Asian Journal of Chemistry; Vol. 24, No. 1 (2012), 47-52

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Corrosion Inhibition Efficiency of Benzimidazole and Benzimidazole Derivatives for Zinc, Copper and Brass

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(*Received*: 28 September 2010; *Accepted*: 9 September 2011) AJC-10368

In this study, 1*H*-benzimidazole, (BIM), 2-methyl-1*H*-benzimidazole (2-CH_3BIM), 5-nitro-1*H*-benzimidazole [5(6)-NO_2BIM] and 5(6)-dinitrobenzimidazole (5,6-diNO_2BIM) were investigated as corrosion inhibitors of copper, zinc and brass in alkaline and neutral media. The inhibition efficiency was calculated by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The frequency range studied was $1\times10^{+5}$ -1×10^{-1} Hz. Surface of the zinc, cupper and brass electrodes were polished with sand paper and etched in 0.15 M HCl solution for 20 s and than immersed in study solutions. Under the experimental conditions, the efficiency of these inhibitors increases in the order BIM > 5(6)-NO_2-BIM >5,6-diNO_2BIM >2-CH_3-BIM in alkaline media (pH:13) and 2-CH_3-BIM >5(6)-NO_2-BIM > BIM in the 0.5 M NaCl the solution.

Key Words: Corrosion, Benzimidazole derivatives, Copper, Zinc, Brass.

INTRODUCTION

Large number of organic compounds are effective inhibitors of the corrosion of many metals and alloys in neutral, alkaline and in acidic media[1-4]. These compounds are generally more environmentally friendly than inorganic corrosion inhibitors and, there is always a need for developing new organic corrosion inhibitors. The benzimidazoles useful structural model in the investigation of the molecules having pharmaceutical or biological activities and some benzimidazole derivatives have been used as antiulcers, antihypertensives, antivirals, antifungals, anticancers and antihistaminics[5-7].

The efficiency of an inhibitor is generally dependent on its molecular structure. Presence of heteroatoms with free electron pairs, aromatic rings with delocalized π electrons and some substituent groups improves inhibition efficiency. Heterocyclic compounds containing nitrogen, sulphur or oxygen atoms are often used for protection metals against corrosion.

Among these, benzimidazole and its derivatives were investigated intensively as effective inhibitors, particularly for copper and zinc. Some of these compounds are known also as inhibitors of general selective corrosion (dezincification) of brass in aqueous solutions.

Benzimidazole (BIM) is a heterocyclic aromatic organic compound. It contains two nitrogen atoms: at the 1-position in the molecule, a pyrrole type nitrogen atom whose unshared electron pair participates in imidazole π electron system and at the 3-position in the molecule, a pyridine type nitrogen atom whose unshared electron pair is free.

The present study is aimed to investigate the efficiency of benzimidazole, (BIM), 2-methyl-1*H*-benzimidazole (2-CH_3BIM) and 5(6)-nitro-1*H*-benzimidazole (5-NO_2BIM) as corrosion inhibitors for copper, zinc and brass in neutral, alkaline and acidic media (Fig. 1). An attempt was also made to clarify the effect of substituents on the inhibition efficiencies of studied molecules.

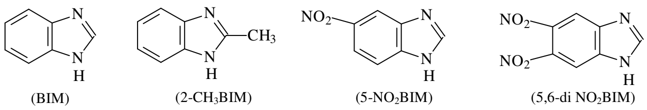


Fig. 1. Molecular structure of BIM, 2-CH_3BIM and 5-NO_2BIM, 5,6-di NO_2BIM

Corrosion inhibition efficiency of benzimidazoles is the same of the other heterocyclic compounds[8]. It has the physical and analytical data of prepared compounds given in Table-1. It is a general assumption that the adsorption of the organic inhibitors at the metal/surface interface is the first step in the mechanism of the inhibitor action and the inhibition efficiency depends to the adsorption properties[9,10]. The adsorption of these molecules can be described by the physisorption or the chemisorption. The physisorption is involved on electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at metal/solution interface. The chemisorption is involved on charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond. It is evident that benzimidazole molecule shows two convenient sites which are the pyridine type nitrogen atom with its *sp*^{2} electron pair and the aromatic rings suitable for the partial shift of electronic density of the molecule to surface of metal[11,12]. The pyridine type nitrogen atom, which gives the basic character to benzimidazole is protonated in acidic media and they become cations, existing in equilibrium with the molecular form.

