



Indole and 5-chloroindole as inhibitors of anodic dissolution and cathodic deposition of copper in acidic chloride solutions

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Abstract

The effect of indole, IN, and 5-chloroindole, Cl-IN, on the anodic dissolution of copper in acidic sodium chloride solutions was studied using voltammetry on a rotating disc electrode (RDE). Both compounds used at 10^{-3} M concentration act as strong inhibitors on the copper dissolution, but indole exhibits better inhibiting properties. The inhibitory action substantially increases with decreasing solution pH. The influence of these organic additives on the electrodeposition of copper on platinum was also investigated using RDE and electrochemical quartz crystal microbalance (EQCM) techniques. The EQCM measurements show that a sparingly soluble layer of the inhibitor is responsible for the protective effects observed in chloride solutions.

List of symbols

A	area (cm^2)
b	Tafel slope
E	electrode potential (V)
$E^{0'}$	formal potential (V)
f	frequency (Hz)
I	current (A)
J	current density (A cm^{-2})

Greek symbols

ω	angular velocity (rad s^{-1})
ϵ_{ie}	inhibition efficiency

Sub- and -superscripts

a	anodic
c	cathodic
inh	inhibited

1. Introduction

Typical corrosion inhibitors for copper are heterocyclic compounds containing nitrogen, oxygen or sulfur. Benzotriazole and its derivatives are highly efficient inhibitors for preventing copper corrosion and its alloys in neutral and alkaline media. However, their inhibition efficiency drops dramatically in acidic solutions. Thus, new efficient and nontoxic inhibitors have recently been sought for copper in aqueous acidic solutions. Stup-

nišek-Lisac and coworkers [1–5] demonstrated that some imidazole derivatives are efficient inhibitors for copper corrosion. Other nitrogen containing compounds were also investigated as potential inhibitors in chloride solutions, among them benzo-hydroxamic acids [6], secondary amines [7] and pyrazole [8].

The aim of this work is to investigate the inhibiting effect of indole (benzopyrazole) and 5-chloroindole on the anodic dissolution of Cu, as well as the cathodic reduction of Cu(II) ions (on Pt electrode). The molecular structures of the inhibitors are shown in Figure 1. The inhibiting properties of indole on the corrosion of copper in aerated 0.5 M sulfuric acid have been demonstrated by Quartarone and coworkers [9]. However, it is known that the mechanism of copper electrodeposition/dissolution strongly depends on the medium. In aqueous noncomplexing solutions, such as sulphates, perchlorates and nitrates, the cathodic deposition and anodic dissolution of copper proceeds according to the overall reaction



In fact, the overall reaction occurs through Cu(I), which is an unstable intermediate. Cu(I) ions were detected and determined during this process using various electrochemical techniques, such as the rotating ring-disc electrode [10]. This behaviour of the Cu(II)/Cu(I)/Cu system is the result of the low thermodynamic stability of Cu(I) ions, which can be expressed in terms of the equilibrium constant of the reproporation reaction

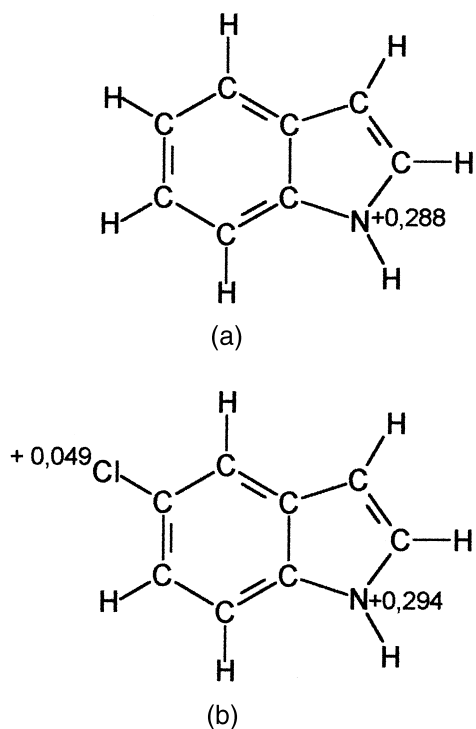


Fig. 1. Molecular structures of the inhibitors studied: (a) indole, IN, and (b) 5-chloroindole, Cl-IN. Electric charge densities are given at nitrogen and chlorine atoms.



