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Comparative study of copper electrodeposition from sulphate acidic electrolytes in the presence of IT-85 and of its components

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Abstract

The effect of a new additive (IT-85) representing a mixture of triethyl-benzyl-ammonium chloride (TEBA) and hydroxyethylated-2-butyne-l,4-diol ('Ferasine') on the kinetics of copper electrodeposition from sulphate acidic electrolytes, as well as on the morphology and structure of copper deposits was investigated and compared with those exerted by its two components, TEBA and Ferasine. Quasi-steady state hydrodynamic voltammetry at a rotating-disc electrode and electrochemical impedance spectroscopy were performed in order to obtain information about the kinetics of the cathodic process. SEM and X-ray diffraction analysis were used to examine the morphology and the structure of copper deposits. The kinetic parameters (α_c, k_0) obtained by both Tafel and Koutecky-Levich interpretations showed that all tested organic additives have an inhibiting effect on copper electrodeposition. Unlike IT-85 or Ferasine, TEBA acts only as a blocking agent in the copper discharge process, without changing the reaction pathway corresponding to the absence of additives. Comparison of the inhibiting effects exerted by IT-85 and its components on the electrodeposition process pointed to the existence of a beneficial complementarity of TEBA and Ferasine when they are used in mixture.

1. Introduction

The most common levelling and brightening agents used in copper electrodeposition are thiourea [1–12], gelatine [8, 13], Cl^- [14–16], benzotriazole [10, 17–20], polyacrylamide [21], polyethylene glycol [22, 23] and mixtures of different additives such as polyethylene glycol and Cl^- [16], thiourea and gelatine [24, 25], etc. Although the beneficial effects of these additives on the properties and quality of the copper deposits are well known, their mechanism of action has not been completely elucidated.

Recently, a new additive, IT-85, representing a mixture of hydroxyethylated-2-butyne-1,4-diol ('Ferasine') and triethyl-benzyl-ammonium chloride (TEBA), which has been successfully used as levelling agent in zinc electrowinning from acidic sulphate electrolytes [26], was proved to be an efficient levelling agent in copper electrodeposition [11, 12].

Taking into account that both IT-85 components, TEBA and Ferasine, behave separately as efficient inhibitors in copper electrodeposition [27–29], the aim of the present study was to examine the simultaneous effect of the two above-mentioned additives on copper electrodeposition from acid $CuSO_4$ solutions. The results obtained in the presence of IT-85 were compared with those exerted by TEBA and Ferasine used separately, in order to better understand the mechanism of action of each component separately and in mixture.

Quasi-steady state hydrodynamic voltammetry at a rotating-disc electrode and electrochemical impedance spectroscopy were used to investigate the influence of the organic additives on the kinetics of copper electrodeposition. The morphology of copper deposits obtained by small-scale electrolysis was examined by SEM and their crystal structure was investigated by X-ray diffraction.

2. Experimental

2.1. *Reagents*

A stock solution of acidic copper sulphate containing 30 g l^{-1} Cu^{2+} as $CuSO_4$ and 100 g l^{-1} H_2SO_4 was prepared by using pure reagents (Merck, Darmstadt, Germany) and distilled water. Various amounts of organic additives were added into the stock solutions

in order to obtain working electrolytes with the following additives concentrations: IT-85: 10; 25, 50 ml l^{-1}; TEBA: 0.2; 0.5; 1 g l^{-1}; hydroxyethylated-2-butyne-l,4-diol (Ferasine 30% solution): 3; 8; 15 ml l^{-1}. The individual concentrations of TEBA and Ferasine were chosen identical with those existing in the working electrolyte with various concentrations of IT-85.

Ferasine and the additive IT-85 (containing 300 g l^{-1} Ferasine and 20 g l^{-1} TEBA) were supplied by the Institute of Physical Chemistry of Bulgarian Academy of Sciences from Sofia. TEBA was purchased from Fluka.

2.2. *Electrochemical measurements*

The experimental set-up consisted of a conventional three-electrode cell connected to a potentiostat (PS 3 Meinsberg, Germany) equipped with a data acquisition system (National Instruments AT MIO16 T5 acquisition board coupled to an IBM PC). The working electrode was a copper disc electrode (Ø = 3 mm), the counter electrode was a platinum foil and a saturated calomel electrode (SCE) was used as reference electrode. To ensure reproducibility between experiments, the exposed surface of the working electrode was polished with 600 and 1200 grit paper and rinsed with distilled water.

