

Corrosion inhibition of brass by thiocarbamides

K K Taha^a, B S Sheshadri^a, M F Ahmed^a & V S Muralidharan^{b*}

^aDepartment of Chemistry, Bangalore University, Central College Campus, Bangalore 560 001, India

^bCentral Electrochemical Research Institute, Karaikudi 630 006, India

Email: varagur@yahoo.com

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Thiocarbamides namely thiocarbamide (TC), ethylenethiocarbamide (ETC) and thiobenzamide (TBA) have been used as corrosion inhibitors for (70/30) brass in 0.1 M HClO₄. The inhibitor efficiency (% *P*) calculated using weight loss, Tafel line extrapolation, linear polarization and impedance methods has been found to be in the order: TBA > ETC > TC. Thiocarbamides adsorbed on the electrode surface inhibited the corrosion of brass. They adsorb following Flory-Huggins isotherms. The number of water molecules displaced was found to increase with molecular size. TC, ETC and TBA displaced 3, 4 and 10 molecules and caused a distortion at the metal solution interface. The inhibitor molecule may form complexes with the dissolved Cu and Zn ions. This may result in the formation of a film.

Keywords: Brass, Corrosion inhibition, Thiocarbamide, Perchloric acid

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Copper, zinc and their alloy (60/40, 70/30 brass) form the most important non-ferrous metals and alloys, widely used in industries and occupy position next to iron as far as commercial importance is concerned, due to their valuable mechanical properties. These materials corrode in corrosive environments especially oxidizing acids are more dangerous. The use of inhibitor to prevent corrosion is a standard practice. Despite a widespread use of inhibitors to control corrosion, still there is need for more comprehensive and systematic study to understand their mode of action. Precise understanding has become important.

Thiocarbamides¹⁻⁴ are well-known for their corrosion inhibition efficiency, especially on transition metals mainly due to the presence of sulphur atom, which has, a high electron density and can therefore easily bind to the metal surface. In thiocarbamides, the presence of α -NH₂ group will further contribute to stronger binding and to the enhanced inhibition³.

Experimental Procedure

Thiocarbamide (TC), ethylenethiocarbamide (ETC) and thiobenzamide (TBA) of analar grade were used without purification. Freshly distilled, double distilled water was used. A piece of (70/30) brass was cut in the form of a disk and fitted in Tygon tubing leaving

about 0.31 cm² area exposed to the corrosive medium. The electrode was polished successively on 200 and 400 emery papers, washed in running tap water, rinsed in distilled water before exposure to stirred 0.1 M HClO₄ and stirred 0.1 M HClO₄ containing 0.01 M of the thiocarbamide. The weight loss data was acquired by spectrophotometric estimation of Cu and Zn in the solution after two hours of immersion time. The experiments were carried out at 293±0.02 K using a thermostat. The polarization (Tafel and linear) and cyclic voltammetric (CV) experiments were carried out using TACUSSEL Potentiostat PR T(10-0.5) driven by a signal generator type GSTP-3. A three compartment cell with brass as working electrode, platinum foil and saturated calomel electrode as counter and reference electrodes respectively, were used for polarization studies. For CV studies the working electrode was the platinum electrode. The CV studies were performed in the potential range of 500 to -500 mV (vs SCE) for CuSO₄ and 0 to -1000 mV for ZnSO₄ with scan rate of 5 mV/s. The FT-IR studies for the pure inhibitors and the scrapping of their films formed on brass after 24 h of exposure, were made in KBr pellet and subjected to IR study using Nicolet Impact 400D, FT-IR spectrophotometer having 4 cm⁻¹ resolution. The A.C. impedance measurements were performed using an electrochemical system SI 1280 B

(SOLARTRON UK) at corrosion potentials over a frequency range of 10 kHz to 0.01 Hz with signal amplitude of 10 mV. The scanning electron micrographs of the polished brass and brass surface after exposure to 0.1 M HClO₄ alone and 0.1 M HClO₄ containing 0.01 M of each inhibitor was taken using scanning electron microscope model JEOL JSM-5600 LV interfaced to a computer and JSM software. For EDAX studies calibration was done with respect to Co K α = 6.9254 keV and Co L α = 0.7763 keV.