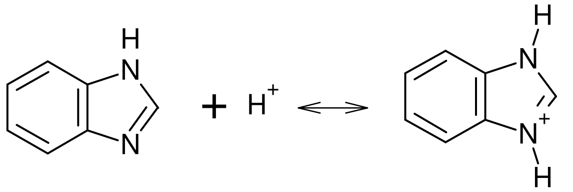


TABLE-1
THE PHYSICAL AND ANALYTICAL DATA OF PREPARED COMPOUNDS

Compounds	Formula	Molecular mass (gmol^{-1})	Melting point (°C)	Solvent
BIM	$C_7H_6N_2$	118.4	171-173	Ethanol-wather
5-NO_2 BIM	$C_7H_5N_3O_2$	163.14	205-207	Ethanol-wather
2-CH_3 BIM	$C_8H_8N_2$	132.17	175-177	Ethanol-wather
5,6- di NO_2 BIM	$C_7H_4N_4O_4$	208.131	232-233	Ethanol-wather

The protective properties of benzimidazole as inhibitors depends also on the substitution on the heterocyclic ring. This means that the inhibition effect can be determined by inductive (I), mesomeric (M) and steric effects of the substituents. The electron-donating substituent groups, such as methyl group -CH_3, having +I and +M effect, increase the negative charge on the benzimidazole ring and would strengthen the interaction with the metal surface. The electron-withdrawing substituent groups, such as nitro groups -NO_2 having both -I and -M effect, increase the positive charge of the reaction center and weaken this interaction. Benzimidazole is commercially available but the usual synthesis involves condensation of *o*-phenylenediamine with formic acid. By altering the carboxylic acid, this method is generally able to afford 2-substituted benzimidazole[13-16].

EXPERIMENTAL

A cylinder pure zinc rod (aldrich, 99.99 % purity, 5 mm diameter), copper (aldrich, 99.99 % purity, 3 mm diameter) and brass ($Cu_{60}Zn_{40}$) were fixed in the Teflon tube with adhesive (Fig. 2). The working electrode was polished with emery papers with 1200 grit etched in 0.15 M HCl solution for 20 s and washed with double distilled water before the experiments. The current-time (20 min), current-potential (scan rate 1 mV/s) and EIS curves were performed by constituted CH-instruments 660B potentiostat, electrochemical work station of computer programme, BAS disc electrode, poly science model 9106 thermostat system using a saturated Ag/AgCl (sat. KCl) as reference and platinium wire as counter electrode. The impedans measurements were performed at the open circuit potential of working electrode with voltage perturbation amplitute of 5 mV in a frequency range between 100 kHz and 0.1 Hz. The inhibition efficiency and capacitance (C) of benzimidazole and benzimidazole derivatives were calculated from the following equation,

$$\mathrm{IE}(\%) = \frac{I_{Corr} - I'_{Corr}}{I_{Corr}} \times 100 \quad (1)$$

$$C = \frac{1}{2\pi f (Z_{im(max)}) R_p} \quad (2)$$

where I_{Corr} and I'_{Corr} are corrosion current densities of the uninhibited and inhibited solutions, respectively, f is the frequency of EIS impedance and R_p is the polarization resistance, respectively.

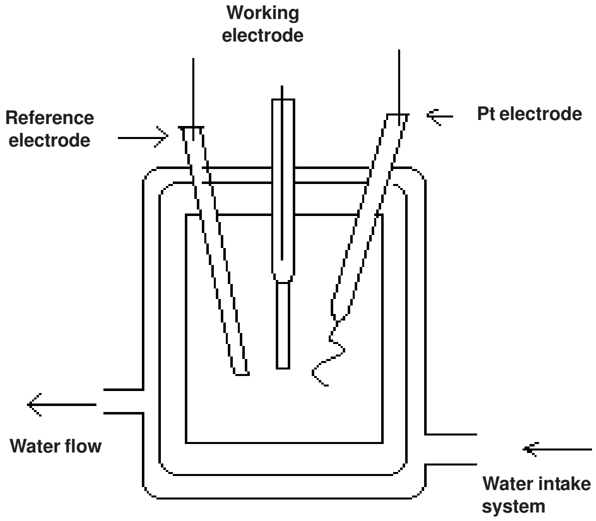


Fig. 2. The cell system.