The quasi-steady state hydrodynamic voltammograms for copper deposition on a rotating disk electrode (RDE, model AMSFRX, Pine, Grove City, PA, USA) were recorded in the potential range 0 and −0.8 mV vs SCE at a rotation speed of 1000 rpm and a scan rate of 20 mV s^{-1}.

The amperometric measurements at the RDE with linear variation of rotation speed were performed at different electrode potential values, chosen in the activation–diffusion control region, by scanning the electrode rotation speed between 100 and 2500 rpm with a 20 rpm increment.

All electrochemical measurements were performed under potentiostatic conditions without ohmic drop compensation. The ohmic drop correction for the applied electrode potential was done by calculus, using the electrolyte resistance obtained from electrochemical impedance diagrams.

The electrochemical impedance spectroscopy measurements were carried out in the 10 kHz–3.2 mHz frequency range, under potentiostatic conditions, at different d.c. electrode potentials situated in the range from −125 to −250 mV vs SCE, using a 'virtual' frequency response analyser, developed in our department, based on a AT-MIO 16F5 National Instruments data acquisition board and an Olivetti 440 PC, connected to specified analogic potentiostat. To control the mass transport, in all measurements, the electrode was rotated at 1000 rpm. In order to improve the accuracy, the measurements were automatically repeated up to 20 times, especially for high frequencies measurements.

2.3. *Preparative electrolysis*

Small-scale potentiostatic electrolysis was performed in the absence and in the presence of different amounts of organic additives, at room temperature, employing a glass cell equipped with one vertical planar brass cathode and a platinum anode. In all cases, the working electrode potential was held constant at a value chosen from the activation controlled region (−175 mV vs SCE) during the deposition time (45 min).

2.4. *Examination of deposits*

Morphological examination of copper deposits involved visual inspection and scanning electronic microscopy (LEICA S 440). The crystal structure was investigated by X-ray diffraction, with a filtered MoK-alpha source. The crystallographic orientation of the deposits was determined by comparing the relative peak intensities of the experimental X-ray diffraction spectra with the standard Cu ASTM diffraction data.

3. Results and discussion

3.1. *Effect of additives on the deposit morphology*

The influence of the organic additives on the copper deposits morphology is illustrated in Figure 1. The grain size varied very little with the thickness after establishment of a stationary state. The copper deposits obtained from solutions without organic additives were rough and granular consisting of relative large, coarse grains (Figure 1a). IT-85 (Figure 1b), TEBA (Figure 1c) and Ferasine (Figure 1d) inhibit the crystal growth process, so that, in their presence a relative enhancement of the nucleation process is induced. This results in a more regular, refined topography of cathodic deposits.

A comparative examination of the morphology of copper deposits showed that the smallest grain size is observed in the case of IT-85. This observation suggested that, when used in mixture, the two components of IT-85 (TEBA and Ferasine) mutually intensify their actions, exerting a synergetic effect on the copper electrodeposition process.

As can be seen from the X-ray diffraction spectra presented in Figure 2, the decrease in grain size of the copper deposits was accompanied by a change in texture from (1 1 1), noticed in the absence of organic additives [12, 27], to (1 1 0) in the presence of TEBA [27], Ferasine and IT-85. This change in texture is the result of inhibition exerted by the additives on the crystal growth process.

3.2. *Quasi-steady state hydrodynamic voltammetry at RDE*

To obtain a better insight into the electrodeposition mechanism, quasi-steady state hydrodynamic voltam-

