



Diffusion coefficients of Cu(II) complexes with ligands used in alkaline electroless copper plating solutions

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Abstract

The diffusion coefficient values of the Cu(II) complex compounds with EDTA, DTPA, NTA, Quadrol, glycerol, saccharose, (+)- and (±)-tartaric acid, OH⁻ ions obtained by polarographic measurements in alkaline solutions lie in the range $(1.2\text{--}5.7) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (at 20 °C and $J = 3$) depending on the size of complex species, and are less than those of free (hydrated) Cu(II) ions and methanediol anion (H₂C(OH)O⁻) determined under the same conditions which are 7.0×10^{-6} and $10 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. The linear dependence of the polarographically determined diffusion coefficient values on the inverse radius of Cu(II) complex species is observed.

1. Introduction

Cu(II) complex compounds are widely used in electroless copper deposition [1–4]. The conventional electroless copper plating solutions are alkaline (the reducing agent, formaldehyde, is sufficiently strong only under these conditions, that is, pH 12–13.5) and Cu(II) ions must be bound into complex compounds to prevent the precipitation of Cu(OH)₂ [1–4]. Polyaminopolycarboxylic and polyhydroxylic ligands are of practical use as Cu(II) ligands in the above-mentioned systems [1–4].

The diffusion coefficient values of Cu(II) complex compounds are of great importance when investigating the kinetics of electroless copper plating, as well as in other areas of solution chemistry. The aim of this work was to systematize the literature data on the diffusion coefficient values of Cu(II) complex species with ligands used in electroless copper plating and to carry out additional experiments in the absence of such information.

2. Experimental details

2.1. Reagents and apparatus

The polarographic curves were recorded using a PU-1 polarograph (Belarus) with a dropping mercury electrode in a thermostated three-electrode cell. The main experiments were carried out at 20 ± 0.1 °C (some measurements were made at 50 ± 0.5 and 70 ± 0.5 °C). The potential scanning rate was 100 mV min^{-1} . The capillary characteristics at 20 °C were as follows: $m = 2.95 \text{ mg s}^{-1}$, $t = 3.73 \text{ s}$. The reference electrode

was a Ag/AgCl electrode filled with a saturated KCl solution. The solutions were deaerated by bubbling Ar. The total concentration of Cu(II) ions was $5 \times 10^{-4} \text{ M}$. The pH of solutions was measured using an EV-74 pH-meter (Belarus).

Carbonate-free solutions of sodium hydroxide were prepared using the method described in [5]. When NaOH concentration exceeded 0.1 M, pH was not measured directly, but was calculated from the equation:

$$\text{pH} = \text{p}K_w - \text{pOH} \quad (1)$$

using the activity of OH⁻ ions and pK_w given in [6].

NaNO₃ and NaOH were used to keep the ionic strength of solutions constant ($J = 3$) and the pH of solutions was controlled using NaOH and HNO₃ solutions. All the reagents were of analytical grade.

2.2. Calculations

The distribution of Cu(II) among the complexes was calculated using the least squares technique and the conditions of the predominance of one kind of Cu(II) complex species were established before the determination of the diffusion coefficient values.

The values of the diffusion coefficient (D) were calculated using the Ilkovic equation [7]:

$$D^{1/2} = \frac{\bar{i}_{\text{dif}}}{607 n c m^{2/3} t^{1/6}} \quad (2)$$

where \bar{i}_{dif} is the limiting diffusion current (μA), n is the number of electrons involved in the electrode reaction,

c is the concentration (mM), m is the flow rate of Hg (mg s^{-1}) and t is the time of the formation of the drop (s).

CPK (Corey–Pouling–Koultumn) molecular models were used for inspecting the possible geometry and size of the complexes ($0.1 \text{ nm} \equiv 1 \text{ cm}$). The diameter of the complex particle is taken as the value of its the highest possible dimension.

3. Results

3.1. *Cu(II) – aminopolycarboxylic and aminopolyhydroxylic ligands*

3.1.1. *Cu(II) – EDTA*

Ethylenediaminetetraacetic acid (EDTA) is widely used for binding of Cu(II) ions into complex compounds [8]. It should be noted that when reviewing the publications dealing with investigations of Cu(II) complexes with EDTA in alkaline medium two kinds of complex species were detected: simple complex CuY^{2-} [9–18] and hydroxycomplex $\text{CuY}(\text{OH})^{3-}$ [10, 16–20] (Y^{4-} is a fully deprotonized anion of EDTA).