The equilibrium constant for Reaction 2 in such media is reported in [11] to be $6 \times 10^{-7} \text{ mol dm}^{-3}$ at 25 °C. Consequently, only a low equilibrium concentration of Cu(I) can exist. Under these conditions, the following ordering of formal potentials is found where the Cu(I)/Cu couple exhibits a formal potential much more positive than the Cu(II)/Cu(I) couple [12]:

$$E_{\text{Cu(II)/Cu(I)}}^{0r} < E_{\text{Cu(II)/Cu}}^{0r} < E_{\text{Cu(I)/Cu}}^{0r}$$

The value of E^{0r} for the Cu(I)/Cu couple was calculated using the Luther rule [13]. Such ordering of potentials is known as inverse [14].

The stability of Cu(I) ions can be significantly changed by adding a ligand that forms strong complexes with Cu(I), but interacts weakly with Cu(II) ions. It is known [15] that Cu(I) and chloride ions form a series of strong complexes. Higher chloride concentrations lead to complexes such as CuCl_3^{2-} and CuCl_4^{3-} . Conversely, only weak complexes are formed by Cu(II) with chloride ions [16]. In Figure 2, a substantial change can be seen in the ordering of the formal potentials for copper when going from the standard conditions [12] to 1 M KCl solution [17]

$$E_{\text{Cu(II)/Cu(I)}}^{0r} > E_{\text{Cu(II)/Cu}}^{0r} > E_{\text{Cu(I)/Cu}}^{0r}$$

Consequently, two well-defined waves of the same height were observed in voltammetric experiments with

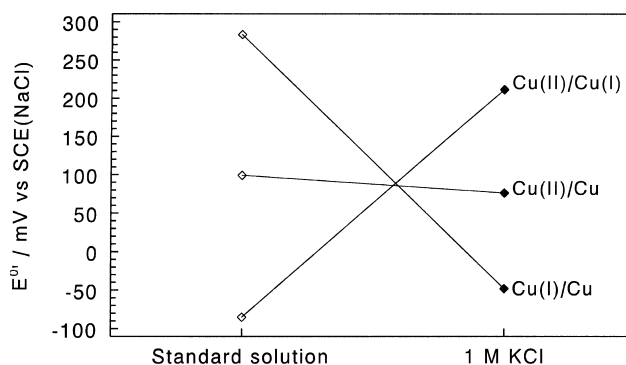


Fig. 2. Placement of the formal potentials for the Cu(II)/Cu(I), Cu(II)/Cu and Cu(I)/Cu redox pairs in aqueous solutions: under standard conditions (left), and in 1 M KCl (right).

the rotating disc electrode during the electrochemical reduction of Cu(II) in the medium considered above [18]. This indicates the occurrence of two clearly separated consecutive one-electron reactions:



It is known [19] that the electrolysis of cupric chloride solutions at low current densities may involve excessive corrosion of the copper cathode. This phenomenon is due to the reproporationation Reaction 2, which yields thermodynamically stable Cu(I) complexes in this medium. Reaction 2 can be considered as a corrosion process, which is a coupling of the cathodic Reaction 3 and Reaction 4, but occurring in the anodic direction.

The present work describes a study of the electrochemical behaviour of copper in acidified 1 M NaCl solutions in the presence of indole and 5-chloroindole, based on rotating disc electrode (RDE) voltammetry. The influence of these additives on the electrodeposition of copper on platinum has also been investigated using RDE and electrochemical quartz crystal microbalance (EQCM) techniques. Recently, EQCM measurements were employed to study metal corrosion and its inhibition [20–23]. The EQCM technique supplies highly sensitive data on mass changes associated with the adsorption or desorption of a species at the electrode surface and allows correlation of these processes with charge transfer reactions.