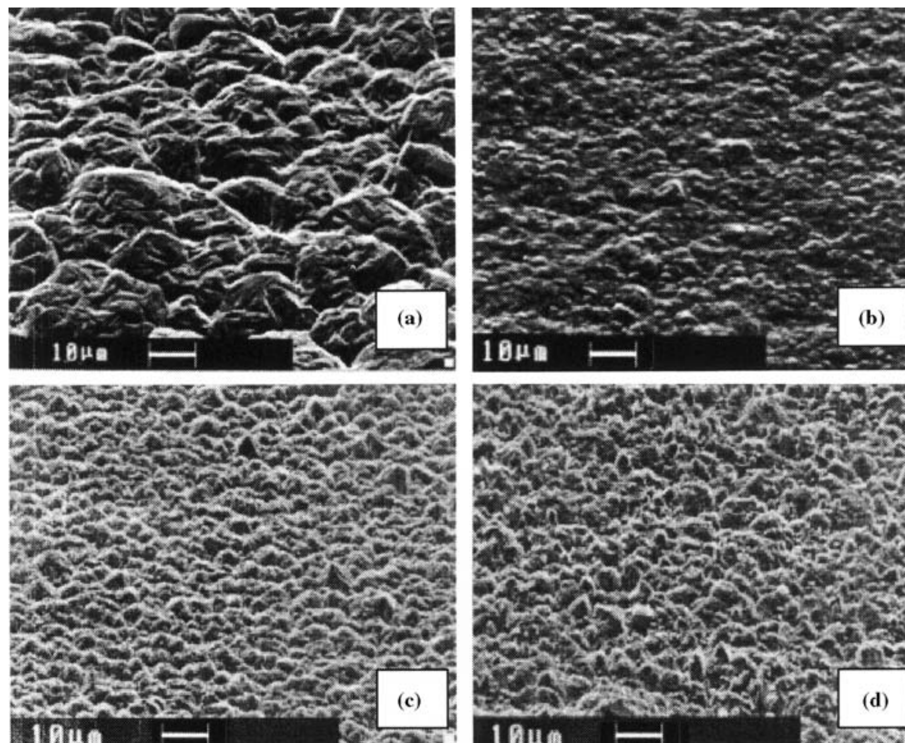


Fig. 1. SEM micrographs of copper deposits obtained at E=−175 mV vs SCE in the absence (a) and in the presence of 10 ml l^{-1} IT-85 (b); 0.2 g l^{-1} TEBA (c); 3 ml l^{-1} Ferasine (d). Experimental conditions: rotation speed, 1000 rpm; electrolysis time, 45 min.

mograms at an RDE in the absence and in the presence of IT-85, TEBA and Ferasine, respectively, were recorded (Figure 3).

The progressive decrease in the cathodic current density for a given value of the electrode overpotential shows that, as expected, all tested organic additives increase the cathodic polarization, due to electrosorption at the electrode interface. However, the shape and characteristics of the hydrodynamic voltammograms depend on the nature of the additives, suggesting differences in the mechanism of action of the investigated leveling agents.

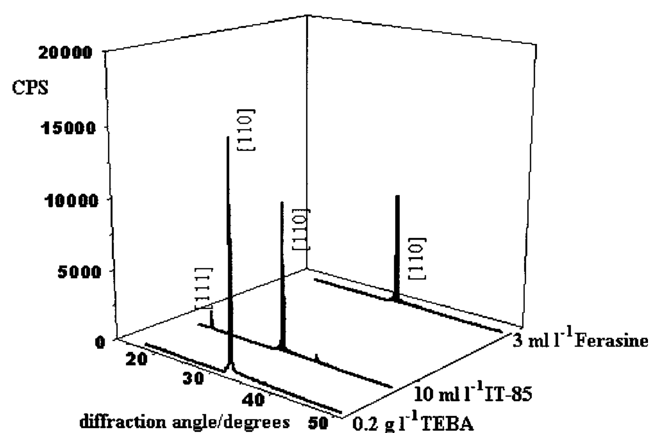


Fig. 2. X-ray difractogramms corresponding to the copper deposits obtained at E=−175 mV vs SCE in the presence of organic additives. Experimental conditions: see Figure 1.

The length of the initial part corresponding to relatively low overpotentials (region I, Figure 3), can be correlated with the nucleation overpotential and its increase observed in the presence of IT-85, TEBA and Ferasine was associated with an increase the number of nuclei leading to finer grained deposits. These conclusions are consistent with the copper deposit morphology (Figure 1).