Results and Discussion

Corrosion rates and other parameters for brass in presence and absence of 10⁻³ M of each thiocarbamides are given in Tables 1-3. The % P = [(w₀ - w) / w₀] × 100, where w₀ and w are the corrosion rates in absence and presence of inhibitors is given in Table 1. The relative inhibitor efficiency was found to be in the order of TBA > ETC > TC. The Tafel polarization curves for brass are given in Fig. 1. The corrosion potential was found to be nobler in presence of thiocarbamides. The polarization curves in presence of inhibitors shifted to higher potential values in cathodic and anodic direction with a change in Tafel slopes. Thiocarbamides were found to inhibit both cathodic and anodic reactions. The polarization curves for the corrosion of brass samples (Fig. 1) not only shift to higher potential values in cathodic and anodic direction but are also accompanied by a change in Tafel slopes. The % P = [(i_{corr'} - i_{corr}) / i_{corr}] × 100 where i_{corr'} and i_{corr} are corrosion current density in absence and presence of inhibitors. The relative inhibition efficiency was found to be in the order: TBA > ETC > TC.

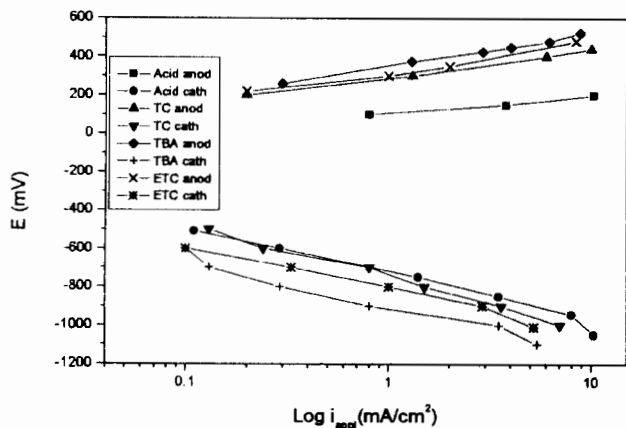


Fig. 1— Polarization curves for brass in HClO₄ containing thiocarbamides

Figure 2 represents the linear polarization curves in presence and absence of inhibitors. R_p values increased considerably in presence of thiocarbamides. Using Stern-Geary equation, i_{corr} was calculated. They decreased in presence of thiocarbamides. The % P was found to be in the order: TBA > ETC > TC. The

Table 1—Corrosion rate and % P for brass in 0.1 M HClO₄ and acid containing 0.001 M thiocarbamides

Medium	Brass	
	Wt. loss(mg/cm ² /h)	% P
0.1 M HClO ₄	0.758	-
0.1 M HClO ₄ + TC	0.215	71.6
0.1 M HClO ₄ + ETC	0.120	84.2
0.1 M HClO ₄ + TBA	0.051	93.2

Table 2—Corrosion parameters for brass in HClO₄ and HClO₄ containing 0.001 M thiocarbamides

Medium	E _{corr} (mV)	β _a (mV/dec)	B _{ba} (mV/dec)	i _{corr} (μA/cm ²)	% P
0.1 M HClO ₄	-150	37	117	52	-
0.1 M HClO ₄ + TC	-105	49	119	14	73.1
0.1 M HClO ₄ + ETC	-100	55	123	8.4	83.8

Table 3—Corrosion parameters for brass in stirred 0.1 M HClO₄ and acid containing thiocarbamides at 25°C by linear polarization

Medium	R _p Ω	i _{corr} (μA/cm ²)	% P
0.1 M HClO ₄	1000	38.6	-
0.1 M HClO ₄ + TC	2080	22.97	40.5
0.1 M HClO ₄ + ETC	3490	14.82	61.6
0.1 M HClO ₄ + TBA	11500	6.28	87.8

