

## STUDY OF ELECTROCHEMICAL PROPERTIES OF THE TERNARY SYSTEM WATER-DIMETHYLSULFOXIDE-COPPER SULPHATE.

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### ABSTRACT

A study of many physical and electrochemical properties such as refractive index and specific conductance of the ternary system water-dimethylsulfoxide-copper sulphate as a function of temperature (in the interval 20 °C-50 °C) is reported, as well as the variations for the peak potentials in the cyclic voltammograms, at several temperatures (between 20 °C and 80 °C) of copper sulphate 1 mM in many water-dimethylsulfoxide mixtures and the galvanic potentials at 20 °C of some metallic electrodes in water-dimethylsulfoxide mixtures.

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### KEY WORDS

Water and dimethylsulfoxide; ternary systems; copper sulphate; refractive index; conductance; galvanic potential; cyclic voltammetry.

### INTRODUCTION

Since a few decades ago, numerous studies concerning solvents of high permittivity (dimethylsulfoxide, dimethylformamide, etc) have been developed. These solvents have a great interest both in electrochemical engineering and hydrometallurgy, as well as in recovering and treatment of metals, organic electrochemistry, etc. Dimethylsulfoxide is a good protophilic solvent, being able to dissolve, at least moderately, a great number of organic substances (hydrocarbons, proteins, heterocycles, cellulose, etc), and inorganic ones (ionic compounds, specially of  $M^+$  and  $M^{2+}$  species). It shows a very high permittivity ( $\epsilon=46.7$ )<sup>1</sup>, and light alkaline properties ( $pK=0.91-1$ )<sup>2</sup>, with an autoprotolysis constant  $pK_s$  of 33.3<sub>3</sub> or 29.0<sub>2</sub> depending on the author. By that reason it reacts with acids and easily coordinates cations, specially  $M^+$  and  $M^{2+}$  species, and has been studied as a ligand<sup>4</sup>. However, it coordinates anions with difficulty due to sterical effects. Its interval of liquid state (17 °C to 189 °C) allows us to work in a wide range of temperatures. It is quite expensive for industrial purposes, but because it is compatible with water (at a very low cost), the employment of a water-dimethylsulfoxide mixture allows to adjust properly the solubilities, conductances and electrode potentials, for an electroactive substance. This is so, because the molar ratio and temperature can be easily and widely modified. It has a very low toxicity<sup>5</sup>. However, most of the studies<sup>6,7,8,9,10,11</sup> about this solvent and its water mixtures have been done at room temperature, and with  $M^+$  species, with some exceptions<sup>12</sup>. By that reason, copper sulphate was employed, and the properties were measured from 20 °C to 50-80 °C. Departing on a solution of an inorganic substance into an organic solvent a precipitate is easily produced with the course of time, due to solubility equilibria, oxidation or ligand substitution reactions, being both of them of slow kinetics. Given that, it becomes important to study the influence of time from the preparation of the solution in the real concentration of the solution at each temperature. In this paper, all the measures of the saturated solutions are referred to the case of solutions prepared three or four days before.

**EXPERIMENTAL**

**Chemical products and solutions**

- \* Pure water deionized in the Milli-Q.
- \* Dimethylsulfoxide **Scharlau** of synthesis grade (min. 99.5% and water content <0.2%).
- \* Pentahydrated copper sulphate **Scharlau** (min. 99%).
- \* Mixtures of both solvents were prepared, in molar fraction intervals of 0.1. From each one of these mixtures, many solutions were obtained, dissolving pentahydrated copper sulphate in increasing quantities, along the entire range of composition, until reaching the saturated solution, bearing in mind the crystallization water. In the case of pure dimethylsulfoxide, anhydrous copper sulphate was employed, which was obtained from the hydrated one drying it in an electric furnace at 300 °C for three hours. All the solutions prepared are shown in Table 1.
- \* Potassium chloride **Merck** (min. 99.5 %), as support electrolyte in cyclic voltammetry.