Quantitative information about the kinetics of the copper electrodeposition in the absence and presence of additives was obtained from the hydrodynamic voltam-

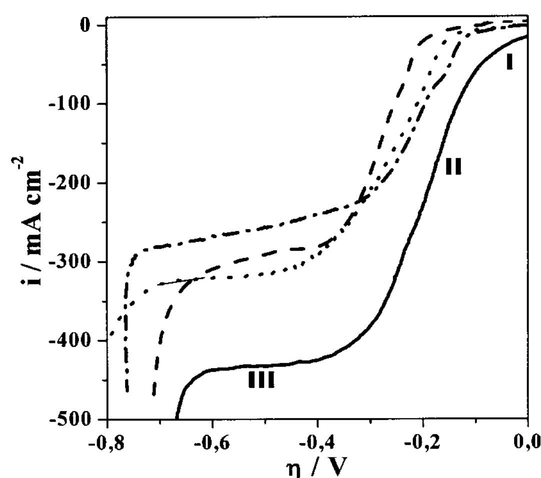
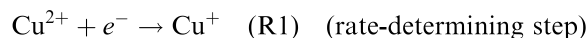
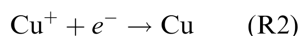


Fig. 3. Influence of organic additives on the hydrodynamic voltammograms at RDE: (–) without additives; (– –) 10 ml l^{-1} IT-85; (•••) 0.2 g l^{-1} TEBA; (–•–) 3 ml l^{-1} Ferasine. The curves were corrected for ohmic drop. Experimental conditions: scan rate, 20 mV s^{-1}; rotation speed, 1000 rpm.

mograms recorded at RDE using Tafel and Koutecky-Levich methods. In a first approach, considering the mechanism for copper electrodeposition proposed by Mattson and Bockris [30, 31]:



$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (R1) \quad \text{(rate-determining step)}$$



$$Cu^+ + e^- \rightarrow Cu \quad (R2)$$

and using the experimental data from the activation domain (region I, Figure 3), the Tafel plots allowed calculation of the cathodic transfer coefficient (α_c and of the standard rate constant (k_0), for the rate-determining step in the absence and presence of different concentrations of IT-85, TEBA [27] and Ferasine (Table 1).

In a second approach, the same kinetic parameters were estimated using Koutecky-Levich interpretation of the RDE measurements performed with linear sweeping of the rotation speed at different potential values chosen from the activation–diffusion region (region II, Figure 3). The electrochemical rate constants (k_E), calculated from the intercept of i^{-1} vs $\omega^{-1/2}$ dependencies, were corrected for the overpotential influence using a Tafel-type equation:

$$k_E = k_0 \exp\left(-\frac{\alpha_C F \eta}{RT}\right)$$

(see insets in Figure 4). The resulting kinetic parameters (α_c and k_0) are summarized in Table 1.

In the absence of organic additives, as well as in the presence of TEBA, both Tafel and Koutecky-Levich methods led to α_c values close to 0.5 (Table 1), in accordance with the classical two-stage mechanism proposed for copper electrodeposition (see reactions R1 and R2) [31]. The α_c values remain essentially unchanged in the presence of TEBA, suggesting that this additive does not change the copper electrodeposition reaction pathway [27].

In contrast, the continuous decrease of the α_c values in the presence of increasing concentrations of Ferasine (Table l) points to a change of the reaction pathway of copper electrodeposition. A possible explanation could be the increasing contribution of an additional reaction, producing Cu^+ ions and influencing the rate-determining step [12], e.g., the following equilibrium:

$$Cu^{2+} + Cu \leftrightarrow 2Cu^+ \quad (R3)$$

As can be observed from Table 1, in the presence of any of the investigated additives, the k_0 values for copper discharge process are considerably lower than those calculated in the solution without additives. This indicates that charge transfer is inhibited in the presence of IT-85, TEBA or Ferasine, which is in good agreement with the decay of the current density observed on the hydrodynamic voltammograms (Figure 3). Furthermore, in the investigated domain of concentrations, as the organic additive concentration increases their inhibiting action also increases. The small differences between the k_0 values, calculated by Tafel and Koutecky-Levich interpretations may be attributed to the pronounced increase in the electrode area during copper electrodeposition at the higher overpotentials used in the case of Koutecky-Levich method [27]. These differences diminish at high additive concentration.

