141[18a]

*Isolated Yield,

Table 2:-(1:1.5 molar ratio of thiocarbohydrazide and acid)

Entry	Comp	R	Time and Yield at different power						Temp (^{0}C)	Mp (^{0}C)	Lit.Mp (^{0}C)
			300 watt		**400 watt**		**500 watt**				
			Time (min.)	Yield* (%)	Time (min.)	Yield* (%)	Time (min.)	Yield* (%)			
1	3a	H	14	72	8	90	10	89	98	168-169	166-167[18a]
2	3b	CH_3	10	75	6	92	7	90	115	201-203	204[18c]
3	3c	C_2H_5	9	77	4	93	6	92	139	141-143	140-141[18a]

*Isolated Yield,

3.2 *Potentiodynamic polarization measurements*

Polarization measurements were scrutinized in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions. Fig.2 (a-c) shows cathodic and anodic polarization curves recorded for Cu in 0.5 M HCl solutions in the absence and presence of various concentrations of AMT, AMMT and AEMT. In hydrochloric acid solution the following mechanism is proposed for the corrosion of copper [25]. The anodic dissolution mechanism of copper is:

$$\mathrm{Cu+Cl^{-}} \rightarrow \mathrm{CuCl_{ads}} + e^{-} \quad (1)$$

$$\mathrm{CuCl_{ads}+Cl^{-}} \rightarrow \mathrm{CuCl_{2}^{-}}_{\mathrm{ads}} \quad (2)$$

$$\mathrm{CuCl_{2}^{-}}_{\mathrm{ads}} \rightarrow \mathrm{Cu^{++}+2Cl^{-}+e^{-}} \quad (3)$$

Table 3:-Spectral data of triazoles derivatives.

Compound	Spectral data
AMT	White solid, (Yield: 90%); mp: 168-169 °C IR, ν_{max} (KBr): 3392 (NH_2), 3250 (CH), 2380 (SH), 1600 (C=N) cm^{-1} ^1H NMR (DMSO-d_6, 300 MHz): δ5.87 (s, 2H, NH_2, D_2O exchangeable), 8.52 (s, 1H, CH), 12.81 (s, 1H, SH) ^{13}C NMR (DMSO-d_6, 75 MHz): δ152.4, 166.1 MS (*m/z*): 117 $[M+H]^+$
AMMT	White solid, (Yield: 92%); mp: 201-203 °C IR, ν_{max} (KBr): 3400 (NH_2), 3246 (CH), 2392 (SH), 1612 (C=N) cm^{-1} ^1H NMR (DMSO-d_6, 300 MHz): δ2.22 (s, 3H, CH_3), 5.79 (s, 2H, NH_2, D_2O exchangeable), 12.67 (s, 1H, SH) ^{13}C NMR (DMSO-d_6, 75 MHz): δ13.3, 151.3, 164.5 MS (*m/z*): 131 $[M+H]^+$
AEMT	White solid, (Yield: 93%); mp: 141-143 °C IR, ν_{max} (KBr): 3396 (NH_2), 3236 (CH), 2382 (SH), 1608 (C=N) cm^{-1} ^1H NMR (DMSO-d_6, 300 MHz): δ2.65 (q, *J*=6.9 Hz, 2H, CH_2), 1.57 (t, *J*=6.9 Hz, 3H, CH_3), 5.73 (s, 2H, NH_2, D_2O exchangeable), 12.61 (s, 1H, SH) ^{13}C NMR (DMSO-d_6, 75 MHz): δ13.9, 21.3, 151.7,164.9 MS (m/z): 145 $[M+H]^+$

This mechanism reflects that $CuCl_{ads}$, represents a cuprous chloride species which is adsorbed onto the copper electrode surface. Insoluble $CuCl_{ads}$ layer on the copper surface in the presence of Cl^- and acts as a protective barrier for copper from its further oxidation. In acidic solutions, the adsorbed CuCl layer is destroyed. Anodic curves in Fig.2 (a-c) unambiguous divided into three regions: (1) the apparent-Tafel region, due to the dissolution of copper into Cu+ (2) the limiting-current region, a region of decreasing currents until a minimum is reached associated with the formation of a CuCl film, and (3) the region beyond the limiting-current plateau, in which the current density increases due to formation of $CuCl^{2-}$ which is responsible for copper corrosion either its dissolution into the bulk solution or its further oxidation to cupric (Cu^{2+}) ions. The anodic dissolution of copper is thus controlled by both electrodissolution of copper and diffusion of $CuCl^{2-}$ to the solution bulk [26]. The inhibition mechanism of triazoles can be explained by the $Cu(inh)_{ads}$ reaction intermediates:

$$Cu + inh \rightleftharpoons Cu\ (inh)_{ads} \rightleftharpoons Cu^{n+} + ne^- + inh \quad (4)$$

$$inh_{aqu} + nH_2O_{ads} \rightleftharpoons inh_{ads} + nH2O_{aqu} \quad (5)$$

At first, when there is not enough $Cu(inh)_{ads}$ to cover Cu surface, owing to low concentration of inhibitors or because the adsorption rate is slow, metal dissolution takes place at sites on the Cu surface free of $Cu(inh)_{ads}$. With a high inhibitor concentration a compact and coherent inhibitor layer is formed over the copper, which reduces chemical attacks on the metal [27]. The cathodic polarization curve may be attributed to the diffusion controlled reduction of dissolved oxygen. The cathodic corrosion reaction in an aerated acidic chloride solution is:

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O \quad (6)$$

From the Fig.2 (a-c) the addition of AMT, AMMT and AEMT inhibitors shifts the potential of the metal in the negative direction due to the decrease in the rate of the cathodic reaction. Since the transfer of oxygen from the bulk solution to the copper/solution interface will strongly affect the rate of oxygen reduction, it can be inferred that the adsorbed layer behaves also a cathodic inhibitor to Cu corrosion by retarding the transfer of O_2 to the cathodic sites of the Cu surface. It is observed that addition of inhibitors affects both the anodic and cathodic parts of the curves, but the cathodic reaction is inhibited to a larger extent. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), in the presence of different concentrations AMT, AMMT and AEMT were calculated from the potentiodynamic polarization curves and tabulated in Table 4. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). It is clear from Table-4 that, the corrosion current densities I_{corr} decreases with increasing inhibitor concentration. From these data one can recognize distinctly higher inhibition of triazoles for concentration 2.58×10^{-3} mol L^{-1} which is the optimum concentration and rank them as follows: AEMT > AMMT > AMT. The inhibition efficiency was calculated from the equation:

$$\eta_{\%} = \frac{I^{0}_{\mathrm{corr}} - I^{\mathrm{i}}_{\mathrm{corr}}}{I^{0}_{\mathrm{corr}}} \times 100 \tag{7}$$

where, I^{0}_{corr} and $I^{\mathrm{i}}_{\mathrm{corr}}$ are the corrosion current density in absence and in the presence of inhibitor, respectively.