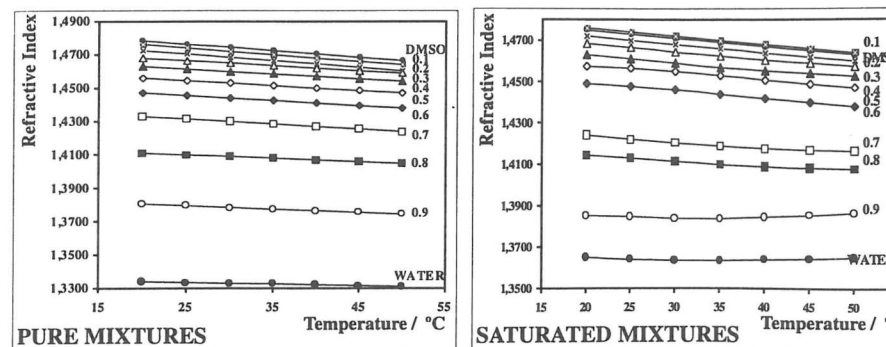
**Table 1.-** List of solutions prepared, in molar concentrations in copper sulphate, for each water / dimethylsulfoxide molar ratio. In the case of pure dimethylsulfoxide, anhydrous copper sulphate was employed.

<b>DMSO</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , and saturated solution.
<b>0.1</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , and saturated solution.
<b>0.2</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , and saturated solution.
<b>0.3</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , and saturated solution.
<b>0.4</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , 10 <sup>-2</sup> and saturated solution.
<b>0.5</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , 10 <sup>-2</sup> and saturated solution.
<b>0.6</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , 10 <sup>-2</sup> and saturated solution.
<b>0.7</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , 10 <sup>-2</sup> , 2.5·10 <sup>-2</sup> , 5·10 <sup>-2</sup> and saturated solution.
<b>0.8</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , 10 <sup>-2</sup> , 2.5·10 <sup>-2</sup> , 5·10 <sup>-2</sup> and saturated solution.
<b>0.9</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , 10 <sup>-2</sup> , 2.5·10 <sup>-2</sup> , 5·10 <sup>-2</sup> , 0.10 and saturated solution.
<b>WATER</b>	0, 10 <sup>-4</sup> , 10 <sup>-3</sup> , 5·10 <sup>-3</sup> , 10 <sup>-2</sup> , 2.5·10 <sup>-2</sup> , 5·10 <sup>-2</sup> , 0.10, 0.15, 0.25, 0.30, 0.50, 0.75, 1.00, 1.30, 1.50, and saturated solution.