A comparative examination of the k_0 values, calculated in the presence of corresponding concentrations of IT-85, TEBA and Ferasine, reveals that the strongest inhibition of copper discharge is induced by IT-85. The decrease in k_0 observed in the presence of TEBA or Ferasine used separately, compared to the k_0 value observed in the additive-free electrolyte, was in both

Table 1. Kinetic parameters for copper electrodeposition from sulphate acidic electrolytes without and with organic additives, estimated with Tafel and Koutecky-Levich methods

Additive conc.	Tafel			Koutecky-Levich		
	α_c*	$10^4 \times k_0$*/cm s^{-1}	Corr. coeff./ No of exp points	α_c*	$10^4 \times k_0$*/cm s^{-1}	Corr. coeff./ No of exp points
Without additives						
0	0.49 ± 0.01	1.32 ± 0.04	0.995/30	0.49 ± 0.01	1.09 ± 0.30	0.993/9
IT-85 ml l^{-1}						
10	0.45 ± 0.02	0.26 ± 0.01	0.998/34	0.44 ± 0.02	0.33 ± 0.05	0.998/9
25	0.42 ± 0.01	0.23 ± 0.01	0.996/30	0.41 ± 0.04	0.29 ± 0.04	0.995/6
50	0.36 ± 0.01	0.21 ± 0.02	0.999/34	0.39 ± 0.03	0.22 ± 0.06	0.988/9
TEBA g l^{-1}						
0.2	0.51 ± 0.02	0.45 ± 0.04	0.987/21	0.50 ± 0.05	0.65 ± 0.02	0.995/6
0.5	0.50 ± 0.02	0.27 ± 0.08	0.995/25	0.49 ± 0.07	0.54 ± 0.01	0.999/7
1	0.49 ± 0.01	0.24 ± 0.02	0.993/25	0.48 ± 0.01	0.30 ± 0.02	0.998/7
FERASINE ml l^{-1}						
3	0.43 ± 0.03	0.48 ± 0.04	0.998/15	0.42 ± 0.01	0.70 ± 0.04	0.997/9
8	0.42 ± 0.01	0.43 ± 0.02	0.998/18	0.40 ± 0.02	0.51 ± 0.03	0.997/7
15	0.40 ± 0.08	0.32 ± 0.02	0.995/19	0.39 ± 0.02	0.35 ± 0.07	0.992/6

* With standard deviation.