RESULTS AND DISCUSSION

Electrochemical impedance spectroscopy (EIS) and current-potential curves obtained in neutral and alkaline solutions by the electrochemical methods for zinc, copper and brass were given in Fig. 3-8. Corrosion parameters, such as corrosion potential (E_{corr}), cathodic (b_c) and anodic (b_c) Tafel slopes, capacitance (C) and corrosion current density (I_{corr}) and inhibition efficiency IE (%) calculated from these curves are listed in Tables 2 and 3. The inhibition potentials mesured in experiments proved that the investigated derivatives of benzimidazole were manifested as a anodic inhibitors. Because, corrosion potentials were changed at the positive direction (Table -3). This means that their corrosion inhibition can be connected with their adsorption onto metal surfaces through nitrogen atoms. So, in alkaline media, the increased electronic density at pyridine nitrogen in particular will affect the coulomb type of adsorption. Furthermore, the NH group of the benzimidazole ring is weakly basic and also relatively strongly acidic. The nitro group, in position 5(6) of the heterocyclic ring affect acidity and consequently, nitrobenzimidazoles are more strongly dissociated in solution leading enhancement of the protective properties of benzimidazoles due to the formation of an ionic bond between metal and the inhibitor as a protective

TABLE-2
CORROSION PARAMETERS FOR THE ZINC, COPPER AND BRASS IN 0.5M NaCl SOLUTION CONTAINING 10^{-3} M BIM, 5(6)-N BIM AND 2-M BIM AT 25 ºC

Neutral media	E_{corr} *vs.* Ag/AgCl (V)	$-b_c$ (mV dec^{-1})	b_a (mV dec^{-1})	I_{corr} (μA cm^{-2})	IE (%)	C (F cm^{-2})
Zinc						
Blank	-1.066	47	306	46.5	-	0.9×10^{-5}
BIM	-0.971	52	427	54.6	-	1.57×10^{-5}
5-NO_2 BIM	-0.938	138	534	118	-	1.70×10^{-5}
2-CH_3 BIM	-0.992	18	269	19.7	57	1.90×10^{-5}
Copper						
Blank	-0.159	446	63	7.6	-	9.455×10^{-5}
BIM	-0.208	133	51	1.4	82	2.534×10^{-5}
5-NO_2 BIM	-0.195	131	50	1.2	84	2.266×10^{-5}
2-CH_3 BIM	-0.188	307	231	0.4	95	0.196×10^{-5}
Brass						
Blank	-0.184	1502	130	4.5	-	6.931×10^{-6}
BIM	-0.166	230	75	2.6	42	5.516×10^{-6}
5-NO_2 BIM	-0.128	260	341	4.7	-	1.930×10^{-4}
2-CH_3 BIM	-0.206	310	77	6.6	-	2.863×10^{-5}

TABLE-3
CORROSION PARAMETERS FOR THE ZINC, COPPER AND BRASS IN 0.4M NaCl + 0.1M NaOH SOLUTION CONTAINING 10^{-3} M BIM, 5(6)-N BIM, 5,6-diN BIM AND 2-M BIM AT 25 ºC

Alkaline media	E_{corr} *vs.* Ag/AgCl (V)	$-b_c$ (mV dec^{-1})	b_a (mV dec^{-1})	I_{corr} (μA cm^{-2})	IE (%)	C (F cm^{-2})
Zinc						
Blank	-1.368	191	120	174	-	3.94×10^{-3}
BIM	-0.936	196	265	36.5	79	1.87×10^{-5}
5-NO_2 BIM	-0.745	320	393	34.0	81	1.18×10^{-5}
2-CH_3 BIM	-0.889	250	221	35.0	80	1.23×10^{-5}
5,6-dinitro BIM	-0.690	243	323	24.0	86	0.12×10^{-5}
Copper						
Blank	-0.194	324	286	41	-	18.8×10^{-5}
BIM	-0.180	206	312	1.5	96	0.83×10^{-5}
5-NO_2 BIM	-0.206	158	127	2.0	95	2.40×10^{-5}
2-CH_3 BIM	-0.170	185	255	3.0	93	2.02×10^{-5}
5,6-dinitro BIM	-0.160	201	195	2.5	94	2.60×10^{-5}
Brass						
Blank	-0.437	483	136	118	-	2.11×10^{-4}
BIM	-0.273	206	335	3.0	97	0.53×10^{-5}
5-NO_2 BIM	-0.344	238	113	4.5	96	3.34×10^{-5}
2-CH_3 BIM	-0.319	262	892	9.0	92	3.43×10^{-5}
5,6-dinitro BIM	-0.274	253	208	6.5	94	3.14×10^{-5}