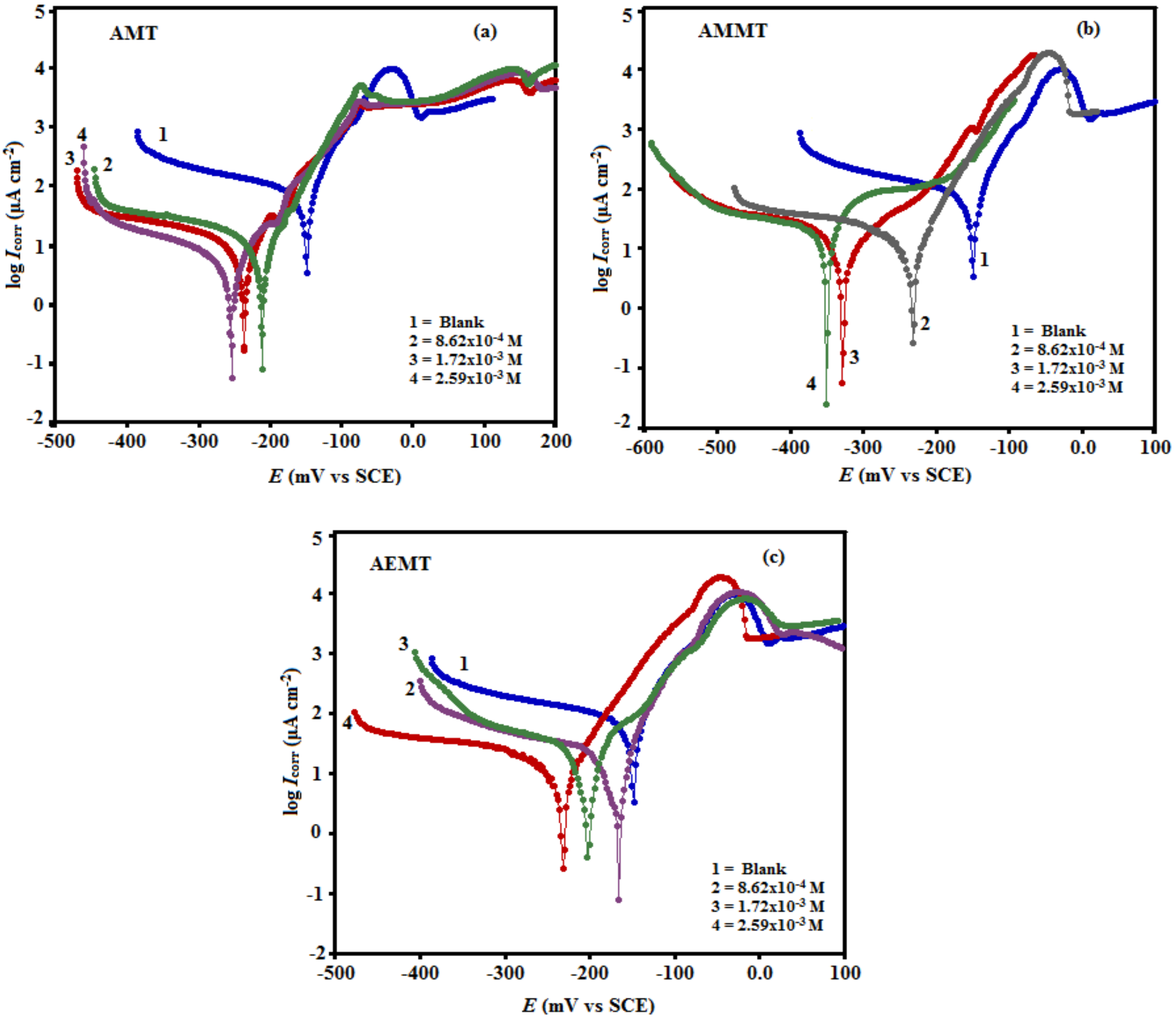


Figure 2: Potentiodynamic polarization curves for copper in 0.5 M HCl containing different concentrations of (a) AMT (b) AMMT (c) AEMT at 303 K temperature

Table 4:- Parameters obtained by Tafel polarization technique for copper in 0.5M HCl solutions in the absence and presence of (a) AMT (b) AMMT (c) AEMT at 303 K temperature.

Acid solution	Conc. of inhibitor (mol L^{-1})	E_{corr} (mV vs. SCE)	I_{corr} (µA cm^{-2})	Inhibition **e**fficiency $(\eta_{\%})$
0.5 M HCl	-	-149.0	92.90	-
AMT	8.26 x 10^{-4}	-211.2	14.50	84.39
	1.72 x 10^{-3}	-236.5	11.20	87.94
	2.58 x 10^{-3}	-254.1	7.38	92.05
AMMT	8.26 x 10^{-4}	-232.3	7.84	91.56
	1.72 x 10^{-3}	-329.5	6.54	92.96
	2.58 x 10^{-3}	-350.3	3.92	95.78
AEMT	8.26 x 10^{-4}	-166.0	8.78	90.54
	1.72 x 10^{-3}	-203.0	5.85	93.70
	2.58 x 10^{-3}	-232.3	3.63	96.09

Conclusions

Potentiodynamic polarization measurements indicate that all three (AMT, AMMT and AEMT) examined compounds are cathodic type inhibitors. We developed a single-step, efficient and green synthesis of 3-substituted-4 amino-5-mercapto-1, 2, 4-trizole derivatives under microwave irradiation. Avoidance of excess use of acid, short reaction times and good yields are the outstanding advantages of the present protocol. All measurements showed that the triazoles derivatives have good inhibition properties for the corrosion of copper in hydrochloric acid (0.5 M HCl) solutions.

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