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Scientific paper
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Study of inhibition properties of some thiazole derivatives against copper corrosion

The inhibitor efficiency of some thiazole derivatives against copper corrosion in acidic sulfate solution were investigated using polarization and electrochemical impedance spectroscopy (EIS) methods. Protection efficiency of four organic molecules: 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (5-BDT), 5-(4′-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-IPBDT), 5-(3′-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-TDT) and 5-(3′,4′-dimetoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-MBDT) were investigated on copper electrode in 0.1moldm^{-3} Na_2SO_4 solution at pH=2.95. Polarization measurements indicates that all investigated thiazole derivatives could reduces the cathodic reaction rate on copper electrode surface in 0.1 mol dm^{-3} acidic Na_2SO_4 solution. In investigation range concentration 0.01mmoldm^{-3} has the best inhibitor efficiency in case of all investigated thiazole. The best protection is obtained in presence of 5-IPBDT derivatives. EIS results showed that investigated thiazole derivatives formed a film on copper surface which was able to protect copper against corrosion in acidic media. 5-IPBDT derivative only formed closely packed inhibitor film, which is able to protect copper surface during the time.

Key words: *inhibitors, corrosion, copper, properties*

INTRODUCTION

Copper and its alloys are used extensively in much kind of chemicals equipment. Copper normally does not displaced hydrogen from acid solutions and the presence of oxygen is essential for its dissolution [1,2].

Several organic molecules have been investigated as potential inhibitors for copper corrosion in acidic media. The thiazole derivatives are an interesting group of nitrogen and sulphor containing organic compounds which act as inhibitors in the dissolution of copper in acidic media. This kind of organic molecules can be adsorbed at the metal-solution interface as a result the metal reduces the corrosive attack in acidic media [3-5].

In this paper, protective effect of thiazole derivatives: 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (5-BDT), 5-(4′-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-IPBDT), 5-(3′-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-TDT) and 5 - (3′,4′-dimetoxybenzylidene)-2,4-dioxotetrahydro -1,3- thiazole (5-MBDT) on copper corrosion were testified in acidic Na_2SO_4 solution using polarization and electrochemistry impedance specroscopy (EIS) techiques.

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EXPERIMENTAL

All the experiments were carried out with a polycrystalline copper (99.99%) electrode in the form of a cylinder (with an exposed area of 0.7 cm^2) embedded in an epoxy resin. Before each experiment the electrode was wet-polished with SiC papers (grit sizes of 800 and 1200), the immersed in the solution. Saturated calomel electrode (SCE) was used as reference, and Pt as counter electrode. A computer-controlled potentiostat (Model Solartron ECI-1286) were applied for the electrochemical measurements. The polarization measurements were performed in room temperature (298K) at five different inhibitor concentration in range of 0.001 mmoldm^{-3}- 0.01 mmoldm^{-3}. The measurements were carried out when open circuit potential (OCP) was stabilized to 5 mv per 5 minute. The potential was scanned between OCP and 500 mV in both catodic and anodic directions at the scan rate of 10 mV min^{-1}. The EIS measurements were performed at the open circuit potential at room temperature (298K) with Zahner electric IM 5d, after 30 minute relaxation time, in each hour during the 24 hour. The impedance measurements were carried out over a frequency range of 0.01-10 KHz, using 10 mV amplitude of sinusoidal voltage. The impedance spectra were analyzed using program Boukamp EQUIVCRT [6].

RESULTS AND DISCUSSION

Using polarization measurements, we were obtained that all investigated derivatives act as catodic

inhibitors against copper corrosion hindered the oxygen reduction in acidic solutions (Fig.1.). 5-IPBDT derivative, in addition to of inhibiting the reduction of oxygen, slows also down the dissolution of copper. The inhibition efficiency of investigated thiazole derivatives decrease in the following order: 5-IPBDT> 5-BDT > 5-MBDT > 5-TDT. In investigation range concentration of 0.01mmoldm^{-3} has the best inhibitor efficiency in case of all investigated hiazole (Fig.2.).

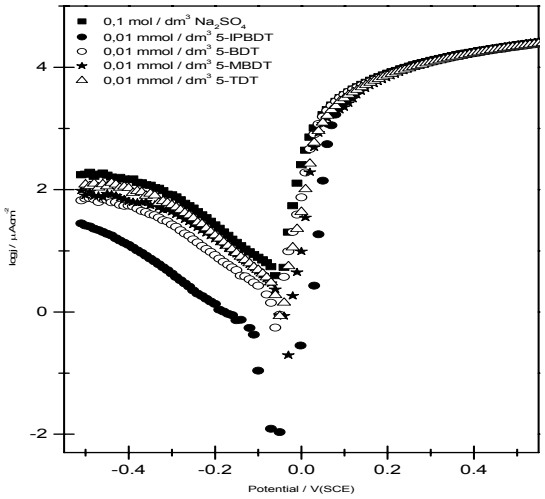

Figure1 - Polarization curves for copper electrodes without and with thiazole derivatives (c=0.01mmoldm^{-3})