2. Experimental details

Indole, IN (>99%), and 5-chloroindole, Cl-IN (>98%), were purchased from Merck (Darmstadt, Germany). The electrolytes were prepared using analytical grade reagents (Merck) and triply distilled water. NaCl solutions were adjusted to appropriate pH values using HCl.

The working electrode was a home made rotating disc electrode (RDE) of specpure copper (Johnson Matthey Chemicals) with $r = 0.213 \text{ cm}$, $A = 0.181 \text{ cm}^2$. The elec-

trode was mechanically polished with alumina powders of different grain sizes down to $0.05 \mu\text{m}$, using water as lubricant, and was then repeatedly rinsed with water. Such pretreatment of the electrode was repeated after each voltammetric measurement. Another rotating disc electrode made of polycrystalline platinum (99.99% Pt) with a geometric area of 0.196 cm^2 was employed to study the cathodic copper deposition. The disks were used in some experiments as stationary electrodes.

All voltammetric experiments were carried out in a three-compartment glass cell. Electrode potentials were measured and reported against an external saturated calomel electrode with NaCl solution, SCE(NaCl), which exhibits potential 6 mV more negative than that filled with saturated KCl solution. A platinum wire gauze (surface area $\sim 5 \text{ cm}^2$) was used as auxiliary electrode. Reference and auxiliary electrodes were individually isolated from the test solution by glass frits.

The electronic setup for voltammetric experiments consisted of a model EP 20A potentiostat and a model EG 20 function generator (ELPAN). Responses were recorded with a Servogor model 790 recorder (Goerz). Electrode potentials were measured using a V-540 digital voltmeter (Meratronik).

EQCM experiments were performed with an apparatus constructed in the Institute of Physical Chemistry (Warsaw) [24]. The quartz crystal had a geometric area of 0.432 cm^2 , and was operated at the fundamental frequency of 5 MHz. The changes in resonant frequency of the quartz oscillator due to mass change were measured on a Philips PM 6685 frequency counter furnished with a frequency-to-voltage converter. The frequency resolution of the measurement was approximately 0.2 Hz. Platinum film electrodes (0.323 cm^2 area) were sputtered on to the crystals (Institute of Physics, Warsaw). The roughness factor of the electrode surface was determined from the measurement of the quantity of charge required to form a layer of adsorbed oxygen [25]. Typical roughness factors calculated on this basis were about 1.4. The mass sensitivity, k_f , of the EQCM was determined experimentally to be $5.65 \times 10^7 \text{ Hz cm}^2 \text{ g}^{-1}$. Other details of the EQCM system used in this study were similar to those previously described [26, 27].

The solutions were purged with argon for 30 min prior to use and an Ar atmosphere was maintained in the cell during all electrochemical experiments which were carried out at $25 \pm 0.2 \text{ }^\circ\text{C}$.

The distribution of charge densities in the inhibitor molecules was calculated by the PM3 semi-empirical methods using a HyperChem[®] version 5.01 computer program from Hypercube Inc.

3. Results and discussion

3.1. Anodic dissolution of copper

Anodic polarisation curves at a Cu rotating disc electrode (RDE) were recorded over a range of rotation

frequency from 8.0 to 30.0 Hz (50.3 to 188.5 rad s^{-1}). The potential was scanned from -350 mV towards the anodic direction at a rate of 5 mV s^{-1} ; such a low scan rate provided polarisation behaviour equivalent to steady-state conditions. This procedure gave good reproducibility. The measurements were performed in acidified NaCl solutions, at a total chloride concentration of 1.0 M, without and with the presence of the inhibitors.

Figure 3 displays a series of RDE voltammograms for the anodic dissolution of Cu in the absence and presence of $1 \times 10^{-3} \text{ M}$ indole (IN) at various pH at a rotation frequency of 30 Hz. As known from the ring-disc voltammetric measurements of Lee and Nobe [28], the disc currents in the potential range applied correspond to Reaction 4 occurring in the anodic direction. The electrodisolution of Cu in the absence of inhibitor is practically independent of pH. In the presence of IN, the polarization curves are shifted in the anodic direction, the greatest effect being observed in a solution of pH 1.0.

