Potentiometric Studies on Chemically and Electrochemically Prepared Sulfide Active Materials for Determination of Copper(II)

Marija Bralić[1], Marijo Buzuk[2,], Maša Buljac[1], Slobodan Brinić[2]*

[1]Department of Environmental Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia
[2]Department of General and Inorganic Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia
[*]E-mail: buzuk@ktf-split.hr.

Three electrodes have been prepared by mixing and pressing different materials: Ag_2S + Cu (electrode 1); Ag + Cu (electrode 2); pure Cu powder (electrode 3). Prepared electrodes were chemically or electrochemically sulfidated and its suitability for potentiometric determination of Cu^{2+}, in water and mixed organic solvent-water solutions, have been investigated. Depending on electrode composition, differences in potentiometric characteristics between chemically prepared sensitive layers were noticed. Unexpected potentiometric behaviors, including deterioration in linear range, deterioration in detection limit (for chemically sulfidated electrode 1 and electrode 2) and super-Nernstian behavior (only for chemically sulfidated electrode 1) are observed and explained by physical characteristics of the prepared sulfide layers. Also, processes responsible for these behaviors are suggested and explained.. Improvements in potentiometric characteristics, for electrodes with electrochemically prepared sulfide layers, when compare to untreated and chemically treated electrodes are reported. Obtained detection limit, linear range and slope, for electrochemically sulfidated electrode 1 were 1.5×10^{-7} M, 3.0×10^{-7} - 0.1 M and 29.5 mV dec^{-1}, respectively. These improvements are discussed in the light of physical and chemical processes that take place in sensitive layers and electrode bulk. In addition, study performed in solutions containing different acetonitrile-water ratio revealed that not only solubility of Cu_xS, but also Ag_2S leaching (which depends on the nature and a way of its incorporation in membrane) is responsible for super-Nernstian responses in mixed solvents. Also, comments to appearance of the super-Nernstian response with increasing acetonitrile content are given.

Keywords: chemical and electrochemical sulfidation, potentiometry, mixed organic solvent-water solutions, super-Nernstian

1. INTRODUCTION

Ion-selective electrodes (ISEs) are established tools that are capable of determining the activities of many analytes. Since metal sulfide membranes were introduced as ion-selective electrodes for copper (II), cadmium(II) and lead(II) ions, many authors have published different methods for the preparation of Cu^{2+} ion-selective electrodes. The characteristic of these electrodes will depend of two main aspects, i.e. the way of preparing the electroactive material and the way in which this material is applied to construct the actual electrode [1, 2]. Potentiometric responses, in dependence of the phase structure of different prepared copper-silver sulfides, were reported by Brinic et. al [3]. In addition, prepared electrode materials and electrode were characterized using impedance spectroscopy, potentiometry and EIS techniques.

Although, different materials for preparation of copper-selective electrode were used (chalcogenide glasses [4-6] and ionophores [7-12]), most common commercial copper ISE are based on mixed metal sulfides, mainly silver-copper sulfides. The selectivity of the last mentioned electrodes is connected with solubilites of corresponding sulphides, as also as on the ratio of the used electroactive components [13]. Response mechanism of these electrodes was explained using single-crystal electrode, based on precipitated and pressed Cu_2S [14]. In these kind of electrodes, for providing transfer of electrical signal from ionic to electronic, it is necessary for membranes to contain some species that posses such capability. Although it is known that Cu_2S is mixed (electronic and ionic) conductor [15], most of sulfide-based crystal electrodes also contains Ag_2S. It is known that Ag_2S is mixed conductor and can provide selective charge distribution across a membrane, by some mobility (causing disturbance in crystal lattice) of Ag^+ ions through a crystal, which is monitored as potential. In addition, transfer from ionic to electronic conductivity can take place through whole electrode body, thus facilitated electron transfer at the interface metal /membrane, which results in more stabile signal.

Excellent review of solid state electrodes, with emphasis on electrodes based on simultaneously precipitated silver-copper sulfides (mainly consisted of the ternary compound called jalpaite - Ag_3CuS_2), with Nernstian response to Cu^{2+}, ions was presented by Gulens [16]. High detection limit of these electrodes were attributed to membrane oxidation [17], dissolution of the electrode and contamination of diffusion layer [18, 19], or to the contamination of electrode surface, in the presence of halide ions, by formation of amorphous sulphur [20].