layer on the metal surface. On the other hand, the addition of methyl group to benzimidazole ring particularly at position 2 leads to the increased the electron density over that of benzimidazole ring and the adsorption onto metal surfaces through nitrogen atoms is hindered. Thus 5(6)-1*H*-nitrobenzimidazole should be a better inhibitor than 2-methyl-1*H*-benzimidazole which is in fact experimentally verified.

The metal surface is positively charged and the interaction with the protonated species would be restricted in acidic media. This results in reduced inhibition efficiencies of substituted benzimidazole derivatives in acid solutions. In neutral solution, the inhibition is based on the adsorption of molecules on metal surface and particularly formation of protective complex. Introduction of groups influences the efficiency but not the inhibition mechanism. As a electron-withdrawing substituent, the nitro group decrease the electron density of the benzimidazole ring and the participation of this molecule in complexation is hindered and contrary, the methyl group enhances the ability of the ligand to interact with metal which forms coordinative bonds with atoms able to donate electrons (Table-3). So, the methylated derivatives are expected to exhibit good inhibitive properties. The experimentals results obtained show also that the derivatives of benzimidazole have not the same inhibition effect on the different metals. 5(6)-1*H*-nitrobenzimidazole is a more efficient inhibitor of copper and brass but a weaker inhibitor of zinc and; 2-CH_3-BIM is an efficient inhibitor of zinc (Figs. 3-8 and Table-3). This opposite effect of substituents on the corrosion efficiency can be due to the stability of the metal complexes. The copper complexes formed by σ bonds and those of zinc formed by π bonds. It is clear that increasing of the electron density of the benzimidazole ring facilitated the formation of the zinc complexes.

It is known that 5-nitro-1*H*-benzimidazole is more efficient inhibitor of copper but a weaker inhibitor of zinc and electron donating substituents increase the protection of zinc, whereas electron withdrawing substituents increase that of copper depending on the ability of zinc and copper to form σ- and π-bonds in complexes[4]. In fact, when considering the