The voltammetry of Cu in solutions containing $1 \times 10^{-3} \text{ M}$ Cl-IN as an additive (not shown) is similar to that observed in the presence of IN, but the inhibiting effect is somewhat smaller.

The disc currents measured at a constant potential and various rotation frequencies were plotted in coordinates I^{-1} against the reciprocal square root of the angular frequency, $\omega^{-1/2}$, in order to determine the activation currents by extrapolating to infinite frequency, $\omega \rightarrow \infty$. An example of the procedure employed is given in Figure 4. The activation currents thus determined were used to construct Tafel plots for Reaction 4 occurring in the anodic direction (Figure 5).

As shown in Figure 5, the logarithms of activation currents are linear functions of electrode potential. A Tafel slope of 59.4 mV per decade of current density was

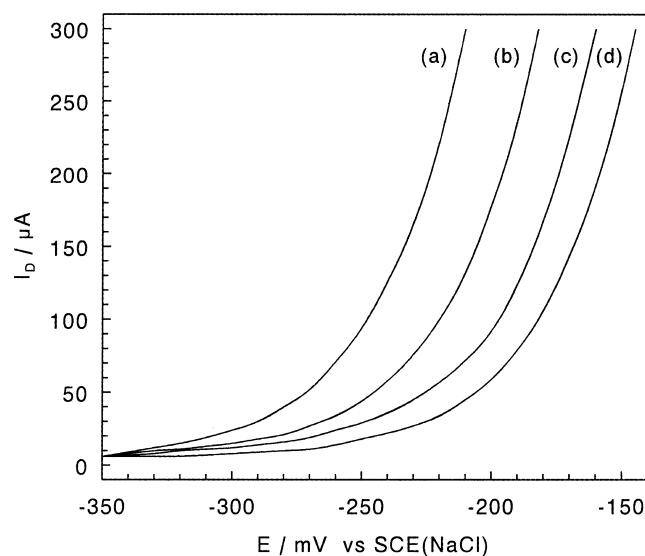


Fig. 3. Polarization curves of a Cu-RDE in 1 M NaCl solutions (a) without, and (b), (c) and (d) with $1 \times 10^{-3} \text{ M}$ IN at pH: (b) 3.0, (a, c) 2.0, (d) 1.0. Rotation frequency 30 Hz; potential scan rate 5 mV s^{-1} .

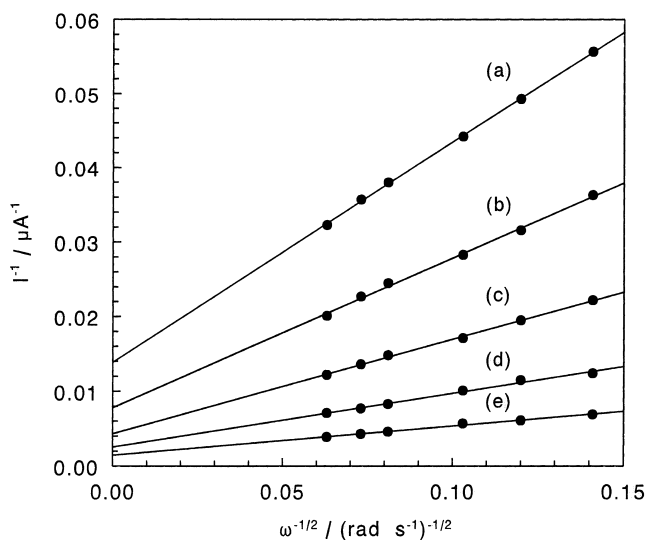


Fig. 4. Plots of reciprocal anodic disc current against reciprocal square root of the circular frequency in the solution containing 1 M NaCl and 1×10^{-3} M IN (pH 2.0). Electrode potential: (a) -250, (b) -230, (c) -210, (d) -190 and (e) -170 mV.