However, limited information are available regarding electrodes for determination of Cu^{2+} based on the chemically or electrochemically prepared sensitive layers, composed of the silver and copper sulfides. In this work, three electrode (Ag_2S+Cu; $Ag+Cu$; Cu) have been chemically and electrochemicaly treated, in a sulfide solution, in order to gain a sensitive layers. Deviation from Nernstain response were assign not only to a method of preparation of the sensitive layer, but also to the way of the incorporation of various membrane components, which was found to have significant influence on kinetics, range and types of the physical and chemical processes responsible for potentiometric response. Also, it was founded that behaviors of different prepared electrodes in mixed (water-organic solvent) media can provide some information useful for interpretation and understanding response mechanism of prepared electrodes.

2. EXPERIMENTAL

2.1. Reagents

All chemical were of analytical reagent grade. All solutions were prepared with doubly distilled water.

Standard solution of Cu^{2+} (0.1 M) was prepared in a calibrated glass flask from copper(II) nitrate trihydrate (Kemika Zagreb, Croatia) diluted in doubly distilled water. The Cu^{2+} solution was titrated by a standardized 0.01 M EDTA solution. EDTA was obtained from Sigma Aldrich (St. Lousi, USA). Common stock solution was used for the preparation of 0.1 and 0.01 M solutions. The sodium sulfide solution was prepared by dissolving a certain amount of $Na_2S \times 9\ H_2O$ (Kemika Zagreb, Croatia) in double distilled water. Concentration of such solution was determined with lead nitrate standard solution.

Silver nitrate solution (0.1 M) was prepared from silver nitrate obtained from Kemika (Zagreb, Croatia). The silver nitrate was standardized with 0.1 M sodium chloride Kemika (Zagreb, Croatia).

Potassium nitrate (p.a.), acetonitrile (p.a.) potassium hydroxide (p.a.), ethanol (96% w/w), methanol (p.a.), ethylen glycole (p.a.) were purchased from Kemika (Zagreb, Croatia), while p-dioxane was obtained from Merck (Darmstadt, Germany)

2.2. Preparation of electrode materials

For the preparation of membranes three reagents have been used: copper fine powder particle size < 63 µm, obtaned from Merck, Darmstadt, Germany; silver powder, extra-fine grade, 99.95%, 500-1200 nm, obtained from Inframat Advanced Materials, Manchester, USA and home-made silver sulfide prepared by mixing stochiometric amounts of silver nitrate ($AgNO_3$) and sodium sulfide ($Na_2S \times 9H_2O$) solutions. Powders were mixed (total mass was 0.5 g), in order to prepare electroactive materials, in ratios presented in Table 1.

Table 1. Composition of electroactive materials

	w/w (%)		
	Cu	**Ag**	**Ag₂S**
Electrode 1	15	-	85
Electrode 2	15	85	-
Electrode 3	100	-	-

2.3. Electrode fabrication

After mixing, electroactive materials (total mass of 0.5 g) were pressed at 5000 kg cm^{-3} in order to achieve membranes thickness of 1 mm. Prepared membrane were placed in specially constructed multi-purpose Teflon® body [21] and electric contact was provided by the stainless steel disk. Before

placing in multi-purpose body, membrane were abraded with fine emery paper and polished with alumina powder down to 0.05 µm and rinsed with distilled water.

Sulfidation of the sensitive part of membranes was performed by chemical or electrochemical sulfidation.

Chemical sulfidation were performed by conditioning of multi-purpose body, containing membrane, in 0.1 M solution of sodium sulfide during 24 hours. After conditioning, electrodes were rinsed with distilled water.

Electrochemical sulfidation were performed using potentiostatic techniques (Autolab, Eco Chemie, combined with General purpose Electrochemical system (GPES)) in deaerated (with N_2) 0.5 M NaOH containing 0.01 M Na_2S at -0.9 V. The experiments were carried out using a standard three-electrode electrochemical cell. The counter electrode was a platinum electrode and the reference electrode was a saturated calomel electrode (SCE).