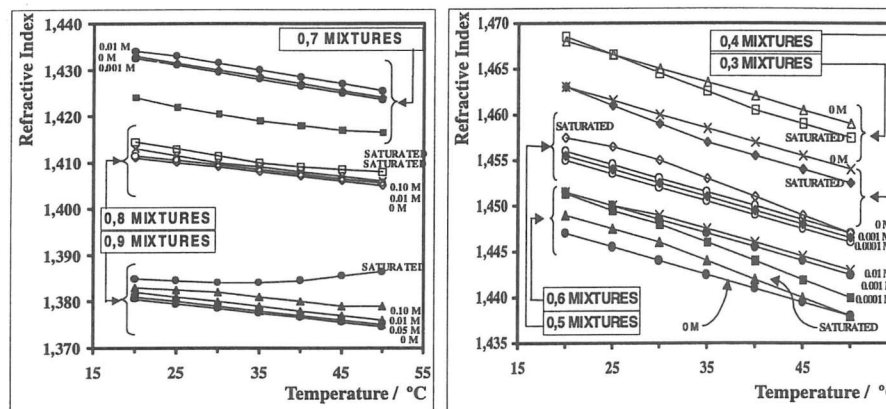
**Results and Discussion**

**Refractive Index**

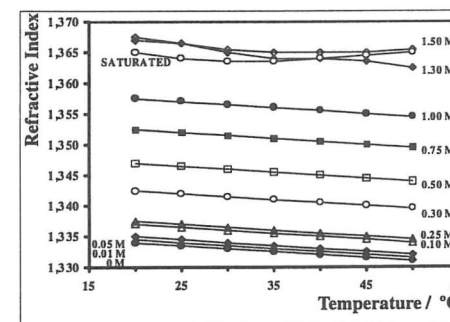
The refractive index for each solution cited in Table 1 was measured between 20 °C and 50 °C. An ATAGO Abbé refractometer was employed, with an accuracy of ±0.0005 units of refractive index. The results obtained for pure mixtures (with no solute) and saturated ones are summarized in Figure 1. For pure mixtures it is observed that the temperature dependence is linear and the values of the refractive index and the slopes depend on the molar fraction. Small additions of dimethylsulfoxide to water bring significant changes in the properties of the medium, but it doesn't happen the other way. Our measures of refractive index for dimethylsulfoxide and water, at different temperatures, agree with the literature<sup>12,13</sup>. In the ranges of temperature and molar fraction studied, the refractive index of pure mixtures has no discontinuities and because of that, its dipolar interaction is broken with no abrupt structural changes in the mixtures<sup>14,15</sup>. In the case of saturated mixtures it is noticed that the concentrations reached at the saturation point are greater with the smaller percentage of dimethylsulfoxide in the mixture. For that reason, the values obtained for saturated mixture of high content in dimethylsulfoxide are similar to the pure ones.



**Figure 1.-** Dependence of the refractive index in water / dimethylsulfoxide mixtures, with no species in solution (left), and saturated with copper sulphate (right), as a function of the temperature and the molar ratio of water.



**Figure 2.-** Dependence of the refractive index in copper sulphate solutions, on the temperature and molar concentration, in water-dimethylsulfoxide mixtures.



**Figure 3.-** Dependence of the refractive index of copper sulphate in water, on the temperature and molar concentration.

In the same way, the higher water proportion in the mixture, the higher the difference of refractive index between pure and saturated mixture. The plot also shows curvature as a function of temperature due to the increase of solubility. Figures 2 and 3 show the refractive index as a function of the temperature and the concentration of copper sulphate, for water and the mixtures of molar ratios between 0.9 and 0.3. For water, dimethylsulfoxide, and the 0.9, 0.8, 0.6, 0.5, and 0.3 mixtures, the refractive index is greater at the saturated solution than the pure solution. On the contrary, the saturated 0.2, 0.4 and 0.7 mixtures have a refractive index smaller than the pure ones, and the 0.1 mixture shows the same value for pure and saturated cases.

**Specific conductances**

A study of the variation of specific conductance with temperature and concentration of copper sulphate was performed with the same solutions and range temperature. It was used a CRISON 522 conductimeter and a conductance cell of constant value  $1.115 \text{ cm}^{-1}$  for this purpose. The results are shown in Figures 4 to 6. In pure mixtures, conductance curves as a function of temperature are concentrated in the same place, from dimethylsulfoxide to the 0.8 mixture, which begins to come closer to water. It is noticed that the specific conductance of the pure 0.9 mixture is larger than that of pure water. Although the mixtures with a great proportion in dimethylsulfoxide have small and similar values of conductance, they have, on the other hand, greater boiling points, and relatively high conductances at high temperatures. (See Figure 4).

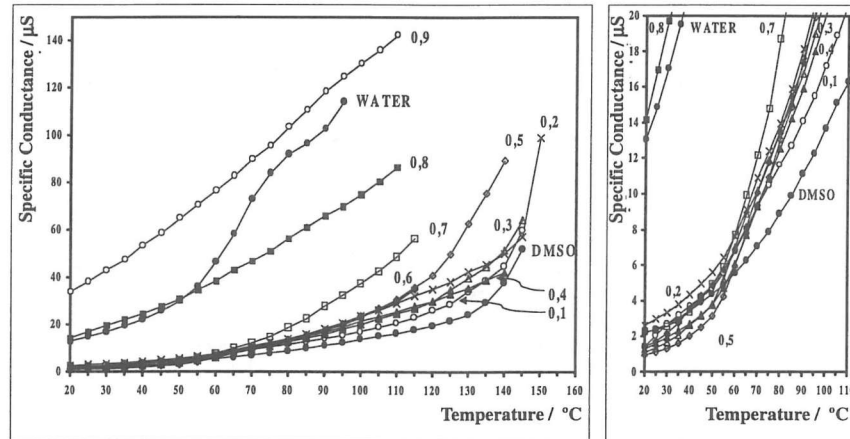


Figure 4.- Specific conductances in microsiemens, as a function of the temperature, of water-dimethylsulfoxide mixtures (left). An enlargement of the previous plot is shown (right).