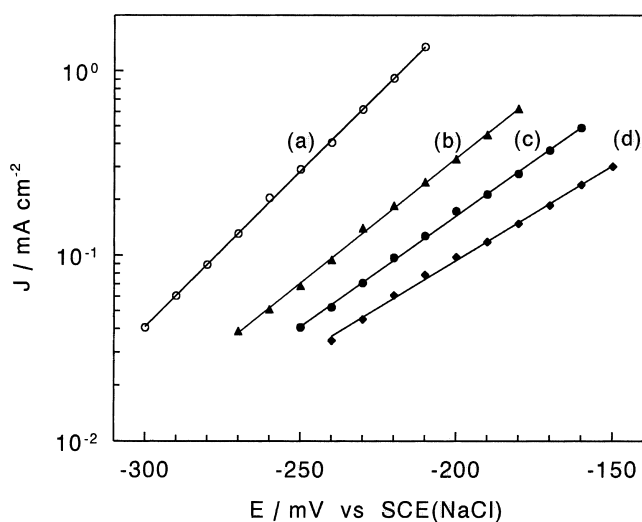


Fig. 5. Tafel plots derived from anodic current-potential curves at Cu electrode, obtained by extrapolation to infinite rotation frequency. Concentration of IN: (a) 0, (b), (c) and (d) 1×10^{-3} M; pH: (b) 3.0, (a) and (c) 2.0, (d) 1.0.

obtained in solutions without IN. The result agrees with those previously reported by several investigators [29–31] in acidic solutions containing 1 M chlorides, and reveals that Cu electrodisso- lution to cuprous species, which takes place in the apparent Tafel region, is mass transfer controlled.

Figure 5 demonstrates that the addition of 1×10^{-3} M IN gives not only a substantial decrease in the rate of copper electrodisso- lution but also changes in the Tafel slope with solution pH (see also Table 1). The Tafel slope changes from 74 to 98 mV (decade) $^{-1}$ as the solution pH decreases from 3 to 1. Figure 6 shows that Cl-IN exerts a similar effect on the anodic dissolution of copper in the apparent Tafel region, but the quantitative changes are smaller than in the case of IN.

Table 1. Tafel slopes, b , and degrees of inhibition, ε_{ie} , for anodic Reaction 4 and cathodic Reaction 3 in 1 M chloride solutions of various pH, in the absence and presence of 1×10^{-3} M IN or Cl-IN

Solution	Anodic		Cathodic
	b /mV (decade) $^{-1}$	ε_{ie} /%	ε_{ie} /%
1.0 M NaCl, pH 2.0, without inhibitor	59.4		
IN, pH 3.0	74.1	55	27
IN, pH 2.0	83.4	74	85
IN, pH 1.0	97.5	85	92
Cl-IN, pH 3.0	71.8	28	25
Cl-IN, pH 2.0	79.9	47	40
Cl-IN, pH 1.0	98.5	61	95

Data were estimated at potentials of -220 and -100 mV for the anodic and cathodic process, respectively.

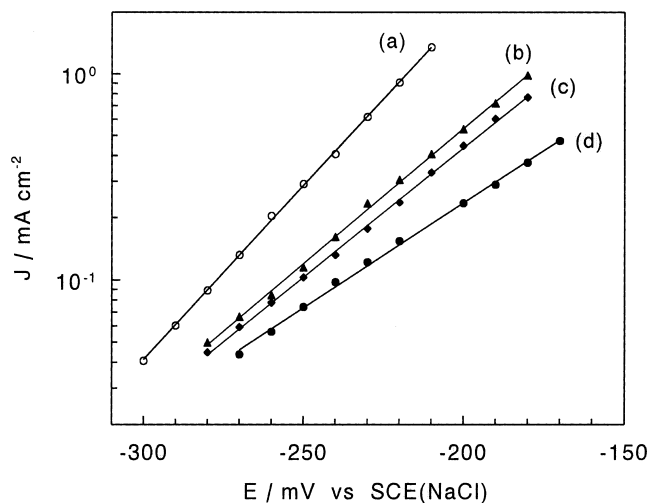


Fig. 6. Tafel plots derived from anodic current-potential curves at Cu electrode, obtained by extrapolation to infinite rotation frequency. Concentration of Cl-IN: (a) 0, (b), (c) and (d) 1×10^{-3} M; pH: (b) 3.0, (a) and (c) 2.0, (d) 1.0.