There are few data for the diffusion coefficient values of CuY^{2-} complex compounds: from the results of polarographic investigations carried out at 20, 30 and 50 °C calculated values of $D_{\text{CuY}^{2-}}$ are 4.5×10^{-6} , 5.8×10^{-6} and $10.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively [21].

It must be noted that the data for the diffusion coefficient values of $\text{CuY}(\text{OH})^{3-}$ are absent.

Our previous investigations carried out at 20–70 °C showed that polarographic waves of Cu(II) reduction in alkaline EDTA solutions are quasi-reversible and diffusion-controlled (the limiting current temperature coefficient is $1.7\% \text{ grad}^{-1}$) [22, 23]. Based on these and spectrophotometrical experiments the conditions for the predominance of the individual complex species, that is, CuY^{2-} or $\text{CuY}(\text{OH})^{3-}$, were determined [18, 23]. The diffusion coefficient values of CuY^{2-} and $\text{CuY}(\text{OH})^{3-}$ species determined at 20, 50 and 70 °C are 5.2×10^{-6} and 4.6×10^{-6} ; 12.2×10^{-6} and 11.3×10^{-6} ; 21.8×10^{-6} and $19.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively [22, 23].

3.1.2. *Cu(II) – DTPA*

Diethylenetetraaminepentaacetic acid (DTPA) forms a more stable complex compound with Cu(II) than EDTA does ($\log \beta_{\text{CuZ}^{4-}} = 21.0$) [24]. The majority of authors indicates the existence of the simplest Cu(II)–DTPA complex compound CuZ^{3-} (Z^{5-} is a fully deprotonized anion of DTPA) [23–29]. The existence of the hydroxy-complex $\text{CuZ}(\text{OH})^{4-}$ was detected recently [30].

The data for the diffusion coefficient values of the complex species mentioned are not numerous. The values of CuZ^{3-} determined by means of direct current polarography at 50 and 70 °C are 10.5×10^{-6} and $13.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively [23].

It was shown that the polarographic waves of Cu(II) reduction in alkaline DTPA solutions are diffusion-controlled [23]. Therefore the values of the diffusion

coefficient can be measured and calculated at 20 °C. After the determination of the predominance conditions of the individual complex species the values of the diffusion coefficient were determined as $D_{\text{CuZ}^{3-}} = 4.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{CuZ}(\text{OH})^{4-}} = 3.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (this work).

3.1.3. *Cu(II) – NTA*

The formation of the simplest Cu(II)–NTA (nitrilotriacetic acid) complex compound CuX^- (X^{3-} is a fully deprotonized anion of NTA) was established, and the stability constant value was determined in [31–38]. The formation of the hydroxycomplex $\text{CuX}(\text{OH})^{2-}$ was detected in [38–41]. The possibility of the existence of CuX_2^{4-} and $\text{CuX}(\text{OH})_2^{3-}$ complexes has been suggested [39, 41]. Investigations carried out in an alkaline medium at tenfold excess of NTA using dc-polarography and spectrophotometry did not confirm this, only the complexes CuX^- and $\text{CuX}(\text{OH})^{2-}$ were found [38]. The diffusion coefficient values determined in the same work at 20 °C are: $D_{\text{CuX}^-} = 5.4 \times 10^{-6}$ and $D_{\text{CuX}(\text{OH})^{2-}} = 5.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

3.1.4. *Cu(II) – Quadrol*

N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine, which also is known as Quadrol (Q), is used as a Cu(II) ligand in alkaline solutions [1–4]. The investigations carried out in weakly acid – weakly alkaline solutions (pH 5–8) showed that Cu(II) forms two kinds of complex compounds with Quadrol: CuQ^{2+} and CuQ_2^{2+} [43–46]. The existence of the dihydroxycomplex species $\text{CuQ}(\text{OH})_2$ and $\text{CuQ}_2(\text{OH})_2$ was described recently [46]. In the same work the distribution of Cu(II) among the complexes with Quadrol was calculated over a wide pH range.