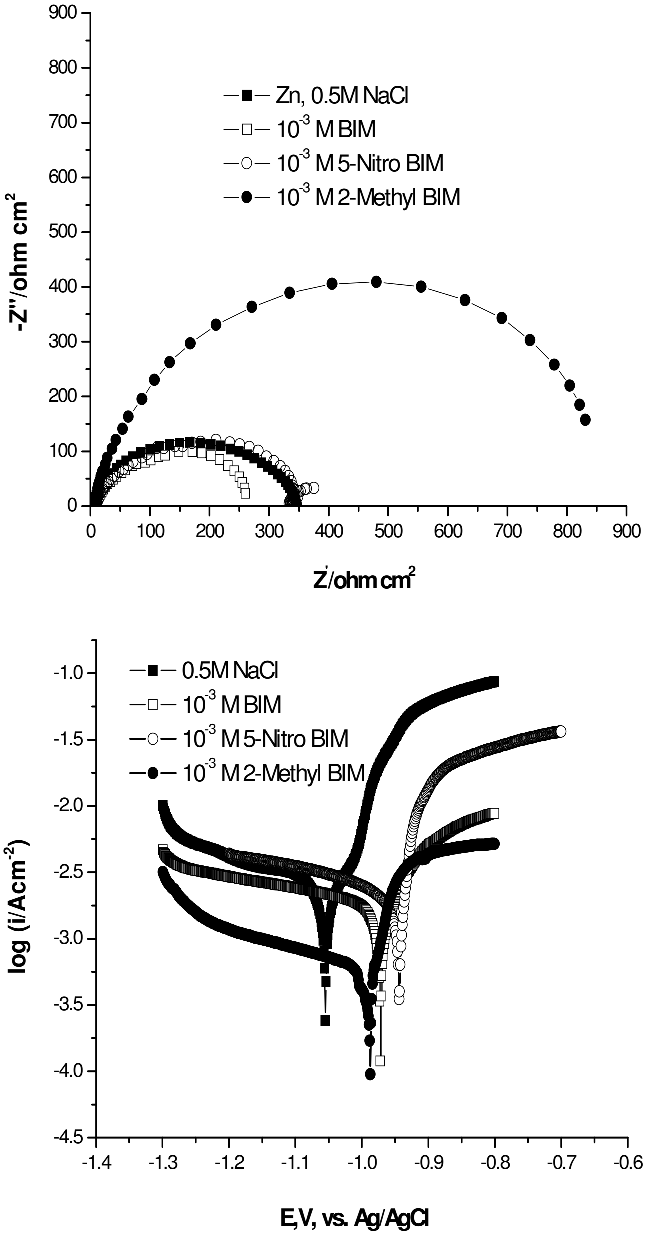
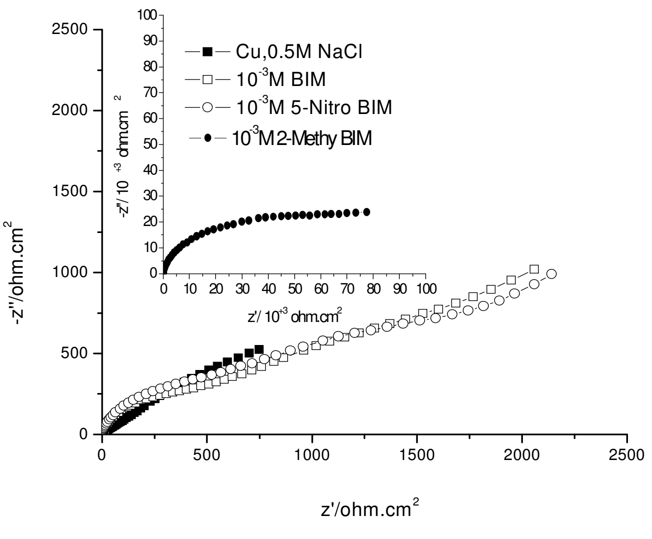


Fig. 3. EIS and current-potential curves of zinc for benzimidazole derivatives in 0.5 M NaCl solution



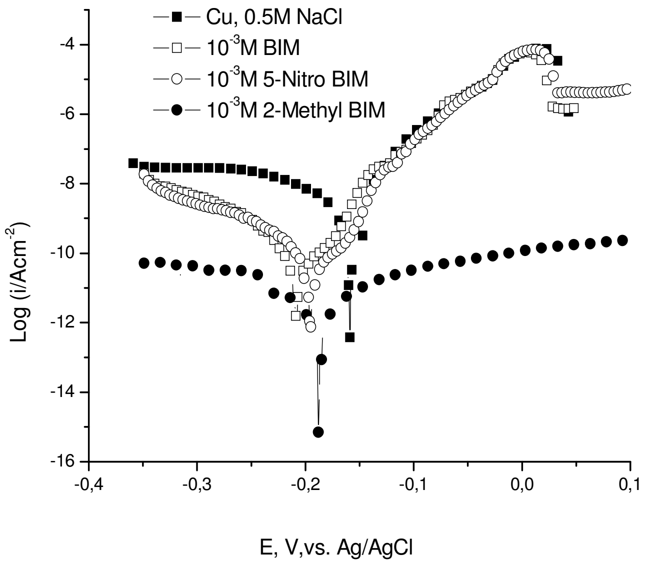


Fig. 4. EIS and current-potential curves of copper for benzimidazole derivatives in 0.5 M NaCl solution