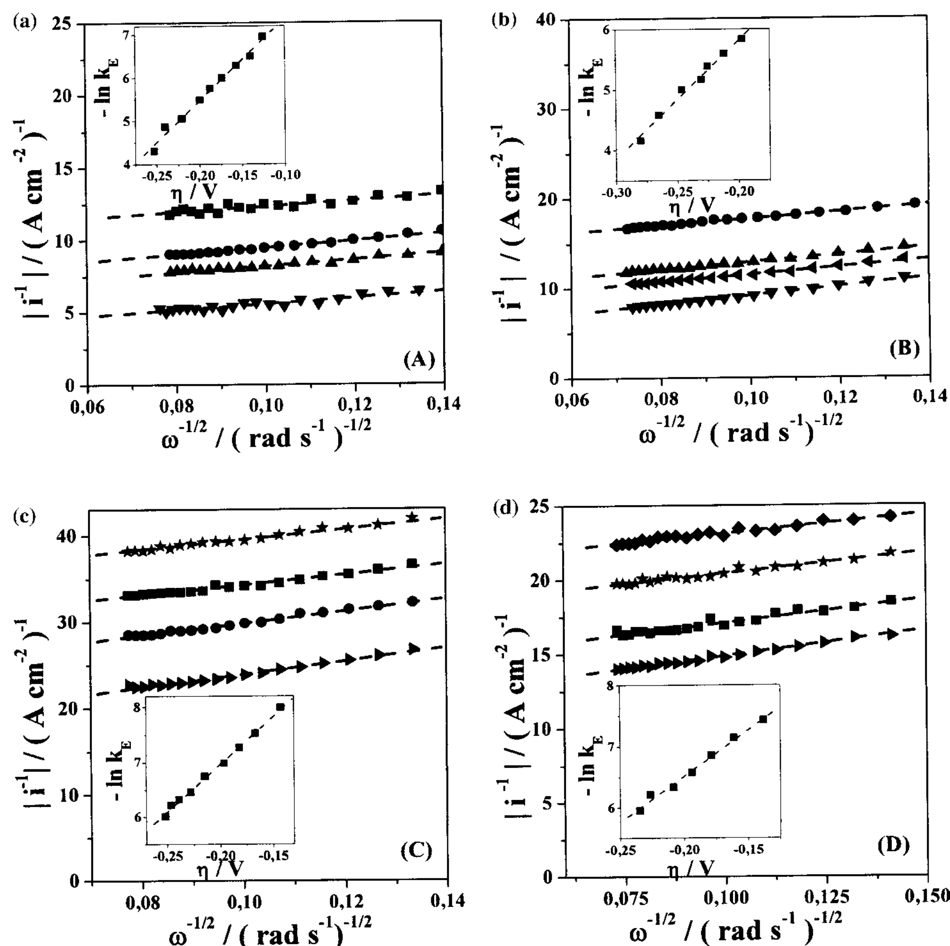


Fig. 4. Variation of i^{-1} with $\omega^{-1/2}$ in the absence (a) and in the presence of 10 ml l^{-1} IT-85 (b); 0.2 g l^{-1} TEBA (c); 3 ml l^{-1} Ferasine (D) at constant potentials chosen from the activation–diffusion control region: (6) −175; (φ) −200; (■) −225; (●) −250; (▶) −275; (▲) −300; (◀) −325; (▼) −375 mV vs SCE. *Insets*: Variation of heterogeneous rates constant (k_E) with the overpotential (η).

cases smaller than in the presence of IT-85, pointing to a complementary action of TEBA and Ferasine.

3.3. *Impedance measurements*

The influence of IT-85 and its components TEBA and Ferasine on the complex-plane impedance diagrams is illustrated in Figure 5. In the absence of organic additives (Figure 5A) and in the presence of TEBA (Figure 5C and C′), the complex-plane impedance diagrams exhibited two capacitive loops and a low-frequency inductive loop. The high-frequency capacitive loop was attributed to the charge transfer across the interface, and the second to a relaxation process of a charged adsorbed intermediate (Cu^{+}_{ads}) [27, 32–34].

In the case of IT-85 (Figure 5B and B′) or Ferasine (Figure 5D and D′), the impedance diagrams exhibit two capacitive loops in the intermediate-frequency domain, more clearly separated at high additive concentration, suggesting that at least two adsorbed species participate in the copper electrodeposition process. Thus the addition of IT-85 or Ferasine into the electrolyte solution changes the copper electrodeposition mechanism.

For all investigated additives. as well as in their absence, the product of charge transfer resistance (R_{ct}) and current density (i) is relatively independent of the d.c. potential value (Figure 6). On the other hand, in the investigated potential range, the iR_{ct} product corresponding to the presence of TEBA tends towards approximately the same values as for the additive-free electrolyte, suggesting that the additive has no effect on the charge transfer mechanism. It is interesting to note that this conclusion is in accordance with the invariance of the α_c values, calculated using the Tafel and Koutecky-Levich methods (Table 1). Consequently, the TEBA inhibition effect on the copper electrodeposition appears to be due to its action as a surface-blocking agent [27].

The presence of Ferasine induces a significant increase in the iR_{ct} product as compared to the additive-free electrolyte. This behaviour may be explained by the inhibition effect exerted by Ferasine on the charge transfer process, probably by changing the reaction pathway. This is in accordance with the observed decrease of the transfer coefficient for the rate-determining step involved in copper electrodeposition in the presence of Ferasine (Table 1).