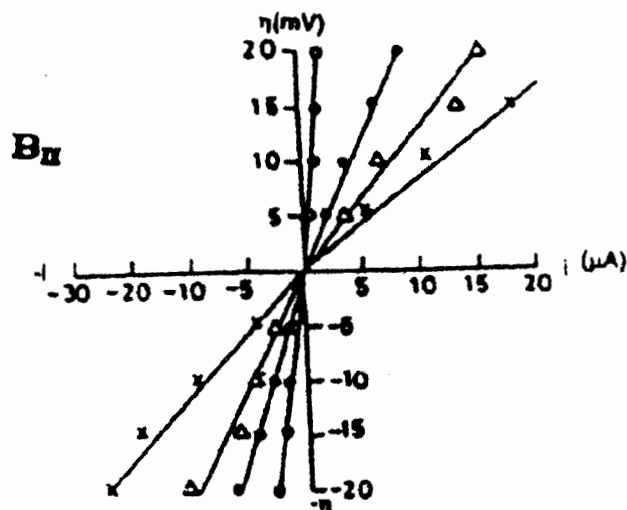


Fig. 2— Linear polarization of brass in 0.1 M HClO₄ (x), and the acid containing TC (Δ), TEC (●) and TBA (○)

Nyquist and Bode plots for brass in presence of thiocarbamides (Fig. 3) revealed semicircular loops which loose their shape in the presence of thiocarbamides. The appearance of an additional loop at higher frequency in Bode plots suggest an adsorption of the organics and the formation of a film. This adsorption caused the distortion in the semicircular loops^{4,5}. The charge transfer resistance values were found to increase for inhibitors while capacitance values decreased (Table 4). i_{corr} values decreased and % P was found to be in the order TBA > ETC > TC.

Thiocarbamides inhibit the corrosion of brass in HClO₄. They retard the anodic and cathodic reactions by adsorption on the surface. If % P is taken as the extent of adsorption “θ”. A relationship between θ and concentration of thiocarbamides will explain the adsorption isotherm.

The Florry Huggins adsorption isotherm⁶ suggest the relation,

$$\left\{ \frac{\theta}{e^{n-1}(1-n)^n} \right\} = \frac{C_{org} \exp \left\{ \frac{-\Delta G_a}{RT} \right\}}{55.4}$$

where constants have usual meaning.

Figures 4a-c present the adsorption isotherms for TC, ETC and TBA respectively. The ‘n’ number of

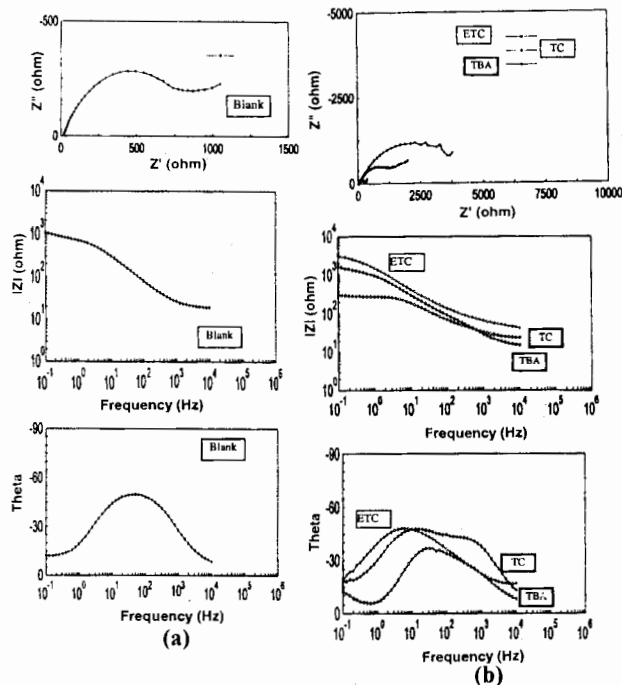


Fig. 3—Nyquist and Bode plots for brass (a) in HClO₄ and (b) in 0.1 M HClO₄ containing thiocarbamides

Table 4—Corrosion parameters brass in stirred 0.1 M HClO₄ and acid containing thiocarbamides at 25°C by EIS

Medium	R_{ct} Ω	C_{dl} μF/cm ²	i_{corr} (μA/cm ²)	%P
0.1 M HClO ₄	900	629	42.84	-
0.1 M HClO ₄ + TC	2450	-	19.11	55.4
0.1 M HClO ₄ + ETC	3920	514	13.54	68.4
0.1 M HClO ₄ + TBA	11700	424	5.14	88.0