By polarographic investigation at 20 °C the diffusion coefficients of the complex compounds were determined [47]: $D_{\text{CuQ}^{2+}} = 4.5 \times 10^{-6}$, $D_{\text{CuQ}_2^{2+}} = 3.5 \times 10^{-6}$, $D_{\text{CuQ}(\text{OH})_2} = 3.0 \times 10^{-6}$ and $D_{\text{CuQ}_2(\text{OH})_2} = 2.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

3.2. *Cu(II) – polyhydroxylic and polycarboxy-polyhydroxylic ligands*

3.2.1. *Cu(II) – glycerol*

Investigations of Cu(II) complex formation with glycerol are not numerous. It was established that the complex formation occurs only in alkaline solutions. The molar ratio Cu(II):glycerol in complexes is 1:1 and 1:2, respectively, and complexes have negative charge [48–51]. A more detailed investigation of the composition and stability of these complex compounds was carried out [52, 53]. From the spectrophotometric and polarographic measurements it was determined that, in alkaline glycerol solutions, two kinds of Cu(II) complex compound predominate: $\text{CuGl}(\text{OH})_3^{2-}$ and $\text{CuGl}_2(\text{OH})_2^{2-}$ (Gl^- is a glycerol anion) and diffusion coefficient values calculated from the polarographic data are: $D_{\text{CuGl}(\text{OH})_3^{2-}} = 4.3 \times 10^{-6}$ and $D_{\text{CuGl}_2(\text{OH})_2^{2-}} = 3.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [53].

3.2.2. *Cu(II) – saccharose*

Synthesis of Cu(II)–saccharose complex compounds was described in [54]. The results of quantitative investigations of copper(II) complexes with saccharose in aqueous alkaline solutions are reported in [52, 55]: the formation of $\text{CuSa}(\text{OH})_2^-$, $\text{CuSa}(\text{OH})_3^{2-}$ and $\text{CuSa}_2(\text{OH})_2^{2-}$ species was established (Sa⁻ is a saccharose anion). Due to the complicated distribution of Cu(II) among the complexes in alkaline saccharose solutions the values of the individual complex compounds were not determined, but by means of dc-polarography it was shown that the diffusion coefficient values of Cu(II) complex species are in the range $(1.2\text{--}3.4) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (20 °C) depending on saccharose concentration [55].

3.2.3. *Cu(II) – (+)- and (±)-tartaric acid*

Most investigations of Cu(II) complex formation with tartarates in alkaline medium were carried out using (+)-tartrate. The dihydroxycomplex $\text{CuT}_2(\text{OH})_2^{4-}$ was found to be predominant at pH > 13, and to transform to $\text{Cu}(\text{OH})_4^{2-}$ at pH greater than 14 [56]. The Cu(II) complex compound of the similar composition was detected by means of the optical rotation method [57]. When using pH-metric titration, spectrophotometry and NMR methods, it was determined that the complex of $\text{CuT}(\text{OH})_2^{2-}$ dominated within the pH range 11 to 13.5 at the ratio of Cu(II):tartrate from 1:1 to 1:4 [58]. Investigations using the ESR method showed that the CuT_2^{2-} complex dominated at pH 10–11, while $\text{CuT}(\text{OH})_2^{2-}$ dominated at pH 11–12; and the complex CuT_2^{2-} (it differed in structure from the complex dominating at pH 10–11) was predominant at pH 13–14 and transformed to $\text{Cu}(\text{OH})_4^{2-}$ at pH greater than 14 [59].

When investigating the formation of Cu(II) ion complexes with (+)-tartrate and (±)-tartrate in alkaline solutions ($14.4 \geq \text{pH} \geq 11.5$) by means of dc-polarography and vis-spectrophotometry (20 °C, ionic strength $J = 3$) it was shown that three kinds of the complex compounds $\text{CuT}(\text{OH})_2^{3-}$, CuT_2^{4-} and $\text{CuT}_2(\text{OH})_2^{6-}$ (T³⁻ is tartrate anion) were formed for both tartrate isomers [60]. It must be noted that in this work it was shown that in the complex formation in alkaline solutions not T²⁻ (as was reported in [58, 59]), but the T³⁻ anion took part.

In the same work of the diffusion coefficients were determined. It was established that the diffusion coefficient values of Cu(II) complex species with (+)-tartrate and with (±)-tartrate are the same: $D_{\text{CuT}_2^{4-}} = 2.2 \times 10^{-6}$ and $D_{\text{CuT}_2(\text{OH})_2^{6-}} = 1.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [60].

3.3. *Cu(II) – OH⁻ ions*

The literature reveals that OH⁻ can take part in Cu(II) complex formation (forming hydroxycomplexes) or, in the case of the complex decomposition, can form tetrahydroxycuprate(II) ions [18, 30, 38–41, 46, 51–53, 55–60].