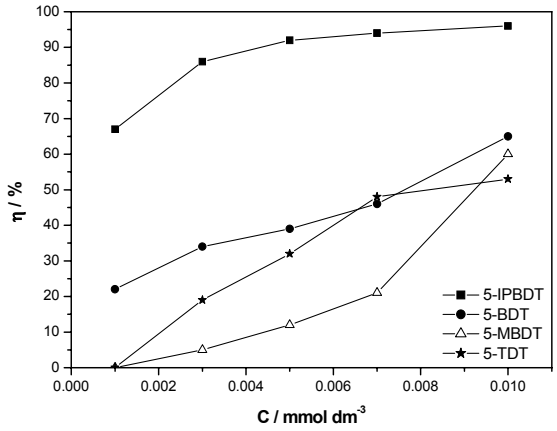

Figure 2 - Concentration dependence of inhibitor efficiency

Electrochemistry Impedance Spectros

Electrochemistry Impedance Spectroscopy measurements

Fig. 3a. and 3b. present Nyquist polts for copper electrodes in 0.1 moldm^{-3} Na_2SO_4 solution without and with 0.01 mmoldm^{-3} thiazole derivatives, after 30 minute and 24 hour. In all cases depressed semicircles were found, what was characteristic for copper in acidic sulfate solution [7-10].

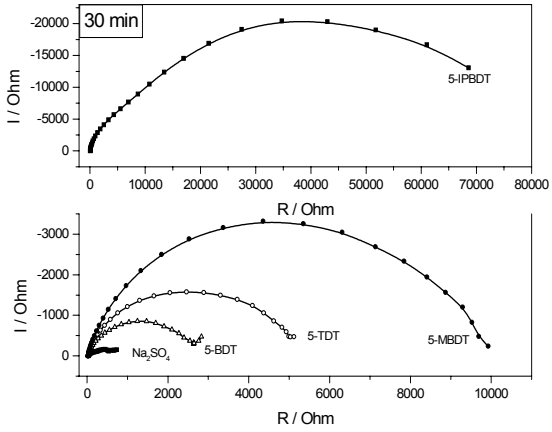

Figure 3a - Nyquist plots for copper electrodes without and with thiazole derivatives (c=0.01mmoldm^{-3}) after 30 minute

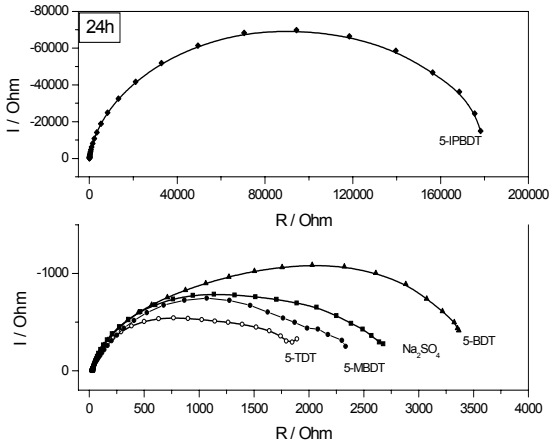

Figure3b - Nyquist plots for copper electrodes without and with thiazole derivatives (c=0.01mmoldm^{-3}) after 24 hour

EIS data were analyzed using equivalent circuit, given in Fig 4. In the equivalent circuits R_Ω is the solution resistance, Rt the charge-transfer resistance, CPE_{dl} represent the double-layer constant phase elements, Ra the pseudo-resistance corresponding to the discharge of adsorbed species, and CPE_a the pseudo-constant phase elements. Constant phase elements (CPE) are used to substitute for capacitors to fit the depressed semicircle more exactly. The impedance of a CPE is given by

$$Z_{\mathrm{CPE}} = \frac{1}{\mathrm{Y}_0}(j\omega)^{-n}$$

Where Y_0 is the magnitude of CPE and n an empirical exponent ($0 \leq n \leq 1$), which value indicate the distribution of time constants caused by inhomogenities in the inhibitor film formed on copper surface [11-13].

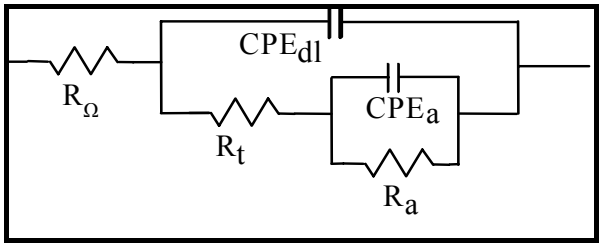

Figure 4 - Electrical equivalent circuit for copper electrode

Given model describe electrochemical process in both cases, in blank and inhibitor solution with two relaxation time constants. The first relaxation time constant describe the fast charge transfer process, taking place in the high frequency range. The second constant in low frequency arc is arises from a charge transfer intermediate adsorption [8, 9]. This result indicated the corrosion process was controlled mainly by the second time constant in the low-frequency region.