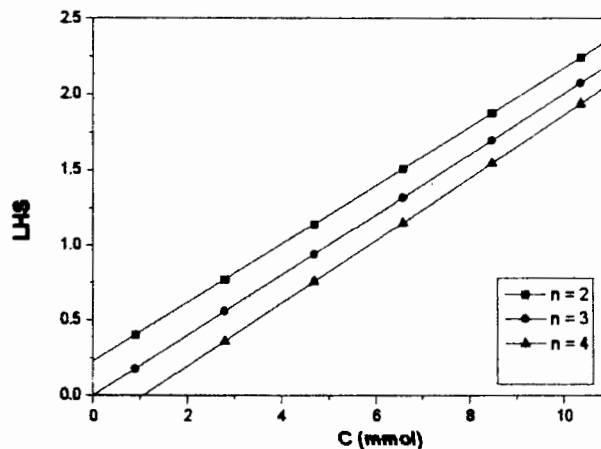


Fig. 4a—Flory-Huggins adsorption isotherm for TC on brass

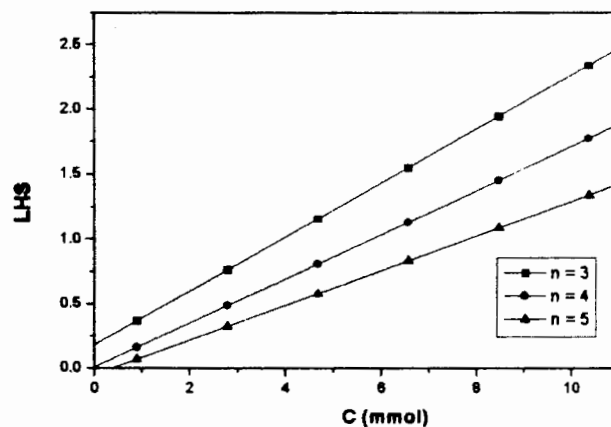


Fig. 4b—Flory-Huggins adsorption isotherm for ETC on brass

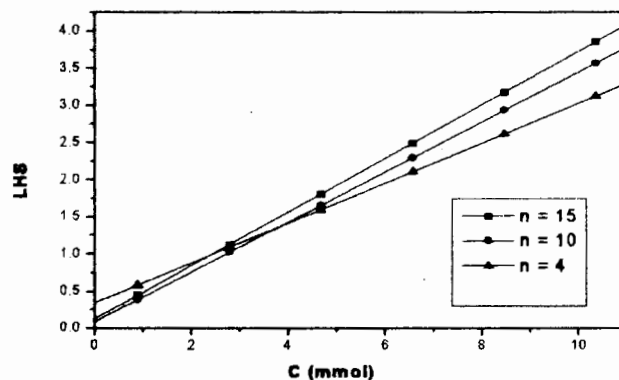


Fig. 4c—Flory-Huggins adsorption isotherm for TBA on brass

water molecules displacement were found to be 3, 4 and 10 for TC, ETC and TBA respectively. Using the 'n' value ΔG_a was calculated for a given temperature, ΔS_a was obtained from the slope ΔG_a versus T graph (Fig. 5). Gibbs-Helmholtz relation was used to calculate the enthalpy of adsorption (Table 5). The increase in the ΔG_a in presence of inhibitors, suggest the spontaneous adsorption on brass surface. The ΔS_a increased in presence of thiocarbamides and TBA was found to exhibit higher value. The increase in ΔS_a suggest an increase in the disorderliness at the metal solution interface. The displacement of water molecules and their removal caused a decrease in capacitance and the re-orientation of the interface.

Structure and inhibition

The structures of thiocarbamides studied are given in Fig. 6: Thiocarbamide has three heteroatoms (two N and one S). These heteroatoms have an ability to coordinate with transition metals such as Cu and Zn via the empty p - or d -orbitals of heteroatoms in