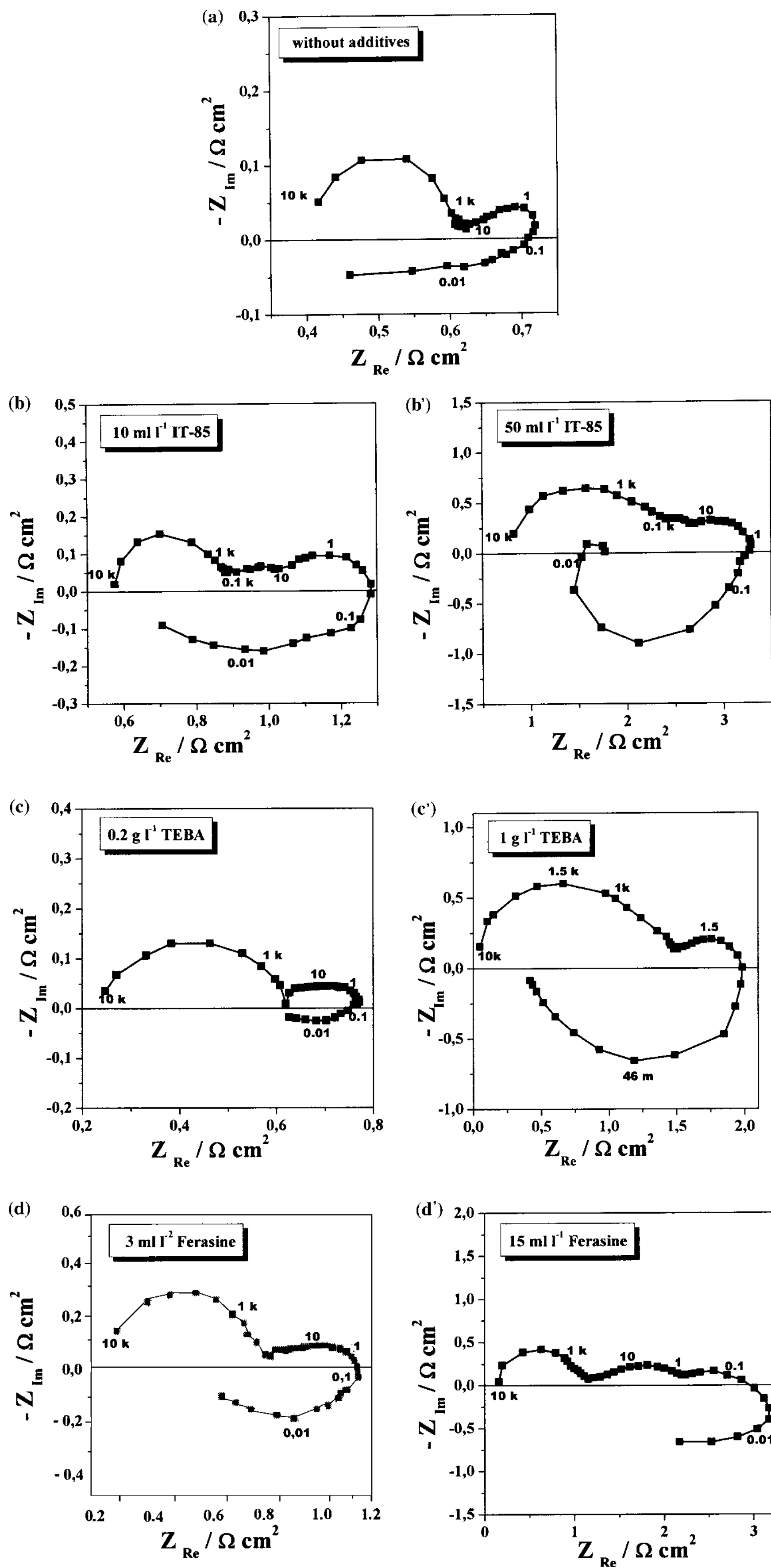


Fig. 5. Complex-plane impedance diagrams for copper electrodeposition at $E = -175$ mV vs SCE in the absence (a) and in the presence of different concentrations of IT-85 (b, b′); TEBA (c, c′); Ferasine (d, d′). Experimental condition: rotation speed, 1000 rpm. Frequencies are in Hz.

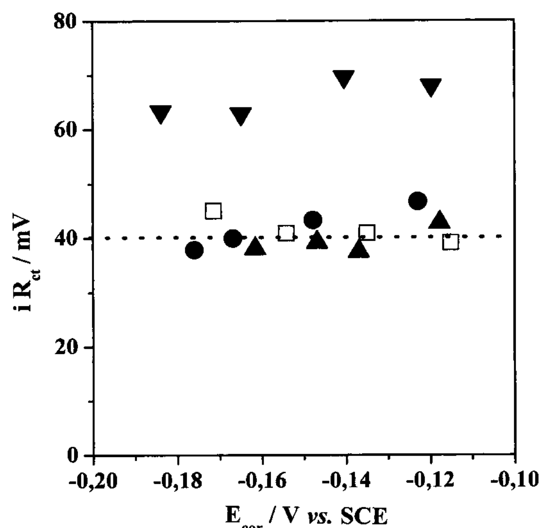


Fig. 6. Influence of the d.c. potential on the iR_{ct} parameter: (□) without additives; (●) 50 ml l^{-1} IT-85; (▲) 1 g l^{-1} TEBA; (▼) 15 ml l^{-1} Ferasine.

