Sensing
in Electroanalysis

Vol. 5 (K. Vytřas, K. Kalcher, I. Švancara, Eds.), pp. 77-84
© 2010 University Press Centre, Pardubice, Czech Republic.
ISBN 978-80-7395-348-5 (printed); 978-80-7395-349-2 (on-line)

Influence of Alkylammonium Cation on Multisweep Cyclic Voltammetry of Cu(II) on Carbon Paste Electrode Modified with Montmorillonite

Zuzana Navrátilová[1]* and Zuzana Hranická[2]

[1] Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22,
701 03 Ostrava, Czech Republic
[2] Bochemie a.s., Lidická 326, 735 95 Bohumín, Czech Republic

---

Abstract: Cyclic voltammetry of Cu^{2+} on the carbon paste electrode modified either with montmorillonite SAz-1 or with montmorillonite SAz-1 pretreated with hexadecyltrimethylammonium cation was performed to find the hexadecyltrimethylammonium cation influence on the Cu^{2+} sorption. In addition, the hexadecyltrimethylammonium presence in the sorption solution was studied, too. In this case, a significant inhibition on the Cu^{2+} sorption was found. The inhibition is supposed to be a consequence of the competitive sorption of HDTM and Cu^{2+}.

Keywords: Modified carbon paste electrode; Montmorillonite; Hexadecyltrimethylammonium-montmorillonite; Copper adsorption.

---

* To whom correspondence should be addressed.
E-mail: zuzana.navratilova@osu.cz ; Tel.: +420-597092195

Introduction

Alkylammonium cations play a little bit controversial role in term of the sorption processes. On the one hand they have been used for preparation of organo-clay composites with the improved properties (e.g. better mechanical stability, thermal stability, sorption ability) [1-4]. A typical phyllosilicate montmorillonite has been mostly studied for preparation and application of its alkylammonium derivatives [2,5]. On the other hand, surfactants of an alkylammonium type represent the typical environmental problems connected with waste water treatment. Their presence in the waste waters can affect removing of other substances (metals, organics).

Several studies have been dealing with the mutual relations of alkylammonium cations and metals in the sorption processes, for example [6]. All these studies were performed by means of batch technique, which is a time-consuming experiment. On the contrary, voltammetry on carbon paste electrodes modified with various sorbents was proved as fast and suitable method for the sorption studies [7]. In addition, a beneficial role of surfactants on some electrochemical measurements as well as for the electrodes modification has been described in detail [8]. In our last work [9] the hexadecyltrimethylammonium (HDTM) cation influence was found in the case of Cu^{2+} sorption on bituminous coal as well as on montmorillonite. The influence of HDTM was more significant when montmorillonite as a sorbent was used; a lower sorption of Cu^{2+} was found. However, the mentioned study dealt with montmorillonite pre-treated with HDTM before its use as an electrode modifier.

This work is aimed at study of the Cu^{2+} sorption on montmorillonite in the presence of hexadecyltrimethylammonium bromide in the sorption solution in comparison with montmorillonite modified with hexadecyltrimethylammonium. The Cu^{2+} sorption was studied by means of the carbon paste electrode (CPE) modified with untreated MMT,SAz-1 and with MMT,SAz-1-HDTM.

Experimental

Materials and Chemicals

Montmorillonite standard - MMT,SAz-1 (Apache County, USA) – was acquired from Source Clay Repository (The Clay Minerals Society, USA) [10]. Mineralogical characterization (IR and X-ray diffraction) [11] proved this material as a pure montmorillonite with cation exchange capacity 0.56 mol kg^{-1}.

Hexadecyltrimethylammonium bromide (Sigma-Aldrich) of analytical reagent grade was used to prepare the modified montmorillonite MMT,SAz-1-HDTM according the procedures described in [12].

All the chemicals used - sodium acetate and acetic acid for the preparation of acetate buffer pH 3.6 were of analytical reagent grade (Merck). Stock standard copper solution (0.0157 M Cu^{2+}) was prepared from *Titrisol*® standard (Merck). Redistilled water in glass apparatus was used throughout the experiments. The redox system $[Fe(CN)_6]^{3-/4-}$ in 1 M KCl solution was used.