2.4. Potentiometric measurements

External reference electrode was double junction electrode (Mettler Toledo InLab 301 electrode). The potentiometric measurements were carried out by means of Mettler Toledo SevenEasy pH meter, which was connected to a computer. The potential build up across the membrane electrode was measured using the following electrochemical cell assembly:

ISE | test solution | external reference electrode. The potential was recorded after addition of standard Cu^{2+} solution in magnetically stirred 0.1 M KNO_3 (pH around 5.5) if not mentioned otherwise .The investigated potentiometric concentration range was from 1.0 x 10^{-7} M to 0.1 M.

Detection limits were estimated according IUPAC [22], as the intersection of two linear lines, the one extrapolated from high concentration range and the other parallel to the x-axis drawn through the mean potential value of the lowest metal ion concentration used in plot of the potential change and the concentration of copper(II) ion.

3. RESULTS AND DISCUSSION

To maintain a constant ionic strength, potentiometric measurements were performed in 0.1 M KNO_3 at 25 °C with constant stirring, as it well known that different stirring rate have a effects on electrode surface adsorption and on diffusion rate [23]. Figure 1 shows the potentiometric responses of untreated (withouth sulfidation) electrodes, toward Cu^{2+}. As it can be seen, electrode 1 and electrode 2 have shown similar near-Nernstian responses with the slopes. However, potentiometric responses of the electrodes were accompanied with significant drift (1 to 3 mV), so stable potential could not be achieved. This can be attributed to insufficient kinetics of reaction that provides potentiometric response, primary to the lack of layer that is responsible for potentiometric response, according accepted theories presented in excellent review by Gulens [16], which included following reaction:

$$Ag_2S(s) + Cu_2S(s) + 2\ Cu^{2+} \leftrightarrows 2\ CuS + 2\ Cu^{+} + 2\ Ag^{+}\ [24] \qquad (1)$$

$$Cu^{2+} + Cu_2S \leftrightarrows CuS(s) + 2\ Cu^{+} \qquad [16] \qquad (2)$$

$$Cu^{2+} + CuS(s) \leftrightarrows 2Cu^{+} + S(s) \qquad [25] \qquad (3)$$

Proposed reactions include exchange mechanism for reactions (1) and (2), as also as redox process (3).
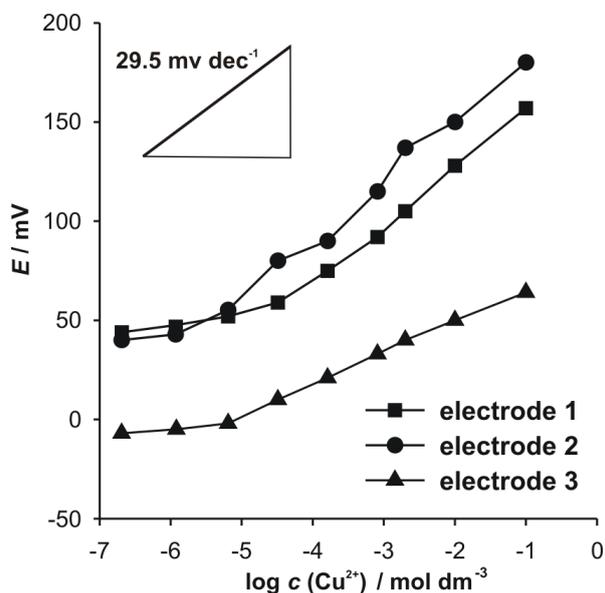
Figure 1. Calibration curves obtained by successive increasing of Cu^{2+} concentration for untreated electrodes.

However, as untreated electrodes did not have formed sulfide layer, it can be assumed that its behaviors toward Cu^{2+} follow those predicted for electrode of the first order. For this reason, the electrode, composed only of copper powder, has been prepared. Surprisingly, this electrode showed sub-Nernstian response (obtained slope was 16 mV per decade^{-1}), probably due to the lack sufficient time within fast and termodinamically reversible equilibrium can be reached. Also, outward fluxes of Cu^{2+} from membrane to solution interphase, cause disturbation in lattice of metal, thus causing unstable response.