In the case of saturated solutions (after some days of repose), the conductances showed a peculiar arrangement. From saturated dimethylsulfoxide to the saturated 0.4 mixture, the conductance decreases, with the exception of the saturated 0.2 mixture, that shows a notorious rise in conductance. The saturated 0.5 mixture shows also a great value of conductance, that overcomes the values of the saturated 0.6, 0.7 and 0.8 mixtures. The saturated 0.9 mixture and water have great conductances due to their higher concentrations of copper sulphate in the saturation. (See Figure 5). The rise in conductance with temperature is linear and very low in the first group of solutions (DMSO-0.4), increasing and obtaining curvature when increasing the proportion of water in the mixture, due to the higher solubility of copper sulphate.

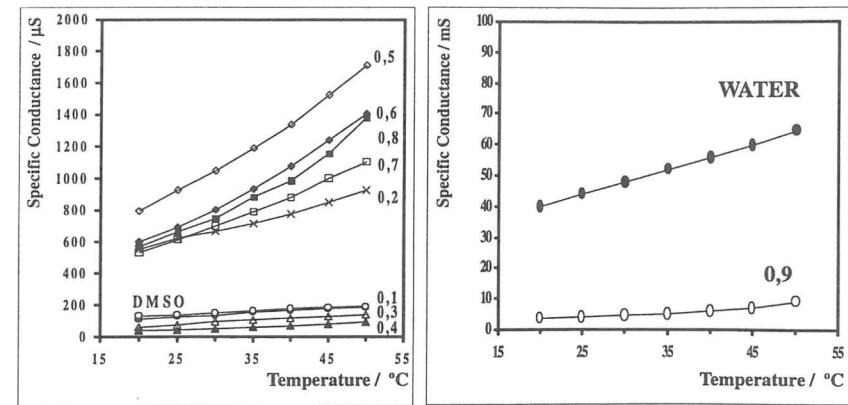


Figure 5.- Specific conductances of the saturated solutions of copper sulphate, as a function of the temperature and the molar ratio of water, in water-dimethylsulfoxide mixtures.

When variation of the conductance with temperature and concentration for each molar ratio is studied, a linear dependence of the conductance with temperature is noticed, except for the saturated mixtures, which are curved. The solubility of copper sulphate decreases with the rise of proportion for dimethylsulfoxide, and the conductances acquire similar values with the same concentration of copper sulphate in the 0.6 and 0.5 mixtures, and the 0.4 and 0.3 mixtures, except for the saturated ones (See Figure 6a and 6b).

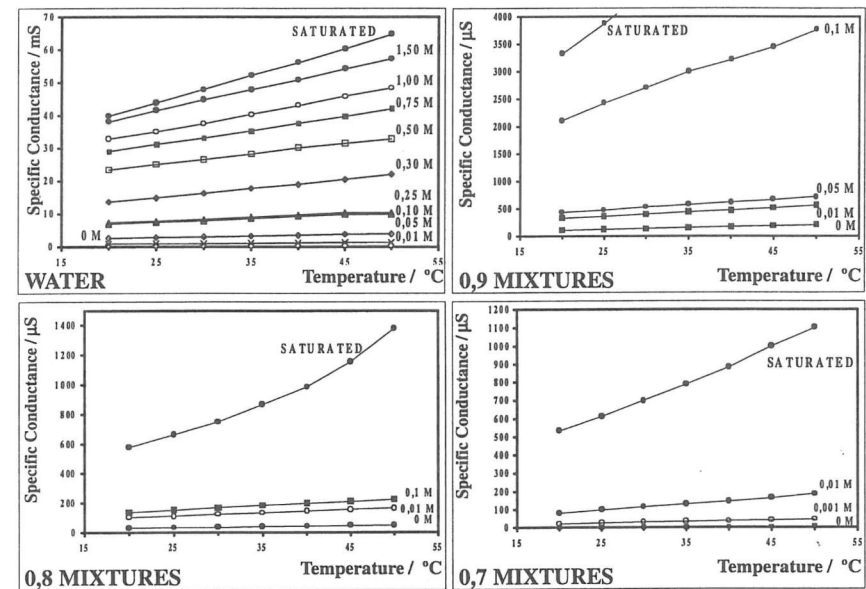


Figure 6a.- Specific conductances as a function of the temperature and the molar concentration of copper sulphate solutions in water and water-dimethylsulfoxide mixtures (molar ratios from 0.9 to 0.7).