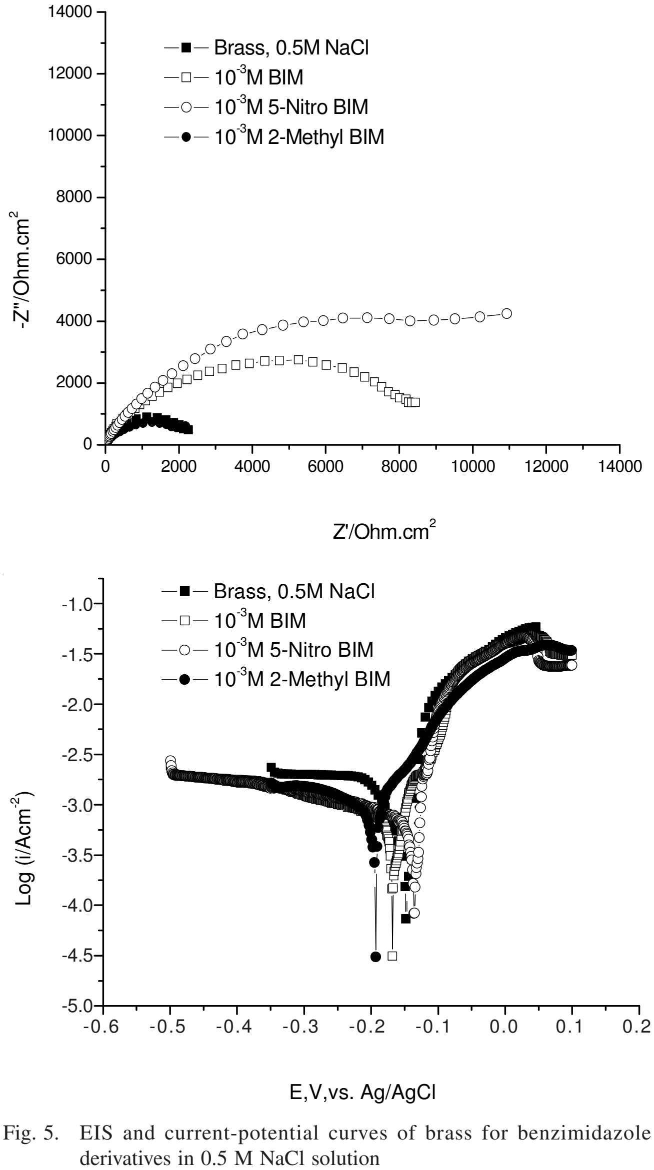


Fig. 5. EIS and current-potential curves of brass for benzimidazole derivatives in 0.5 M NaCl solution

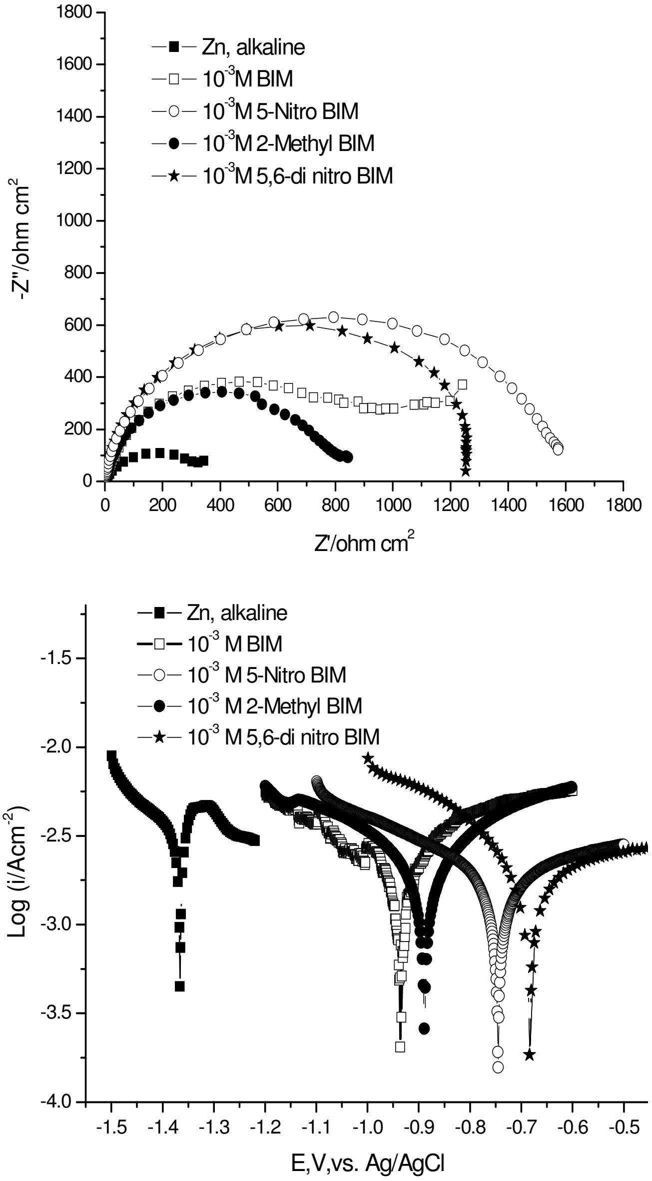


Fig. 6. EIS and current-potential curves of zinc for benzimidazole derivatives in 0.4 M NaCl + 0.1 M NaOH solution