The inhibition efficiency ε_{ie} , for copper electrodisso- lution was calculated in the apparent Tafel region by comparing currents at constant potential, in the absence of inhibitor, I_0 , with those with inhibitor, I_{inh} , by using the simple relation:

$$\varepsilon_{ie} = \left(\frac{I_0 - I_{inh}}{I_0} \right) \times 100 \quad (5)$$

The results at -220 mV and rotation frequency 8 Hz are presented in Table 1. With decreasing pH, the inhibition efficiency increases in the presence of 1×10^{-3} M IN up to value of 85%. Somewhat lower inhibition efficiencies were obtained with 1×10^{-3} M IN-Cl in the same potential range. Values of ε_{ie} remain constant for both additives in the potential range from -250 to -200 mV.

The high inhibition efficiency of IN and Cl-IN is probably caused by the formation of an adherent and compact inhibitor film on the copper surface.

3.2. Cathodic reduction of Cu(II) on Pt-RDE

Much previous work has been devoted to the inhibiting effect of organic compounds on the anodic dissolution of copper, while relatively few data are available concerning its electrodeposition in the presence of additives. In this study we have also examined the effect of IN and Cl-IN on the cathodic reduction of Cu(II) from chloride solutions.

Figure 7 shows the influence of IN at different pH on the reduction of Cu(II) on a Pt RDE. The voltammogram for an additive-free solution shows two distinct waves of nearly the same height at about 0.18 and -0.35 V, which are attributable to electrode Reactions 3 and 4. The significant potential separation between the waves is caused by the high thermodynamic stability of Cu(I) ions in the medium investigated. At potentials negative of -0.5 V, hydrogen evolution commences.

The addition of IN causes a considerable decrease in the limiting current of the first wave. It is noteworthy that the current decreases with reduction in pH. The inhibiting effect is most pronounced at pH 1.0 (curve (d) in Figure 7). The voltammogram recorded under these conditions shows the almost complete suppression of the limiting current. Indeed, the second wave of Cu(II) reduction moves towards more negative potentials with decreasing pH, and the sum of the waves diminishes steeply at the same time. Similar results were obtained for solutions containing Cl-IN at various pH.

Considering changes in the limiting current of the first cathodic wave upon the addition of the inhibitors used, the inhibition efficiency values for cathodic Reaction 3 were calculated. The results are listed in Table 1.

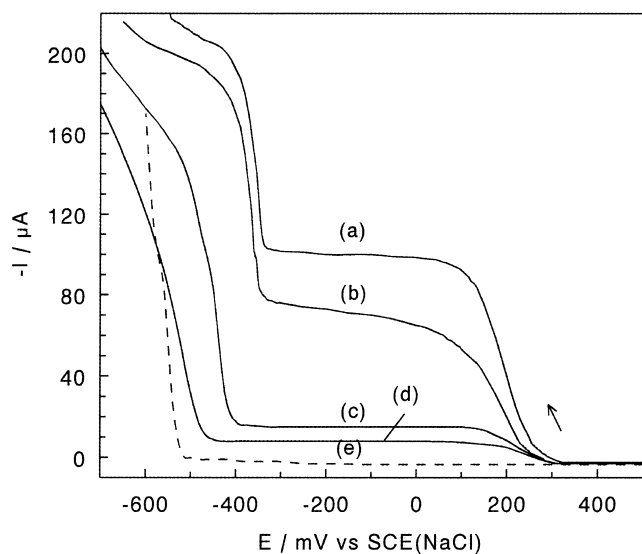


Fig. 7. Voltammograms for the reduction of 1×10^{-3} M Cu(II) on a Pt-RDE from the solutions containing 1 M NaCl in the absence (a) and presence of 1×10^{-3} M IN (b), (c) and (d). Voltammogram labelled (e) is the residual current recorded for background electrolyte without inhibitor. pH of solutions: (a), (b) and (e) 3.0, (c) 2.0 and (d) 1.0. Rotation frequency 30 Hz; potential scan rate 5 mV s^{-1} .