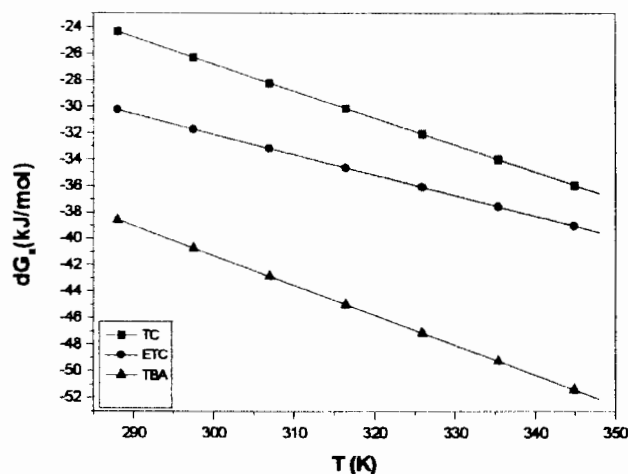


Fig. 5—Plot of G^0 versus temperature for various thiocarbamides

inhibitor molecule and d -orbitals of transition metals^{7,8}. The tendency of S atom to form stronger coordination bond is on the basis of electronegativity grounds. The shift in C=N, C-N, C-S and N-H stretching frequencies obtained for the inhibitor-alloy films when compared to those for pure compounds (Table 6), confirm that the TC is chemisorbed on the surface through these links. The relatively enhanced inhibitor efficiency obtained with ETC can be explained due to the change from an open chain TC to a cyclic ETC³ and the replacement of two primary amines in the former, by two secondary amines in the latter. These in addition to the increase in molecular size due to the two $-CH_2-$ groups, relatively enhance the binding and surface coverage of the molecule leading to increased inhibition. The presence of benzene ring as in the case of TBA⁷ may lead to stronger bonding through the overlap of the π -orbitals of the benzene ring with the metal d -orbitals resulting in firmer adsorption. This is supported by the larger shift in the stretching frequencies and bending modes seen in IR data⁸ (Table 6 and Figs 7a & b). The presence of the benzene ring also increases the size of the molecule leading to greater surface coverage by its adsorption⁸. This is evident from different values of 'n' namely 10, 4 and 3 obtained for TBA, ETC and TC respectively. The relative order of inhibitor efficiency observed agrees with the size factor. This contention is further substantiated by the CV studies (Table 7 a & b). The cyclic voltammograms

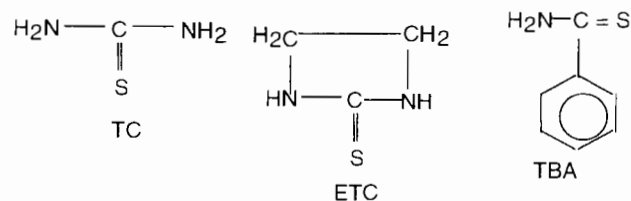


Fig. 6—Structures of thiocarbamides

Table 5—Free energy of adsorption (ΔG_a), Entropy of adsorption (ΔS_a), Enthalpy of adsorption (ΔH_a) and Energy of activation (ΔE_a) values for the adsorption of inhibitors on brass from 0.1 M $HClO_4$ containing 0.001 M thiocarbamides.

Inhibitor [M]	Thermodynamic Parameters	Temperatures					
		293K	303K	313K	323K	333K	343K
TC	ΔG_a kJ/mol	-24.4	-28.6	-29.3	-32.1	-33.1	-35.4
	ΔS_a J/K/mol	150					
	ΔH_a kJ/mol	19.6	16.9	17.7	16.3	16.9	16.1
ETC	ΔG_a kJ/mol	-31.7	-34.1	-33.9	-35.4	-37.1	-39.2
	ΔS_a J/K/mol	188					
	ΔH_a kJ/mol	23.2	22.7	24.8	25.2	24.7	25.2
TBA	ΔG_a kJ/mol	-40.0	-43.4	-43.2	-46.3	-46.0	-51.2
	ΔS_a J/K/mol	227					
	ΔH_a kJ/mol	26.5	25.4	27.9	27.1	29.0	26.7

Table 6—IR spectral data for thiocarbamides and their films formed on brass in 0.1 M HClO₄
v/cm⁻¹