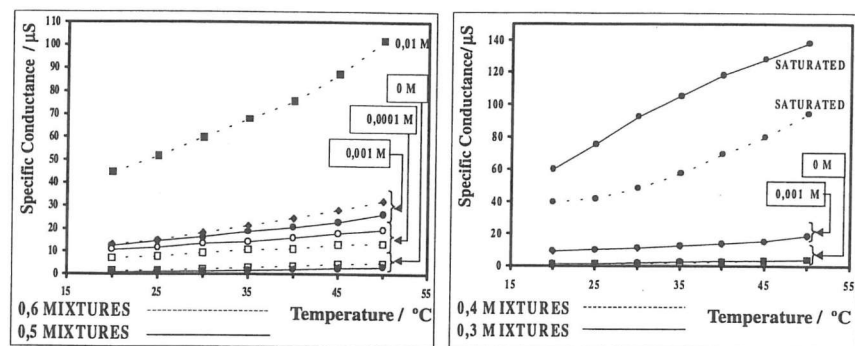


Figure 6b.- Specific conductances as a function of the temperature and molar concentration of copper sulphate solutions in water and water-dimethylsulfoxide mixtures (molar ratios from 0.6 to 0.3).

**Galvanic potentials**

The galvanic potentials of some metallic electrodes, in water, dimethylsulfoxide and their mixtures, with no electrolytes in solution, were measured at room temperature of 20 °C, with the Ag/AgCl (KCl 3 M) as a reference electrode, and a pH-meter / millivoltmeter CRISON 501.

Before each measurement, the surface of the electrode was sandpapered and immersed in diluted nitric or hydrochloric acid (depending on the electrode) as well as degreased with acetone, washed with water of milli-Q, and dried with paper.

The values presented in Table 2, for each electrode and mixture, are the mean value for ten measurements. As a general rule, galvanic potentials of these electrodes in dimethylsulphoxide are, with some exceptions, lesser than in water. It is clearly seen that the galvanic potential of silver electrode decreases significantly from water to dimethylsulfoxide, being the larger decrease of its value placed from water to the 0.7 mixture. The other electrodes show a similar linear behaviour, in the range from water to molar fraction 0.8.

Table 2.- Galvanic potentials, in mV, of some metallic electrodes in water, dimethylsulfoxide, and their mixtures, at 20 °C, with the Ag/AgCl (KCl 3M) as reference electrode.

R	0,0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0
Silver	-310	-280	-260	-240	-210	-220	-200	-180	-120	-60	10
Copper	-290	-260	-220	-240	-230	-230	-240	-220	-210	-200	-180
Nickel	-850	-770	-740	-780	-770	-740	-790	-780	-800	-810	-820
Lead	-590	-550	-520	-530	-480	-430	-460	-430	-530	-490	-460
Graphite	-380	-410	-370	-340	-320	-300	-370	-320	-250	-350	-430
Zinc	-950	-890	-870	-850	-800	-870	-970	-820	-850	-790	-740
Cadmium	-920	-890	-870	-870	-860	-850	-840	-870	-790	-800	-820
Tin	-610	-590	-570	-580	-570	-510	-570	-500	-470	-490	-520
Antimonium	-730	-690	-660	-640	-600	-570	-650	-520	-550	-580	-540

**Cyclic Voltammetry**

A wave generator HQ INSTRUMENTS-305 and a potentiostat HQ INSTRUMENTS-Model 105 were used to obtain cyclic voltammograms of copper sulphate 1 mM in water and some water / dimethylsulfoxide mixtures, keeping always KCl 0,1 M as support electrolyte, at scan rates of 20 and 50 mV/s, and temperatures between 20 °C and 80 °C, with platinum as working and auxiliary electrodes, and Ag/AgCl (KCl 3 M) as reference electrode. The free-oxygen solutions were prepared by bubbling nitrogen for half an hour. They were placed into a thermostated and well stoppered electrochemical METROHM cell (glass with num. 6.1418.220 and cover with num. 6.1414.010), to prevent vaporization of solvents. During the potential scans dry nitrogen was bubbled too into the solutions.