Table 2. Some potentiometric characteristics of prepared (untreated) electrode

	linear range (M)	slope (mV dec^{-1})	detection limit (M)
electrode 1 (Ag$_2$S+Cu)	1.0×10^{-5} - 0.1	28.0	7.0×10^{-6}
electrode 2 (Ag+Cu)	6.5×10^{-6} - 0.1	28.5	5.0×10^{-6}
electrode 3 (Cu)	8.5×10^{-6} - 0.1	16.0	4.0×10^{-6}

In order to improve sensitivity, stability and other potentiometric characteristics, surface modification of prepared electrodes were done in two ways: by chemical and electrochemical sulfidation. The aim of these modifications was formation of a sensitive layer at the surface of electrode (as Cu_xS), which could be involved in exchange mechanism according to reactions (1) and (2). This layer can meet to requirements needed for satisfying potentiometric response toward metal ions, due it similarity to sensing parts (CuS or Cu_2S) of home-made or commercial electrodes.

Responses of chemically sulfidated electrodes are presented at Figure 2, while potentiometric characteristics are presented in Table 3.
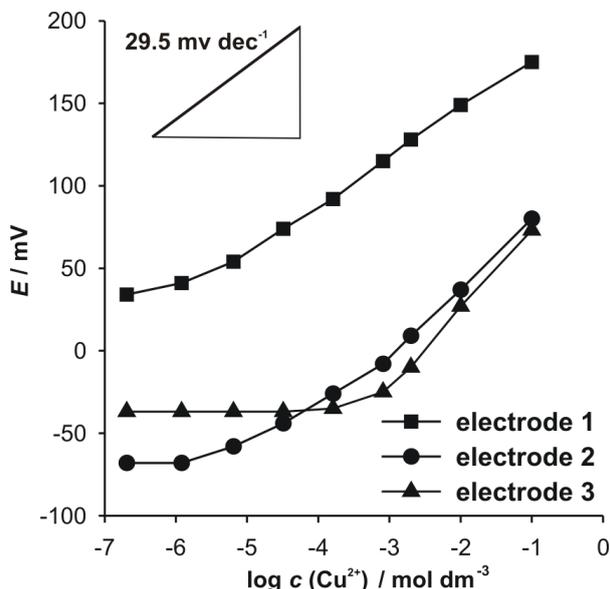

Figure 2. Calibration curves obtained by successive increasing of Cu^{2+} concentration for chemically sulfidated electrodes.

Table 3. Some potentiometric characteristics of chemically sulfidated electrode

	linear range (M)	slope (mV dec^{-1})	detection limit (M)
electrode 1 (Ag_2S+Cu)	3.0×10^{-6} - 0.1	29.5	1.0×10^{-6}
electrode 2 (Ag+Cu)	1.0×10^{-5} - 0.1	41.0	8.0×10^{-6}
electrode 3 (Cu)	8.0×10^{-4} - 0.1	48.6	5.0×10^{-4}

Interestingly, no improvements on potentiometric characteristics can be noticed in the case of electrode 3 (modified Cu), but super-Nernstian response, together with deterioration of the detection limit were obtained. As it previously described [26], by immersion of copper electrode in Na_2S solution, cuprous sulfide and cuprous oxide could be formed. For electrode 3, the main processes that controls detection of Cu^{2+}, at concentrations up to 10^{-3} M, is diffusion of Cu^{2+} through the formed porous structure of the Cu_2S. Insufficient kinetics of reaction (2), effected by slow diffusion can be the main reasons for increase of detection limit. Also, one of the reasons can be specific adsorption (fouling) inside porous structure of the Cu_2S. Above concentrations of 10^{-3} M of Cu^{2+}, reaction (2),

which is placed in porous structure of formed Cu_2S, is not hampered due to increase in concentration gradient. However, outward flux of formed Cu^+ is limiting factor for establishing fast and termodinamically reversible equilibrium for reaction (2). As pores contain relatively high concentration of Cu^+ toward O_2, oxidation of Cu^+ by O_2 is limited, and electrode response is consequence of disequilibrium Cu^+ concentration inside pores and super-Nernstian response has been observed.

For chemically sulfidated electrode 2 (Ag + Cu) slightly deterioration of detection limit can be noticed, primarily attributed to the same reasons as in the case of electrode 3 (see Figure 2). However, potential drift did not noticed. Stability of potentiometric response can be related to formed sulfides (Ag_2S and Cu_2S), which are known as relatively good mixed conductors (ionic and electronic) [15, 16], thus transfer from ionic to electronic conductivity is feasible. This transfer take place in sulfide layers, as also at the interface between surface formed Ag_2S-Cu_2S and Cu-Ag in the bulk of the electrode.