ETC	TC + brass	Assignment	ETC	ETC +brass	Assignment	TBA	TBA + brass	Assignment
3240	3421	v NH ₂	3270	3359	v NH ₂	3364, 3291	3431	Amide – NH ₂ Pair
2955	2940	v C-H	2955 2878	2893	v C-H	3162	2852 2919	v C-H
2883	2862	v C-H	2572	-	v C-H	2759	-	v C-H
2572	2360	v C-H	1522	1528	v C=N Amide I	1631	1641	v ring
1528	1466	Amide I	1502	-	δN-H in-plane	1491	-	δNH in-plane
1284	1380	v N-CS-N<	1372	1326		1450	1388	v C=N Amide I
1316	1290	V _{C-N} , δ _{N-H} Amide II	1502 1471	-	δN-H in-plane	1326	-	v C-N Amide II
1502	1466	δN-H in plane	1316 1207 1119	-	v C-N Amide II in plane δCH	1134		BZ in-plane δCH
-	467	M – S	1000		Thiamide III	1072		BZ in-plane δCH
-	1025	ClO ₄ ⁻	- 690 617	1109 - 455	ClO ₄ Out-of-plane δCH M – S	1000 772 690 576		Thioamide III BZ out -of- plane bend v C-S NH wag
							1119 452	ClO ₄ ⁻ M – S

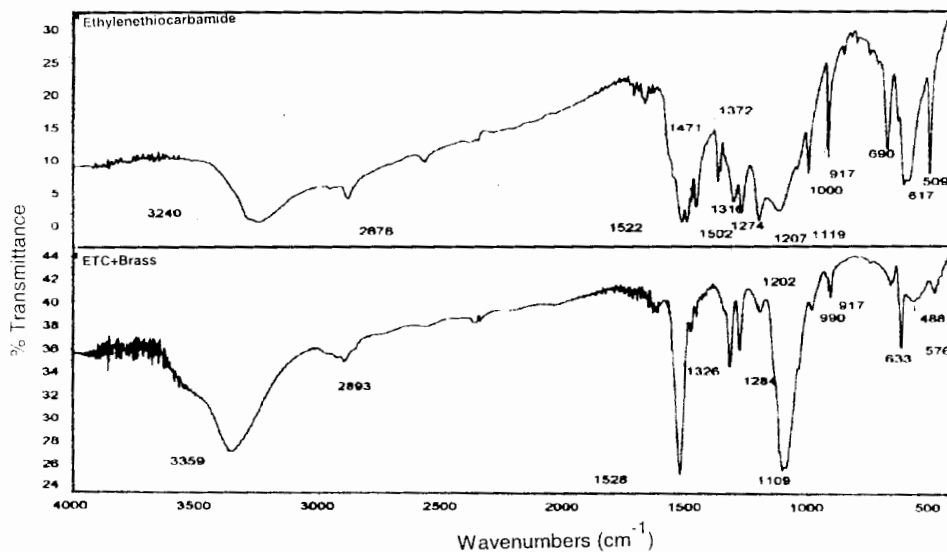


Fig. 7a— Stacked IR spectra of ETC and its film on brass

revealed that the anodic and cathodic peak potentials for Cu and Zn undergo shift in negative and positive directions respectively, and the cathodic and anodic current decrease (except for ETC) in intensity in the presence of inhibitors may also be attributed to complexation of Cu and Zn with inhibitor molecules (Fig. 8). The surface films on brass as seen from SEM images (Fig. 9a-d)

when compared with the corroded surface may lead to reduction of the corrosion process. The surface composition of the alloy exposed to inhibitors, as determined from EDAX spectrum (not shown) exhibited the presence of significant amounts of “S” and “N” which may support the arguments that there is strong chemisorption of inhibitors on the surface of brass.