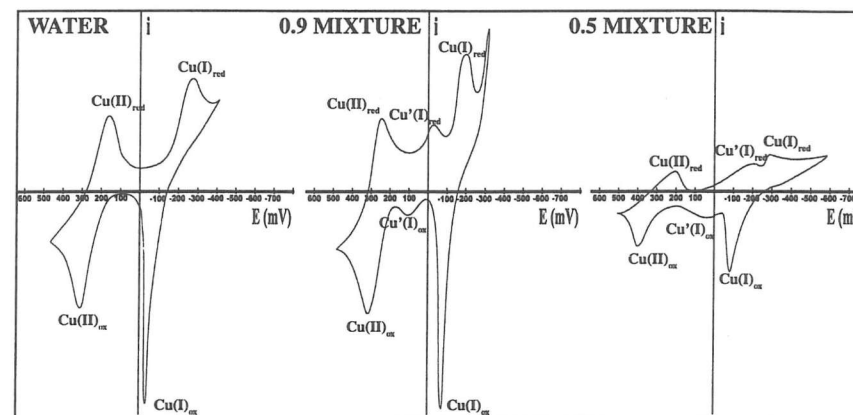


Figure 7.- Shapes of cyclic voltammograms at 25 °C, of CuSO<sub>4</sub> 1 mM in water and two water / dimethylsulfoxide mixtures (0.9 and 0.5 molar ratio of water), with KCl 0,1M as support electrolyte. Scan rate was 50 mV/s.

Typical shapes of the voltammograms are shown in Figure 7. Peak potentials and peak potential differences for all redox couples founded are listed in Table 3, as a function of temperature at both scan rates. Temperature correction was applied to the values obtained. Good voltammograms were obtained in water and mixtures from 0.9 to 0.5 molar ratios. From the 0,4 to 0,1 mixtures, the increasing ohmic resistance of solutions causes a poor quality in the voltammograms, but little distinguishable peaks. In water two species (of Cu(II) and Cu(I)) appears, whose peak potentials considerably defer of the values of the redox potentials of aquocomplexes. We supposed that the complexes are saturated with chlorine anions, due to the high concentration of support electrolyte. In water / dimethylsulfoxide mixtures, a new peak appears between the other two. Its height increases with concentration of dimethylsulfoxide and time (hours or minutes, depending on the proportion of dimethylsulfoxide in the mixture). At the same time, peak heights of the other Cu(I) complex decrease, with no changes in the Cu(II) ones. It means that at least one Cu(I) complex with dimethylsulfoxide is formed, and a ligand substitution reaction occurs in the system. Peak potentials and peak potential differences depends on the molar ratio of water, as is noticed in Table 3. In Figure 7 is noticed that the higher proportion of dimethylsulfoxide, the higher displacement of peaks of the two Cu(I) species to more negative potentials and higher peak potential differences. In the case of the Cu(II) specie, peak potential differences increases too with the proportion of dimethylsulfoxide, but the middle point of each pair of peaks displaces more slowly that in the case of the Cu(I) species. Peak differences increases with temperature only in water, and decreases in all water / dimethylsulfoxide mixtures. The mixture of molar ratio 0,9 has a minimum peak difference compared with the other mixtures in all molar ratio interval.

**Table 3.-** Peak potentials in volts ( $\pm 0.01$  V) and their differences for species detected in cyclic voltammograms. Reference electrode was Ag/AgCl (KCl 3M), and support electrolyte was KCl 0,1 M. Subscript (1) refers to the Cu(II) specie, and subscripts (2) and (3) refer to the Cu(I) species. Temperature corrections were applied to the potential values.