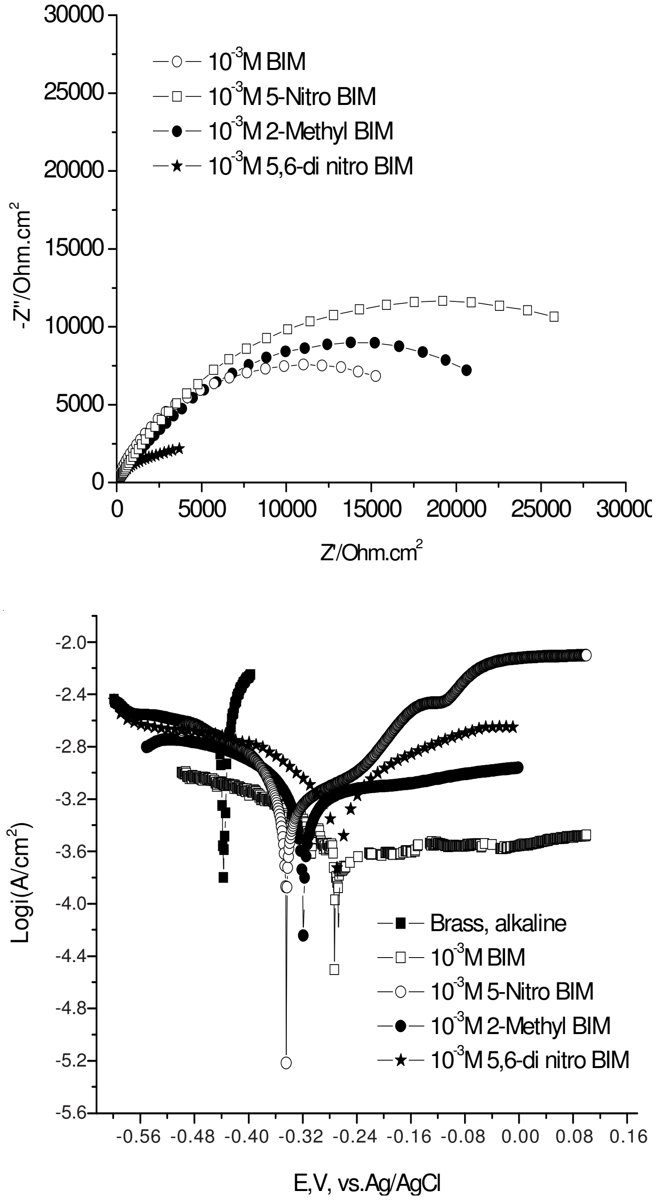
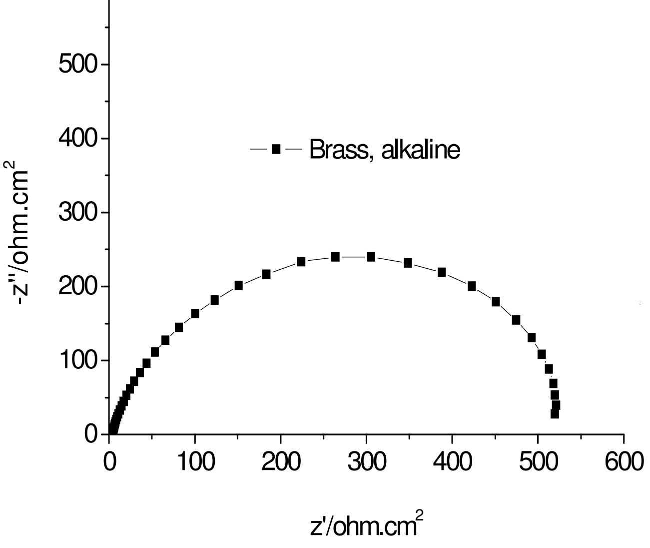
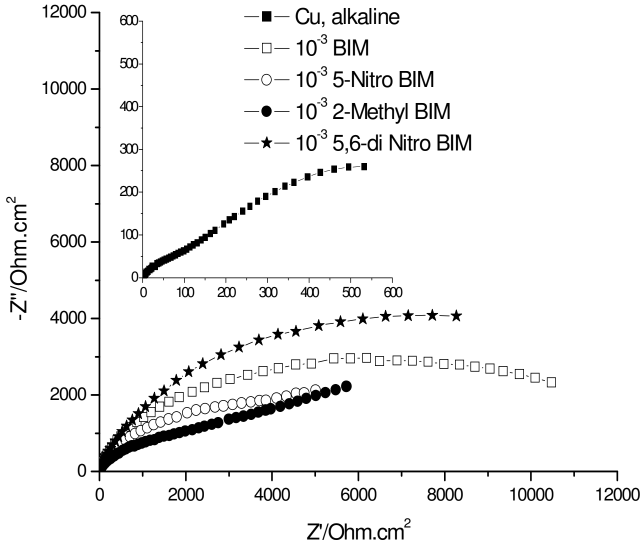