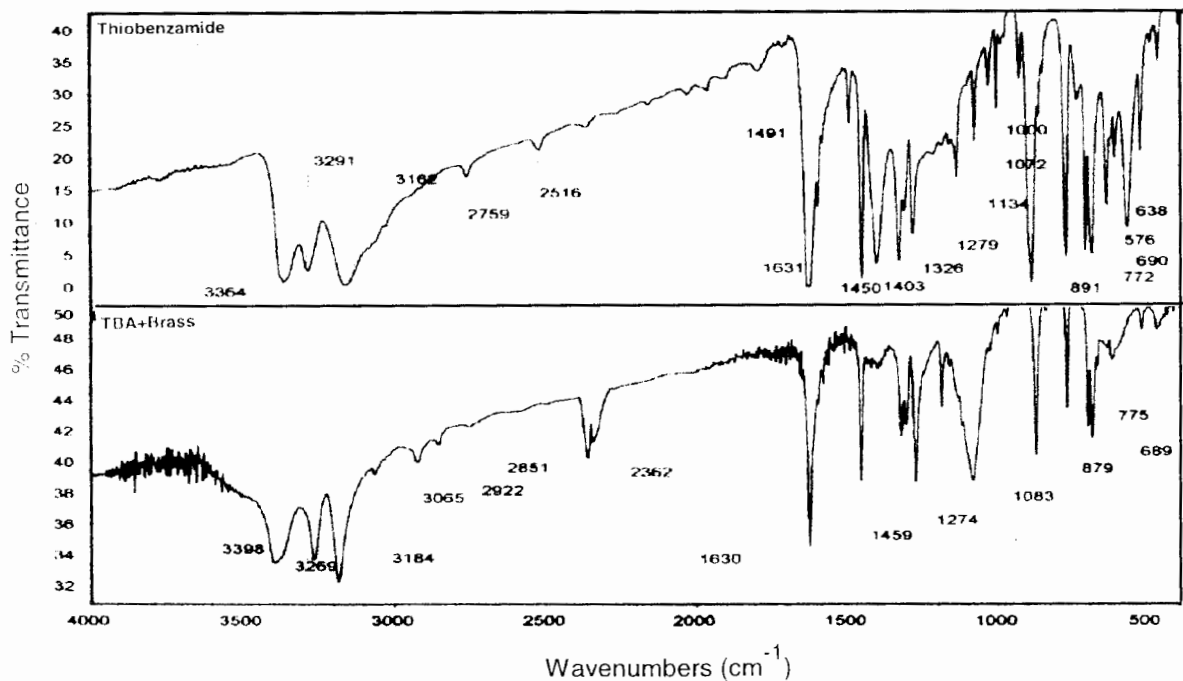


Fig. 7b— Stacked IR spectra of TBA and its film on brass

Table 7 a—Peak potentials (E_p) and peak currents (I_p) from the cyclic voltammograms of 2 mM CuSO_4 and 2 mM CuSO_4 containing optimum concentrations thiocarbamides recorded at a scan rate of 5 mV/s.

Medium	Cathodic response			
	Peak I		Peak II	
	E_{Pc1} (mV)	I_{Pc1} (μA)	E_{Pc2} (mV)	I_{Pc2} (μA)
CuSO_4	0	-2.0	-200	-40.0
..+TC	-80	-2.0	-240	-2.0
..+ETC	250	-2.0	-	-
..+BTA	-40	-0.8	-180	-1.0
Medium	Anodic response			
	Peak I		Peak II	
	E_{Pa1} (mV)	I_{Pa1} (μA)	E_{Pa2} (mV)	I_{Pa2} (μA)
CuSO_4	100	28.0	-100	80.0
..+TC	20	6.0	-280	24.0
..+ETC	470	84	-	-
..+ETC	420	30.0	260	13.6
..+BTA	400	0.40	-20	0.8

Table 7 b—Peak potentials (E_p) and peak currents (I_p) from the cyclic voltammograms of 2 mM ZnSO_4 and 2 mM ZnSO_4 containing optimum concentrations of thiocarbamides recorded at a scan rate of 5 mV/s

Medium	Cathodic response		Anodic response	
	E_{Pc} (mV)	I_{Pc} (μA)	E_{Pa} (mV)	I_{Pa} (μA)
ZnSO_4	-500	-9.0	-400	9.0
..+TC	-625	-8.0	-480	2.4
..+ETC	-580	-36.0	-	-
..+BTA	-720	-0.8	-	-