To obtain a better insight into the inhibition mechanism, cyclic voltammograms were recorded with the use of RDE. Figure 8 displays some cyclic voltammograms obtained with a successive increase in the cathodic potential limit within the first wave. For comparison, the voltammogram of the additive-free solution (curve (d)) was recorded. This curve shows a poorly defined hysteresis loop upon reversing the potential scan. On the other hand, a small and broad shoulder appears at about 0.35 V when the potential is scanned in the anodic direction. As shown in previously [32], this shoulder corresponds to the dissolution of a thin CuCl layer formed during cathodic Reaction 3. This film exerts also a slight blocking effect on the bulk generation of Cu(I). In comparison with the additive-free solution, the runs made in the solution of 1×10^{-3} M IN show more distinct hysteresis loops. It is seen that the displacement of the reverse curves is affected by the switch potential and, thus, by the polarization time. This feature can be attributed to the formation of an inhibiting film, which accumulates on the electrode surface. Moreover, the formerly mentioned anodic shoulder disappears completely in the presence of indole. The above experiment indicates that the cathodic process (3) is probably not associated with the formation of insoluble Cu(I)-IN complexes on the electrode surface.

Additional measurements with the electrochemical quartz microbalance (EQCM) were performed to obtain complementary information necessary to characterise

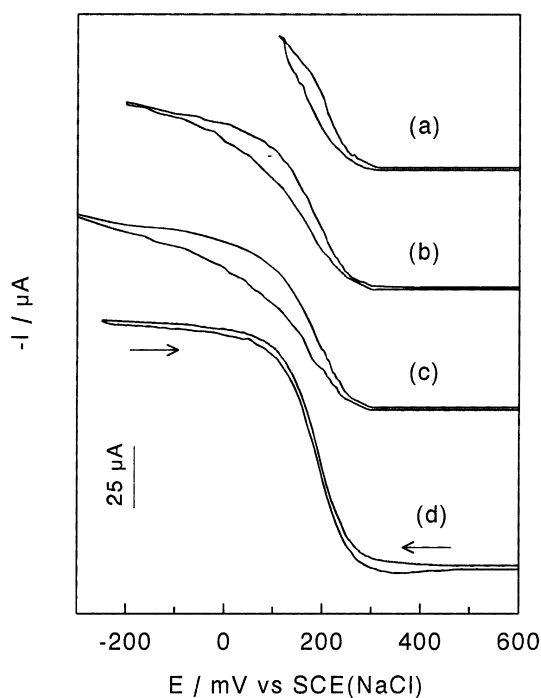


Fig. 8. Cyclic voltammograms for reduction of 1×10^{-3} M Cu(II) at a Pt-RDE in the solution containing 1.0 M NaCl and 1×10^{-3} M IN (pH 3.0). All potential scans were initiated at 600 mV and reversed at (a) 100, (b) -200 , (c) -300 and (d) -250 mV. Voltammogram labelled (d) was recorded in absence of IN. Rotation frequency 30 Hz; potential scan rate 5 mV s^{-1} . Arrows indicate directions of potential scanning.

the electrochemically produced adsorbates, and thus to understand better the nature of electrode Reaction 3.

The frequency response of the EQCM upon the addition of IN is illustrated in Figure 9 by a series of experiments in which the inhibitor concentration was changed from 0 to 1×10^{-3} M at pH 3.0. In the inhibitor-free solution (curve (a)), the start of a frequency decrease (mass increase) coincided with the beginning of the first wave for Cu(II) reduction (see Figure 7). This finding confirms the previous statement that the reduction of Cu(II) to Cu(I) is accompanied by copper underpotential deposition which involves the coadsorption of Cl on the electrode surface [32]. A sharp frequency decrease at potentials negative of -0.3 V is associated with the bulk deposition of copper.