For the chemically sulfidated electrode 1 (Ag_2S + Cu) significant improvements concerning linear range and detection limit can be noticed (Figure 2). Distinction in potentiometric behaviour toward electrode 2 arise from fact that only sulfide layer that can be formed is Cu_2S (since Ag_2S was incorporated in membrane). This implies a lower porosity of formed layer and thus decreased fouling effect. Also, stability of response is improved due to presence of mixed conductor (Ag_2S), in contact with electronic conductor (Cu), within whole bulk of the electrode. Since transducing from ionic to electronic conductivity take place in whole electrode body, transfer of electrical signal through interface stainless steel disk/bulk of membrane (Ag_2S+Cu) is facilitated, enabling stabile and fast potentiometric response.

It is known that properties of surface layer are significantly influenced with kind of preparation process. Electroless deposits are found to be more porous than electrodeposited layers of comparable thickness [27]. Electrochemically sulfidization was performed in order to gain more ordered, compact and less porous layer, thus avoiding the problems described for chemical treated electrode. Obtained voltammograms for all three electrodes in 0.5 M NaOH containing 0.01 M Na_2S were identical to the results reported by Zaky et. al [28] (obtained for copper-silver alloys), so chosen potential for electrochemical sulfidization was -0.9 V vs. SCE. In addition, Zaky et. al. [28] confirmed formation of sulfides by x-ray diffraction analysis.

Table 4. Some potentiometric characteristics of electrochemically sulfidated electrode

	linear range (M)	slope (mV dec^{-1})	detection limit (M)
electrode 1 (Ag$_2$S+Cu)	3.0×10^{-7} - 0.1	29.5	1.5×10^{-7}
electrode 2 (Ag+Cu)	2.5×10^{-6} - 0.1	32.0	1.5×10^{-6}
electrode 3 (Cu)	1.0×10^{-4} - 0.1	35.0	5.0×10^{-5}

All three electrochemically sulfidated electrodes have shown extended linear range and lower detection limits, when compare to chemically sulfidated electrodes, which was in accordance with

expectations. Also, obtained slopes (32 mV dec^{-1} and 35 mV dec^{-1} for electrodes 2 and 3, respectively) tend to Nernstian response, thus indicating decreasing of fouling effect and establishing of the fast equilibrium.
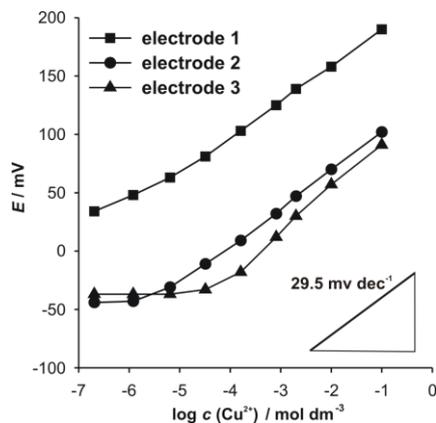

Figure 3. Calibration curves obtained by successive increasing of Cu^{2+} concentration for electrochemically sulfidated electrodes.

Thus, for further investigation and characterization, electrodes 1 and 2 (as electrodes with the best potentiometric characteristics) have been chosen.
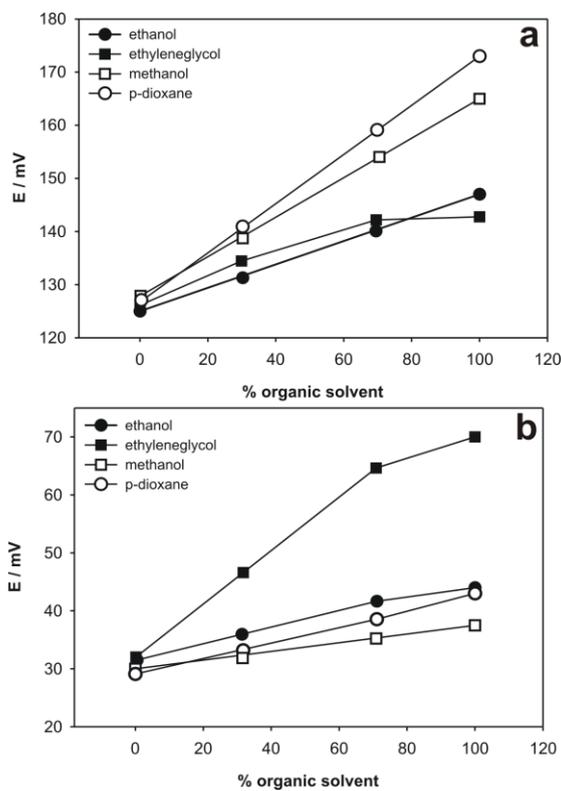
Figure 4. Influence of different organic solvent, in organic-water mixtures, on potential of the electrode 1 (a) and electrode 2 (b). Initial concentration of Cu^{2+} was c (Cu^{2+}) = 1.0×10^{-3} M