Fig. 7. EIS and current-potential curves of copper for benzimidazole derivatives in 0.4 M NaCl + 0.1 M NaOH solution





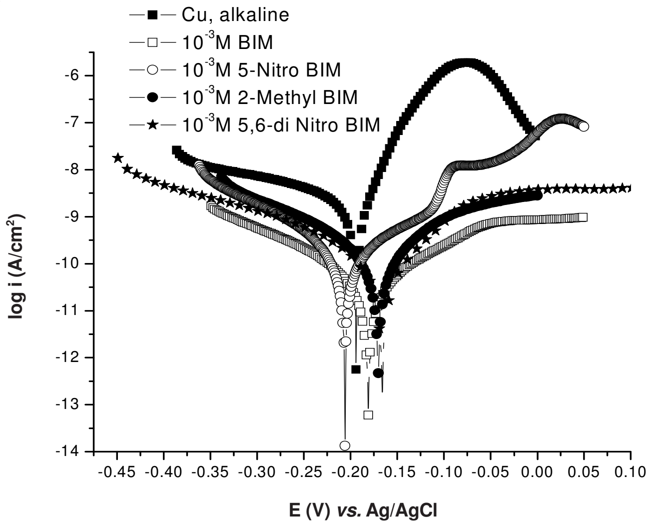


Fig. 8. EIS and current-potential curves of brass for benzimidazole derivatives in 0.4 M NaCl + 0.1M NaOH solution

data presented in Tables 2 and 3 the following conclusion is imposed; the introduction of the second nitro group in benzimidazole molecule, increased the inhibition efficiency for zinc in alkaline media. As a withdrawing group, this substituent decreased strongly electron density on the benzimidazole ring and facilitated the absorption on the metal surface. Consequently, the resulting compound 5,6-dinitrobenzimidazole has better inhibitor activity with respect of 2-methyl-1*H*-benzimidazole for zinc, copper and brass in alkaline media. On the other hand the inhibiton efficiency of 5,6-dinitrobenzimidazole is not significantly different from of 5-nitro-1*H*-benzimidazole due to the steric effect.

Conclusion

The experimental results obtained (Table-2), indicate that in the solution of neutral media, these derivatives are more efficient corrosion inhibitors for copper in the increasing order of 2-CH_3-BIM > 5(6)-NO_2-BIM > BIM. The corrosion inhibition efficiency of 1*H*-benzimidazole, 5(6)-nitro-1*H*-benzimidazole, 5,6-dinitrobenzimidazole and 2-methyl-1*H*-benzimidazole for copper, zinc and brass were investigated depending on the pH. In alkaline media, given in Table-3, at 10^{-3} M concentration of the compounds, the inhibition efficiency increases as follows: BIM > 5(6)-NO_2-BIM > 5,6-diNO_2BIM > 2-CH_3-BIM. The investigated benzimidazole derivatives were not effected as inhibitors on zinc, copper and brass in acidic media. Capacitances decreased with increasing inhibition efficiencies of benzimidazoles derivatives.

ACKNOWLEDGEMENTS

The authors acknowledged the financial support from Ankara University (Project No. 2004-07-05-088).

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