The values of the elements of the equivalent circuit obtained by fitting are given in Table 1.

The total resistance of the copper/electrolyte interphase R_p, includes Rt and Ra values and a real value of the finite diffusion at $\omega \rightarrow 0$ [14]. The total resistance of the system can be used as measure of the inhibiting efficiency.

Table 1 - Values of elements of the equivalent circuits in Fig 3a and fig 3b (after 30 min and 24 hour)

	after 30 min			*after 24 hour*		
	R_{pol} / Ω	C_{ds} / μFcm^{-2}	n	R_{pol} / Ω	C_{ds} / μFcm^{-2}	n
Na_2SO_4	749	19,1	0,77	2840	14,3	0,89
5-IPBDT	74930	5,8	0,93	206200	3,8	0,96
5-BDT	2729	11,1	0,89	3930	13,2	0,86
5-MBDT	10410	10,4	0,92	2100	13,4	0,89
5-TDT	5120	12,4	0,88	2063	26,7	0,86

At the beginning, the effect of investigated thiazole derivatives in copper protection revealed the increases in the total resistance (R_p) and decrease of the double layer capacitance in relation to blank solution. During the time, total resistance (R_p) increase in blank solution and in presence of 5-BDT and 5-IPBDT derivatives but in same time decrease in presence of 5-MBDT and 5-TDT derivatives. That means that the inhibitive efficiency of 5-MBDT and 5-TDT derivatives significantly decrease during the time.

The double layer capacitance during the time, decrease only in 5-IPBDT containing solution. Which indicates that in longer time only 5-IPBDT derivatives has protection efficience. This phenomenon can be explained that only this derivative can formed compact film on copper surface. Layer formed of other derivatives during the time becomes porous and less protective.

CONCLUSION

Four thiazole derivatives were investigated as potential copper inhibitors in acidic 0.1 moldm^{-3} Na_2SO_4 solution. Using potentiostatic polarization measurements it was obtained that in investigation range, concentration of 0.01mmoldm^{-3} has the best inhibitor efficiency in case of all investigated thiazole. All derivatives acts as catodic inhibitors hindered the oxygen reduction. The inhibitor efficiency decrease in the following order: 5-IPBDT> 5-BDT > 5-MBDT > 5-TDT. Using electrochemical impedance spectroscopic measurements an empirical model of electrochemical cell with two relaxation time constants was obtained. The effect of the investigated thiazole derivatives in copper protection is revealed the increase in the total resistance and decrease of the double layer capacitance compared with blank solution. Inhibitor film formed on copper surface was the highest quality in presence of 5-IPBDT derivatives. Only this derivative can protect copper against corrosion in acidic sulphate media during the time.

Acknowledgments

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IZVOD

ISPITIVANJE INHIBITORSKIH SVOJSTVA DERIVATA TIAZOLA NA KOROZIJU BAKRA

Ispitivana je inhibitorska efikasnost odabranih derivata tiazola u odnosu na koroziju bakra u kiseloj sredini snimanjem polarizacionih krivi i impedansnim merenjima. Određivana je zaštitna sposobnost sledećih organskim molekula: 5-benziliden-2,4-dioksotetrahidro-1,3-tiazol (5-BDT), 5-(4′-izopropil-benziliden)-2,4-dioksotetrahidro-1,3-tiazol (5-IPBDT), 5-(3′-teniliden)-2,4-dioksotetrahidro-1,3-tiazol (5-TDT) i 5-(3′,4′-dimetoksibenziliden)-2,4-dioksotetrahidro-1,3-tiazol (5-MBDT) u 0,1mol/dm^{-3} rastvoru Na_2SO_4 pri pH=2,95. Polarizaciona merenja ukazuju da svi ispitivani derivati tiazola smanjuju brzinu redukcije kiseonika, delujući kao katodni inhibitori korozije bakra kiselom u 0,1mol dm^{-3} rastvoru Na_2SO_4. U ispitivanom opsegu, koncentracija od 0,01 mmoldm^{-3} ima najveću inhibitorsku efikasnost kod svih ispitivanih derivata. Najbolja zaštita uočena je kod 5-IPBDT derivata. Merenja impedanse pokazuju da ispitivana jedinjenja formiraju film na površini bakarne elektrode koji je sposoban da štiti bakar od korozije u kiseloj sredini. 5-IPBDT derivat jedino formira dovoljno kompaktan film, koji može da štiti bakar od korozije u dužem vremenskom periodu.

Ključne reči: *inhibitori, korozija, bakar, svojstva*

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