Further investigation was aimed on the behaviour of these two electrodes in mixed organic-water solvent, with emphasis on acetonitrile solution.

Influences of the some organic solvents on stability of potentiometric response, for electrodes 1 and 2, performed in solutions containing various amount of organic solvent, are presented at Figure 4. Although, instability of potential at constant Cu^{2+} concentration can be noticed, Nernstain or sub-Nernstian slopes were obtained when measurements were performed by addition of Cu^{2+} in solution containing constant organic solvent-water ratio (not shown). In addition, slightly deteriorations in detection limits were observed, which is in agreement with previously reported results [24].

Potentiometric responses of electrodes 1 and 2, with different acetonitrile content, are presented at the Figure 5a and 5b, respectively. Decreasing of initial potentials with increasing acetonitrile content can be explained by lower solubility of Cu_2S in acetonitrile (dielectric constant $\varepsilon= 37.5$) than in water ($\varepsilon= 80$). In addition, high stability of Ag/Ag_2S electrode, in various mixed aqueous-organic media, including acetonitrile-water solution, was reported by Ciobianu et. al [29] implying low solubility of Ag_2S in acetonitrile.

As addition of Cu^{2+} promotes a chemical reaction (1), leaching of Cu^+ and Ag^+ in solution becomes more pronounced. Increasing of slope in mixed acetonitrile-water solutions is a results of high stability of released Cu^+ and Ag^+ in acetonitrile [24]. As it can be observed from Figures 5a and 5b, slopes found to increase with increasing acetonitrile, which can be a consequence of lower oxidation rate of Cu^+ to Cu^{2+}. This oxidation is controlled by concentration of dissolved oxygen in solution, which become lower by increments of acetonitrile portion (Henry constant for O_2 in acetonitrile (for mole fraction) is 200 MPa [30]; for O_2 in water (for mole fraction) is 4 315 MPa). Interestingly, for identical contents of acetonitrile, larger slope was observed for electrode 2 than for electrode 1. This implies that the leaching of Ag^+ from electrochemically formed ("*in situ*") Ag_2S is more feasible than from Ag_2S which was directly incorporated in electrode and pressed, if we bear on mind that contents of Cu in both electrodes, as also as preparations of sulfide layer were identical for both electrodes (thus assuming identical solubility of prepared Cu_2S).
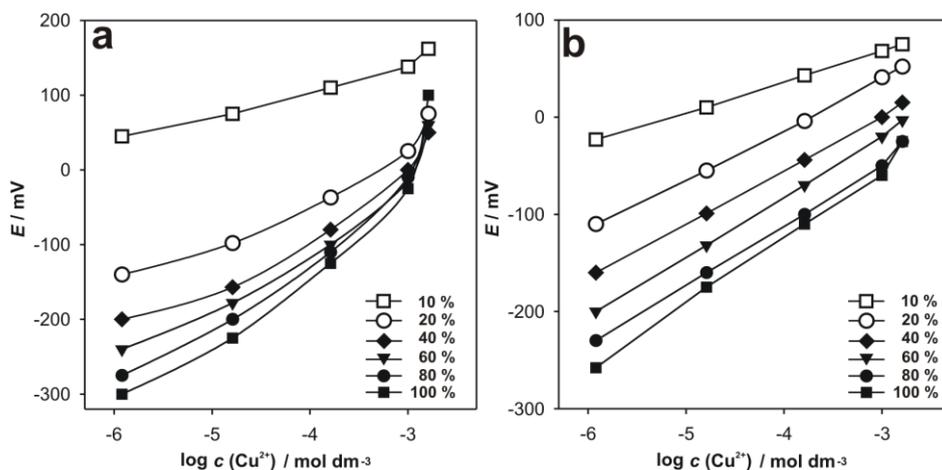