Surprisingly, the average value of the iR_{ct} product, calculated in the presence of IT-85, is close to that observed for the additive-free electrolyte and, in the investigated potential range, iR_{ct} is relatively invariant. This fact is apparently in contradiction with the slight variation of k_0 and α_c values (Table 1). Nevertheless, this behaviour can be explained accepting that in presence of IT-85 the reaction mechanism is not significantly changed and that a large decrease in active surface occurs as a consequence of simultaneous adsorption of TEBA and Ferasine. Moreover, it appears that the influence of Farasine on the overall mechanism is smaller when TEBA is present, while the simultaneous presence of both additives induces a stronger inhibition of the electrodeposition process than when they are used separately.

Concerning the two intermediate-frequency capacitive loops, recorded in the presence of IT-85 and Ferasine, no variation in frequency at their apex with electrode rotation speed was observed. An increase in apex frequency with the electrode polarization was apparent showing that the involved processes are potential activated. Consequently, both intermediate-frequency capacitive loops may be attributed to the relaxation processes of charged adsorbed intermediates.

The low-frequency inductive loop from the impedance spectra recorded in the absence, and presence of additives was interpreted in terms of the electrode area relaxation due to the birth and growth of copper monolayers formed on the facets of crystallites [33–35]. The nucleation time constant τ_n of the inductive loop changes in the presence of organic additives, pointing to an intervention of these compounds in the electrocrystallization step (Table 2). The decrease in τ_n value at a given d.c. electrode potential, in the presence of IT-85, TEBA and Ferasine, suggests an increase in the nuclei renewal rate, leading to a multiplication of nuclei on the

Table 2. The calculated nucleation time constant (τ_n) extracted from the apex frequency of the inductive loops recorded at −175 mV vs SCE in the absence and in the presence of organic additives

Electrolyte composition	Without additives	IT-85/ml l^{-1}		TEBA/g l^{-1}		Ferasine/ ml l^{-1}	
		10	50	0.2	1	3	15
τ_n/s	22.4	7.2	5.0	16.0	2.3	10.6	10.6

electrode surface. The highest nucleation rate corresponds to the presence of IT-85 (Figure 1). This is in accordance with the morphology of the copper deposits, consisting of smaller grains in the presence of organic additives than in their absence, and shows that IT-85, TEBA and Ferasine inhibit crystal growth and promote nucleation.

Although all organic additives promote nucleation, it is interesting to note that increase in additive concentration has different effects on τ_n values. While increased concentrations of IT-85 and TEBA lead to an enhancement of the copper nucleation process, the τ_n values of the inductive loop do not change significantly with Ferasine concentration, suggesting a weaker effect of this additive on copper electrocrystallization. These results are in agreement with the morphology of copper deposits obtained at Ferasine concentrations higher than that corresponding to Figure 1 (results not shown).

4. Conclusions

IT-85, TEBA and Ferasine were found to be efficient levelling agents in copper electrodeposition, leading to finer grained copper deposits, with a preferential growth orientation [1 1 0]. In mixture, the two components of IT-85 exert a beneficial effect, leading to more levelled cathodic deposits than when the TEBA or Ferasine were used separately. The interpretation of the experimental data obtained by hydrodynamic voltammetry at RDE as well as by electrochemical impedance measurements confirmed that:

(i) The inhibiting effect of the investigated additives on the charge transfer decreases in the order IT-85 > TEBA > Ferasine.
(ii) A comparison of the inhibiting effects exerted by IT-85 and its components on the charge transfer step, estimated by the values of the standard rate constants, pointed to the existence of a beneficial effect when TEBA and Ferasine are used in mixture.
(iii) The decrease in cathodic transfer coefficient in the presence of Ferasine proves that the copper electrodeposition mechanism is affected by the presence of the additive. In contrast, TEBA acts only as a blocking agent in the copper electrodeposition, without changing the reaction pathway corresponding to the absence of the additive.
(iv) All tested organic additives inhibit crystal growth and promote nucleation of copper; the effect on

copper the electrocrystallization step decreases in the order: IT-85 > TEBA > Ferasine.

In conclusion, it can be stated that the inhibiting effect of IT-85 on copper electrodeposition is the result of the specific intervention of its components in the different stages of the electrodeposition process.

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