The composition and stability of $\text{Cu}(\text{OH})_4^{2-}$ was investigated in [38, 61–63]. $\text{Cu}(\text{OH})_4^{2-}$ was shown to have a planar structure [59, 64].

The diffusion coefficients of $\text{Cu}(\text{OH})_4^{2-}$ at various temperature were calculated from the polarographic limiting current values giving 5.7×10^{-6} , 12.0×10^{-6} and $19.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively, at 20, 50 and 70 °C [38].

3.4. *Hydrated Cu(II) ions*

The polarographic wave of Cu(II) reduction in 3 M NaNO₃ solution containing 0.5 mM Cu(NO₃)₂ is diffusion-controlled at 20 °C and the value of the limiting current is 4.17 μA. The calculated diffusion coefficient value of hydrated Cu(II) ions in the absence of complexing agents is $7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (this work).

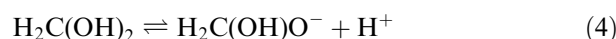
3.5. *Formaldehyde in alkaline solutions*

Generally speaking it would be interesting to compare the diffusion coefficient values of Cu(II) complex compounds with those of formaldehyde, a reducing agent widely used together with the Cu(II) complex compounds mentioned.

Formaldehyde is known to exist largely in the hydrated form of methanediol in solution ($K_e = 2 \times 10^3$) [65]:



The dissociation of methanediol takes place in alkaline solutions forming a methanediol anion ($\text{p}K_a \sim 13$) [66]:



According to [67, 68], the principal reducing agent in electroless copper deposition solutions is the methanediol anion. Its diffusion coefficient value was determined polarographically in [69]: $D_{\text{CH}_2(\text{OH})\text{O}^-} = 10 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (20 °C, 0.1–0.6 M NaOH).

4. Discussion

The results of the investigations show that the diffusion coefficients of the chelated Cu(II) species (Table 1) are less than that of free (hydrated) Cu(II) ions (Section 3.4). Similar conclusion for chelated metal species and free metal ions were also made [70].

When comparing the polarographically determined diffusion coefficients of Cu(II) complexes with approximate diameters (Table 1), the following correlation was found: the diffusion coefficient decreases with the increase in species size.

According to the Stokes–Einstein equation the diffusion coefficient (D) is inversely proportional to the radius of the particle (r):

Table 1. Diffusion coefficient values of Cu(II) complex species calculated from polarographic data*

Ligand and its designation	Cu(II) complex compound	Appr. diameter, /nm	Temperature, /°C	$D \times 10^6$, / $\text{cm}^2 \text{s}^{-1}$	References
EDTA (H_4Y)	CuY^{2-}	0.7	20	4.5	21
			20	5.2	22
			30	5.8	21
			50	10.5	21
			50	12.2	23
		$\text{CuY}(\text{OH})^{3-}$	0.8	20	4.6
			50	11.3	23
			70	19.5	23
DTPA (H_5Z)	CuZ^{3-}	1.0	20	4.2	This work
			50	10.5	23
			70	13.2	23
NTA (H_3X)	$\text{CuZ}(\text{OH})^{4-}$	1.1	20	3.7	This work
	CuX^-	0.6	20	5.4	38
Quadrol (Q)	$\text{CuX}(\text{OH})^-$	0.7	20	5.1	38
	CuQ^{2+}	0.9	20	4.5	47
Glycerol (HGI)	CuQ_2^{2+}	1.2	20	3.5	47
	$\text{CuQ}(\text{OH})_2$	1.2	20	3.0	47
	$\text{CuQ}_2(\text{OH})_2$	1.5	20	2.5	47
	$\text{CuGI}(\text{OH})_3^{2-}$	0.8	20	4.3	53
	$\text{CuGI}_2(\text{OH})_2^{2-}$	1.1	20	3.7	53
Saccharose (HSa)	$\text{CuSa}(\text{OH})_5^-$	1.2	20	} from 1.2 } to 3.4	55
	$\text{CuSa}(\text{OH})_3^{2-}$	1.4	20		55
	$\text{CuSa}_2(\text{OH})_2^{2-}$	2.2	20		55
(+) and (±)-tartaric acid (H_3T)	CuT_4^-	1.6	20	2.2	60
	$\text{CuT}_2(\text{OH})_2^{6-}$	1.8	20	1.7	60
OH^- ions	$\text{Cu}(\text{OH})_4^{2-}$	0.6	20	5.7	38
			50	12.0	38
			70	19.0	38

* Data except [21] were obtained at fixed ionic strength (3 mol l^{-1})

$$D = \frac{RT}{N_A} \frac{1}{6\pi\eta r} \quad (5)$$

where η is the solution viscosity.