Figure 5. Influence of different acetonitrile amount, in acetonitrile-water mixtures, on potential of the electrode 1 (a) and electrode 2 (b). Initial concentration of Cu^{2+} was c $(Cu^{2+}) = 1.0 \times 10^{-4}$ M

Effect of pH on the potential response of electrode was determined at three concentrations of Cu^{2+}. A pH range between 1 and 9 was controlled using HNO_3 and KOH solutions. As it can be seen from Figure 6, a constant potential of the electrode, at initial presence of Cu^{2+} of 1.0×10^{-3} M, was obtained between pH values 2-5. Potential is more affected by pH change, as concentration of the Cu^{2+} decreases. At the pH values below 2, the electrode was affected due to the dissolution of surface sulfide layer. The potential drop in the alkaline media could be consequence of formation of $Cu(OH)_x$ complexes and decreasing of "free" Cu^{2+}, as effect was pronounced at lower Cu^{2+} concentration.
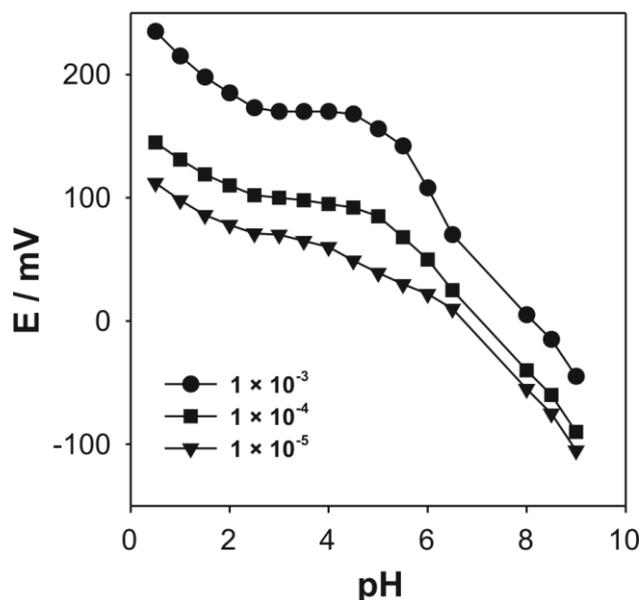

Figure 6. The effect of pH on the potentiometric response of the electrode 1 at different Cu^{2+} concentrations.

4. CONCLUSION

In summary, it was found that types, kinetics and range of processes responsible for potentiometric response were strongly influenced by preparation and incorporation of the membrane components into electrodes. Although untreated electrodes showed near-Nernstian slope toward Cu^{2+}, its potentiometric responses have suffered from significant drift of potential. This behaviour has been attributed to insufficient kinetics of surface reaction, caused by lacking of sensitive layer, which is based on metal sulfides. Deterioration in detection limit, for electrodes with chemically formed sulfide layers, were attributed to the slow diffusion and fouling of porous Cu_2S layers with Cu^{2+}/Cu^+. Super-Nernstian responses observed for electrode 2 and electrode 3 were consequence of hampered oxidation of Cu^+ with O_2, together with limited outward flux of formed Cu^+ in pores. In addition, significant improvement in potential stability for electrode 2 were noticed, which is connected to formation of mixed conductors (Ag_2S and Cu_2S). Improvements concerning linear range and detection limit were noticed for the chemically sulfidated electrode 1. This electrode was characterized with Nernstian slope, thus indicating a lower porosity and decreased fouling effect of formed sensitive layer.

All three electrochemically sulfidated electrodes have shown extended linear range and lower detection limits when compare to chemically sulfidiated electrodes, probably due to formation of more ordered and less porous sulfide layers, thus avoiding problems appeared at electrodes with chemically formed sulfides. However, Nernstian slope was observed only for the electrode prepared with directly incorporated (pressed) Ag_2S (electrode 1), thus indicating that not only a way of preparation, but also way of the incorporation of membrane components into membrane is responsible for potentiometric behaviour.