R	T (°C)	Scan rate: 50 mV / s									Scan rate: 20 mV / s								
		E <sub>1red</sub>	E <sub>1ox</sub>	$\eta_1$	E <sub>2red</sub>	E <sub>2ox</sub>	$\eta_2$	E <sub>3red</sub>	E <sub>3ox</sub>	$\eta_3$	E <sub>1red</sub>	E <sub>1ox</sub>	$\eta_1$	E <sub>2red</sub>	E <sub>2ox</sub>	$\eta_2$	E <sub>3red</sub>	E <sub>3ox</sub>	$\eta_3$
1.0	25	0,16	0,32	0,16	—	—	—	-0,32	-0,08	0,24	0,17	0,30	0,13	—	—	—	-0,28	-0,11	0,17
	40	0,15	0,33	0,18	—	—	—	-0,36	-0,10	0,26	0,17	0,32	0,15	—	—	—	-0,32	-0,12	0,20
	60	0,16	0,36	0,20	—	—	—	-0,41	-0,12	0,29	0,18	0,33	0,15	—	—	—	-0,39	-0,15	0,24
	80	0,16	0,40	0,24	—	—	—	-0,47	-0,13	0,34	0,18	0,35	0,17	—	—	—	-0,45	-0,17	0,29
0.9	25	0,20	0,32	0,12	-0,27	-0,02	0,25	-0,46	-0,22	0,24	0,22	0,31	0,09	-0,24	-0,01	0,23	-0,32	-0,14	0,18
	40	0,22	0,32	0,10	-0,24	-0,03	0,21	-0,47	-0,25	0,22	0,24	0,33	0,09	-0,23	-0,03	0,20	-0,33	-0,17	0,16
	60	0,23	0,32	0,09	-0,22	-0,04	0,19	-0,48	-0,27	0,21	0,25	0,35	0,11	-0,22	-0,05	0,17	-0,35	-0,20	0,15
	80	0,24	0,32	0,08	-0,21	-0,06	0,15	-0,49	-0,29	0,20	0,26	0,36	0,10	-0,18	-0,05	0,13	-0,37	-0,24	0,13
0.8	25	0,19	0,36	0,17	-0,32	-0,02	0,30	-0,45	-0,12	0,33	0,21	0,38	0,16	-0,28	-0,06	0,22	-0,37	-0,12	0,25
	40	0,20	0,37	0,16	-0,30	-0,03	0,27	-0,44	-0,16	0,29	0,22	0,38	0,16	-0,29	-0,07	0,22	-0,36	-0,13	0,23
	60	0,23	0,38	0,15	-0,29	-0,06	0,23	-0,44	-0,19	0,25	0,24	0,41	0,17	-0,29	-0,08	0,21	-0,36	-0,15	0,21
	80	0,26	0,40	0,14	-0,28	-0,09	0,20	-0,44	-0,22	0,22	0,26	0,45	0,19	-0,30	-0,10	0,20	-0,35	-0,14	0,21
0.7	25	0,22	0,37	0,15	-0,36	-0,06	0,29	-0,48	-0,15	0,34	0,24	0,37	0,13	-0,34	-0,10	0,24	-0,52	-0,32	0,21
	40	0,25	0,38	0,13	-0,36	-0,08	0,28	-0,50	-0,17	0,34	0,24	0,35	0,11	-0,32	-0,11	0,21	-0,52	-0,33	0,19
	60	0,26	0,40	0,14	-0,37	-0,11	0,26	-0,53	-0,22	0,31	0,25	0,39	0,14	-0,31	-0,13	0,18	-0,55	-0,37	0,18
	80	0,28	0,41	0,13	-0,39	-0,16	0,23	-0,55	-0,27	0,28	0,27	0,42	0,15	-0,28	-0,15	0,13	-0,58	-0,41	0,17
0.6	25	0,24	0,36	0,13	-0,38	-0,07	0,31	-0,54	-0,22	0,32	0,20	0,40	0,20	-0,35	-0,10	0,25	-0,52	-0,32	0,20