Figure 1 shows the dependence of the polarographically determined diffusion coefficient values on the inverse radius of Cu(II) complex species. This dependence is close to linear, taking into account the possible hydration of the complexes, and the fact that the Stokes–Einstein equation is assigned to uncharged and spherical particles which are larger than the molecules of the solvent, assuming a moderate effect of the surrounding electronic charge on the neighbouring species.

When comparing the $D_{\text{CH}_2(\text{OH})\text{O}^-}$ value with those of Cu(II) complex compounds at the same temperature, it is seen that in all cases the methanediol anion diffusion coefficient value is higher. This is in agreement with the expected size of $\text{H}_2\text{C}(\text{OH})\text{O}^-$, which is $\sim 0.5 \text{ nm}$ (cf. with the data of Table 1).

The diffusion coefficient values of the Cu(II) complexes can also be determined by rotating disc electrode investigations. It was found that $D_{\text{CuY}^{2-}} = 3.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (pH 4, 20°C) [71]; $D_{\text{CuY}^{2-}} = 2.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{CuX}^-} = 2.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ($0.5 \text{ M Na}_2\text{SO}_4$, 25°C) [72]. When comparing the results obtained using the rotating disc electrode with those calculated from polarographic data (Table 1), it can be concluded that

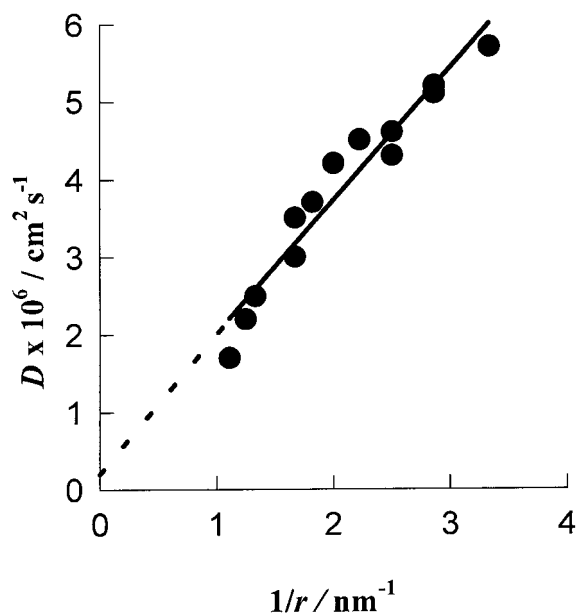


Fig. 1. Dependence of the polarographically determined diffusion coefficient values (Table 1; 20°C , $J = 3$) on the inverse radius of Cu(II) complex species.

the diffusion coefficient values of the same complex species calculated on the basis of the rotating disc electrode in [71, 72] are lower.

We are of the opinion that the results given in [71, 72] are low. This can be confirmed on the basis of the free (hydrated) Cu(II) ion diffusion coefficients; the value of $D_{\text{Cu(II)}}_{\text{free}} = 5.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (25 °C) presented in [72] is considerably lower than that $D_{\text{Cu(II)}}_{\text{free}} = 7.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (25 °C) [73] and $D_{\text{Cu(II)}}_{\text{free}} = 6.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (1 M KCl, 21 °C) [74]. Our investigations carried out at 20 °C gave the value of $D_{\text{Cu(II)}}_{\text{free}}$ as $7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is in good agreement with the data obtained in [73], taking into account the temperature coefficient of the diffusion coefficient being ~3% [7], as well as with the data given in [74].

5. Conclusions

The diffusion coefficients of Cu(II) complex compounds with EDTA, DTPA, NTA, Quadrol, glycerol, saccharose, (+)- and (±)-tartaric acid, OH⁻ ions obtained by polarographic measurement in alkaline solutions lie in the range $(1.2\text{--}5.7) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (at 20 °C). The values of the diffusion coefficients of the complexes investigated are less than that of free (hydrated) Cu(II) ions determined under the same conditions, which is $7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The diffusion coefficients of the Cu(II) complexes investigated decreases with increase in species size. The dependence of the polarographically determined diffusion coefficient values on the inverse radius of the Cu(II) complex species is linear.

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