Further results of Figure 9 indicate that the addition of increasing amounts of IN leads to an increase of the measured resonant frequency in the range of the first reduction wave. This, at first sight, surprising result can be regarded as a quasi-substitution process [33], in which the surfactant replaces cuprous chloride on the electrode surface. The measured mass loss is caused by the gradual replacement of CuCl in the interfacial layer by molecules of the adsorbed inhibitor. This effect can particularly be observed with increase in IN concentration. Because of the large size of the molecules studied, the mass loss due to displaced metal salt is much larger than the mass gain resulting from adsorption of the inhibitor.

The inhibiting effect of IN and Cl-IN both on copper dissolution and electrodeposition increases considerably with decreasing pH. This interesting phenomenon suggests that indole and 5-chloroindole act better as inhibitors in the protonated forms, INH^+ and Cl-INH^+ , than in the molecular forms. On the other hand,

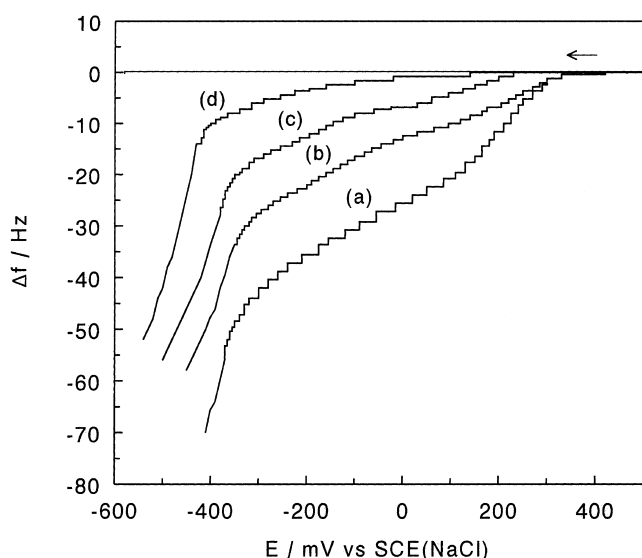


Fig. 9. EQCM frequency responses obtained during the cathodic potential scan at a Pt-coated quartz crystal in the solution containing 1×10^{-3} M CuCl_2 , 1 M NaCl (pH 3.0) and IN: (a) 0, (b) 1×10^{-5} , (c) 1×10^{-4} , (d) 1×10^{-3} M. Potential scan rate 5 mV s^{-1} . Arrow indicates direction of potential scanning.

it is known [34, 35] that indole is a very weak base. As follows from the simulation of the charge density in the indole molecule (Figure 1), this fact can be explained by the large positive charge on the nitrogen atom in the heterocyclic ring, which diminishes its nucleophilicity. Recently, Andonovski and coworkers [36, 37] estimated a value of $\text{p}K_a$ for the protonated form of indole, IN^+ , to be -3.6 ± 0.1 . On the basis of this result it can be assumed that the neutral molecules dominate in solutions of $\text{pH} \geq 1$. However, it is known that the large potential gradient in the electrochemical double layer can considerably change the relative basic strengths of organic compounds [38]. Kwiatek and Kalinowski showed that the electric field in the double layer can decrease the acidity constants of protonated aromatic ketones [39, 40] and aromatic nitro compounds [41, 42] by several orders of magnitude. It is reasonable to suppose that an analogous mechanism explains the facts described here.

4. Conclusions

The following conclusions can be drawn:

- (i) Both indole (IN) and 5-chloroindole (Cl-IN) act as inhibitors of anodic copper corrosion in acidic sodium chloride solutions, but IN presents better inhibiting properties than Cl-IN.
- (ii) The inhibition efficiencies of the both surfactants depend significantly on pH. Surprisingly, decreasing solution pH substantially increases the degree of copper protection.
- (iii) IN and Cl-IN were also found to inhibit copper(II) electroreduction on polycrystalline Pt. The inhibitory action also increases with increasing acidity.
- (iv) The action of inhibitors can be physically interpreted as blockage of the metal surface. An adherent layer of inhibitor is postulated to account for the protective effect.

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