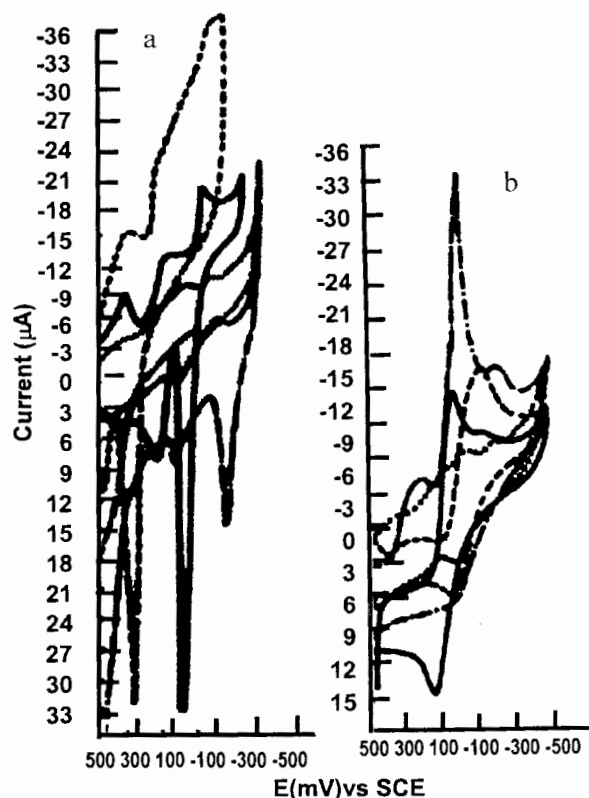


Fig. 8—(a) CV of 2 mM of CuSO_4 (—), CuSO_4 + TC (---), CuSO_4 + ETC (....), CuSO_4 + TBA (— · —) and (b) CV of 2 mM of ZnSO_4 (—), ZnSO_4 + TC (---), ZnSO_4 + ETC (....), ZnSO_4 + TBA (— · —)

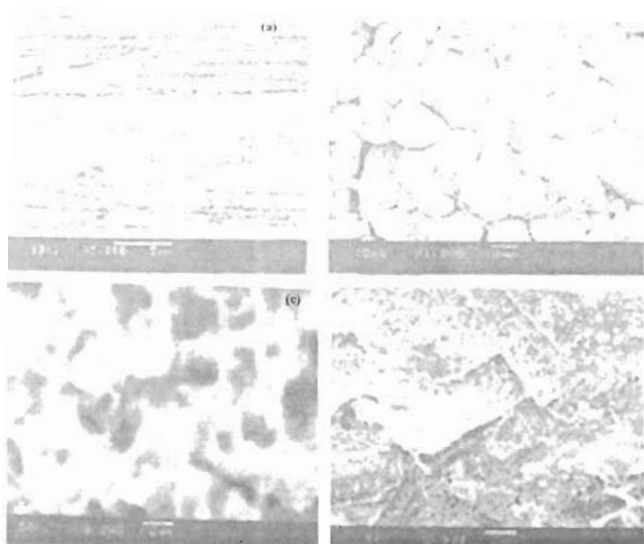


Fig. 9— SEM of a-polished brass surface, b-corroded surface, c-TC film on brass and d-TBA film on brass

Conclusions

Thiocarbamides are adsorbed on the electrode surface and inhibit the corrosion of brass. They adsorb

following Flory-Huggins isotherms. The number of water molecules displaced was found to increase with molecular size. TC, ETC and TBA displaced 3, 4 and 10 molecules and caused a distortion at the metal solution interface. The inhibitor molecule may form complexes with the dissolved Cu and Zn ions. This may result in formation of film.

References

- 1 Jing Chi, Lin Shipcizhon, Yi Ping Wang & Hong Jun Chess, *JPN, Kolcai Tokkvo Koho*, Jp. 11269674 A/ (Oct 1999) 16.
- 2 Stoyanova A, Raicheva S & Sokolava E. *In Symp Electrochem and Inhibitor Protection from Corrosion, Albena, Bulgaria*, 11-14 Oct 1989.
- 3 Raicheva S N, Aleksiev B V & Sokolova E I. *Corr Sci*, 34 (1993) 343.
- 4 Juttner K, *Electrochim Acta*, 35 (1990) 1501.
- 5 Mansfeld F, *Electrochim Acta*, 35 (1990) 1523.
- 6 Flory P J, *J Chem Phys*, 10 (1945) 51.
- 7 Higgins M L, *Ann NY Acad Sci*, 4 (1942) 31.
- 8 Antonia E Stoyanova & Sigrid D Peycrimhott, *Electrochim Acta*, 47 (2000) 1365.
- 9 Rao CNR, *Chemical Application of Infrared Spectroscopy* (Academic Press, NY), 1963, 330.