Super-Nernstian responses in mixed acetonitrile-water solutions are results of higher stability of Ag^+ and Cu^+ in acetonitrile than in water. Increasing of the slopes with increasing of acetonitrile contents in mixed solutions is result of lower oxidation rate of Cu^+ to Cu^{2+}, due to decreasing O_2 concentration in mixed solutions. Also, experiments in mixed solutions revealed that leaching of Ag^+ from electrochemically formed Ag_2S is more feasible than from those directly incorporated (pressed). These findings suggest that experiments carried out in mixed acetonitrile-water can give useful information about porosity and solubility of membrane components, together with information about oxidation rate of Cu^+ with O_2 for electrode with different composition.

References

1. G. J. M Heijne, W. E. van der Linden, G. den Boef, *Anal. Chim. Acta,* 89 (1977) 287
2. G. J. M Heijne, W. E. van der Linden, *Anal. Chim. Acta,* 93 (1977) 99
3. S. Brinić, M. Buzuk, M. Bralić, M. Buljac, D. Jozić, *Int. J. Electrochem. Sci.*, 7 (2012) 5217
4. R. Tomova, G. Spasov, R. Stoycheva-Topalova, A. Buroff, *Sens. Actuators B-Chemical,* 103 (2004) 277
5. S. P. Awasthi, N. S. Shenoy, T. P. Radhakrishnan, *Analyst,* 119 (1994) 1361
6. M. T. Neshkova, A. A. Kirkova, R. W. Cattrall, C. G. Gregorio, A. M. Bond, *Anal. Chim. Acta* 362 (1998) 221
7. M. Buzuk, S. Brinić, E. Generalić, M. Bralić, *Croat. Chem. Acta*, 82 (2009) 801
8. S. Brinić, M. Buzuk, E. Generalić, M. Bralić, *Acta Chim. Slov.*, 57 (2010) 318
9. S. Brinić, M. Buzuk, M. Bralić, E. Generalić, *J. Solid State Electr.*, 16 (2012) 1333
10. L. P. Singh, J. M. Bhatnagar, *Talanta*, 64 (2001) 313
11. A. Abbaspour, M. A. Kamyabi, *Anal. Chim. Acta*, 455 (2002) 225
12. M. M. Ardakani, S. H. Mirhoseini, M. Salvati-Niasari, *Acta Chim. Slov*., 53 (2006) 197
13. E. H. Hansen, C. G. Lamm, J. Růzicka, *Anal. Chim. Acta* 59 (1972) 403
14. A. Hulanicki, A. Lewenstam, *Talanta*, 23 (1976) 661
15. J. C. Barbour et. al, *Mechanisms of Atmospheric Copper Sulfidation and Evaluation of Parallel Experimentation Techniques,* Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550 (2002)
16. J. Gulens, *Selective Electrode Rev.,* 9 (1987) 127
17. R. De Marco, *Anal. Chem.*, 66 (1994) 3202
18. A. Zirino, R. de Marco, I. Rivera, B. Pejcic, *Electroanalysis*, 14 (2002) 493
19. M. G van der Berg, *Marine Chemistry*, 71 (2000) 331
20. A. Lewenstam, T Sokalski, A. Hulanicki, *Talanta*, 32 (1985) 531
21. M. Bralic, Nj. Radic, S. Brinic, E., *Talanta* 55 (2001) 581
22. P. Buck , E. Lindner, *Pure Appl. Chem.,* 66 (1994) 2527
23. A. Zirino, D. A. VanderWeele, S. L. Belli, R. DeMarco, D. J. Mackey, *Mar. Chem.,* 61 (1998) 173
24. J. F. Coetzee, W. K. Istone, M. Carvalho, *Anal. Chem.,* 52 (1980) 2353

25. J. C. Westall, *Anal. Chem.*, 56 (1984) 1792
26. I. Zaafarany, H. Boller, J. Saudi Chem. Soc. 14 (2010) 183
27. G. O. Mallory, J. B. Hajdu, *Electroless plating: fundamentals and applications,* Cambridge University Press, New York (1990)
28. A. M. Zaky, S. S. Abd El-Rehim, B. M. Mohamed, *Int. J. Electrochem. Sci.*, 1 (2006) 17
29. M. Ciobanu, J. P. Wilburn, D. A. Lowy*, Electroanalysis*, 16 (2004) 1351
30. S. Horstmanna, A. Grybata, R. Kato. *J. Chem. Thermodyn*. 36 (2004) 1015