	40	0,24	0,38	0,14	-0,38	-0,08	0,30	-0,55	-0,24	0,31	0,21	0,39	0,18	-0,33	-0,10	0,23	-0,54	-0,35	0,19
	60	0,24	0,39	0,15	-0,38	-0,10	0,28	-0,57	-0,28	0,29	0,24	0,36	0,12	-0,32	-0,12	0,20	-0,56	-0,38	0,18
	80	0,25	0,40	0,15	-0,39	-0,14	0,24	-0,62	-0,35	0,27	0,25	0,36	0,11	-0,31	-0,13	0,18	-0,58	-0,41	0,17
0.5	25	0,15	0,49	0,34	-0,49	-0,12	0,37	-0,60	-0,27	0,33	0,19	0,43	0,24	-0,52	-0,12	0,40	-0,60	-0,30	0,30
	40	0,18	0,48	0,30	-0,49	-0,13	0,36	-0,62	-0,31	0,31	0,22	0,42	0,20	-0,52	-0,14	0,39	-0,61	-0,32	0,29
	60	0,20	0,47	0,27	-0,49	-0,15	0,34	-0,64	-0,34	0,30	0,24	0,43	0,19	-0,56	-0,17	0,39	-0,64	-0,36	0,28
	80	0,24	0,46	0,22	-0,50	-0,17	0,33	-0,66	-0,37	0,29	0,26	0,45	0,19	-0,58	-0,22	0,36	-0,66	-0,39	0,27
0.4	25	0,17	0,54	0,37	-0,57	-0,13	0,44	-0,68	-0,25	0,43	0,20	0,49	0,29	-0,54	-0,10	0,44	-0,72	-0,30	0,42
	40	0,18	0,52	0,34	-0,57	-0,10	0,47	-0,69	-0,29	0,40	0,22	0,49	0,27	-0,55	-0,12	0,43	-0,75	-0,32	0,43
	60	0,19	0,52	0,33	-0,58	-0,09	0,49	-0,72	-0,34	0,39	0,23	0,48	0,25	-0,59	-0,17	0,42	-0,78	-0,33	0,45
	80	0,22	0,51	0,29	-0,58	-0,09	0,49	-0,75	-0,39	0,36	0,25	0,47	0,22	-0,64	-0,22	0,42	-0,80	-0,35	0,45
0.3	25	0,14	0,53	0,39	-0,67	-0,10	0,57	-0,82	-0,32	0,50	0,16	0,46	0,30	-0,54	-0,14	0,40	-0,78	-0,30	0,48
	40	0,16	0,53	0,38	-0,69	-0,11	0,58	-0,83	-0,35	0,48	0,17	0,48	0,31	-0,55	-0,15	0,41	-0,73	-0,28	0,45
	60	0,18	0,54	0,36	-0,70	-0,17	0,54	-0,85	-0,37	0,49	0,23	0,49	0,26	-0,59	-0,21	0,38	-0,72	-0,28	0,44
	80	0,20	0,54	0,34	-0,74	-0,21	0,53	-0,89	-0,43	0,47	0,25	0,50	0,25	-0,63	-0,26	0,37	-0,68	-0,23	0,45
0.2	25	0,16	0,59	0,43	—	—	—	—	—	—	0,14	0,49	0,35	—	—	—	—	—	—
	40	0,17	0,60	0,43	—	—	—	—	—	—	0,17	0,49	0,33	—	—	—	—	—	—
	60	0,18	0,56	0,38	—	—	—	—	—	—	0,19	0,49	0,30	—	—	—	—	—	—
	80	0,20	0,55	0,35	—	—	—	—	—	—	0,22	0,49	0,27	—	—	—	—	—	—
0.1	25	0,00	0,71	0,70	—	—	—	—	—	—	0,07	0,49	0,42	—	—	—	—	—	—
	40	0,00	0,65	0,65	—	—	—	—	—	—	0,08	0,52	0,44	—	—	—	—	—	—
	60	0,06	0,63	0,58	—	—	—	—	—	—	0,12	0,52	0,40	—	—	—	—	—	—
	80	0,07	0,63	0,56	—	—	—	—	—	—	0,17	0,53	0,37	—	—	—	—	—	—

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