Carbon Paste Electrodes

Preparation of the carbon paste electrodes and the measurement techniques were performed as they were already described [7]. The electrodes are labeled as follows: CPE(MMT,SAz-1) modified with 10 % (w/w) of MMT, SAz-1; CPE(MMT,SAz-1-HDTM) modified with 10 % (w/w) of MMT,SAz-1-HDTM.

Procedures

EKO-TRIBO-Polarograph (EKOTREND, Prague, CZ) was employed for all the voltammetric measurements. A three-electrode cell was equipped with a carbon paste electrode (CPE) (working), an Ag/AgCl (sat. KCl) reference electrode and a Pt wire counter electrode. Multisweep cyclic voltammetry (MCV) at a scan rate 20 mV s^{-1} was applied in the potential range from –1.5 V to +1.0 V and –1.3 V to +0.2 V for $[Fe(CN)]^{2-/3-}$ and Cu^{2+}, respectively.

Results and Discussion

An Influence of the HDTM Presence on Cyclic Voltammetry of $[Fe(CN)_6]^{3-/4-}$

Cyclic voltammetry of the redox system $[Fe(CN)_6]^{3-/4-}$ exhibited significantly different voltamogram in the presence of HDTM in the solution. The electrochemical behavior of $[Fe(CN)_6]^{3-/4-}$ on both modified CPEs is relatively comparable to its behavior on the unmodified CPE(0) in the absence of HDTM (Fig. 1). However, the modification with either MMT,SAz-1 or MMT,SAz-1-HDTM caused the lower value of ΔE, the higher cathodic response resulted in the lower anodic-to-cathodic peak current ratio (I_a/I_c) (Table 1). The presence of HDTM in the solution had more considerable influence as it is seen on Fig. 2

demonstrating cyclic voltammetry on CPE(MMT,SAz-1) in the solutions of various HDTM concentrations. The cathodic and anodic current responses increased, the former increased more significantly, especially in the case of the lower HDTM concentration. With increasing HDTM concentration both responses decreased, probably due to an occupation of the electrode surface with the surfactant. However, the current decrease is not too enormous even in the case of the relatively high concentration 1.19 x 10^{-3} mol l^{-1} HDTM for CPE(0) as well as for CPE(MMT,SAz-1).

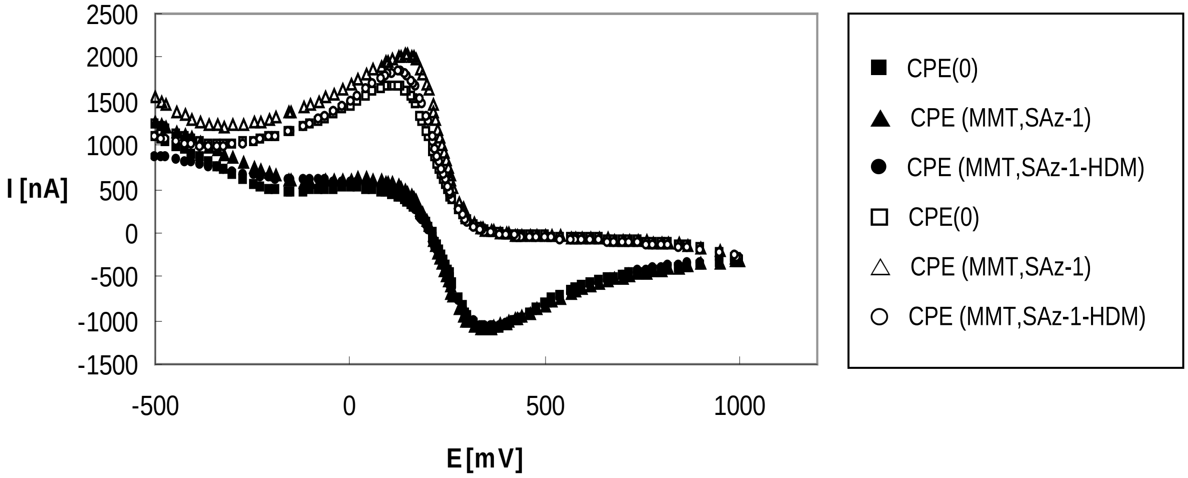

Figure 1. *Cyclic voltammetry of 0.001 M* $[Fe(CN)_6]^{3-/4-}$ *in 1M KCl* (empty symbols: cathodic current, bold symbols: anodic current)

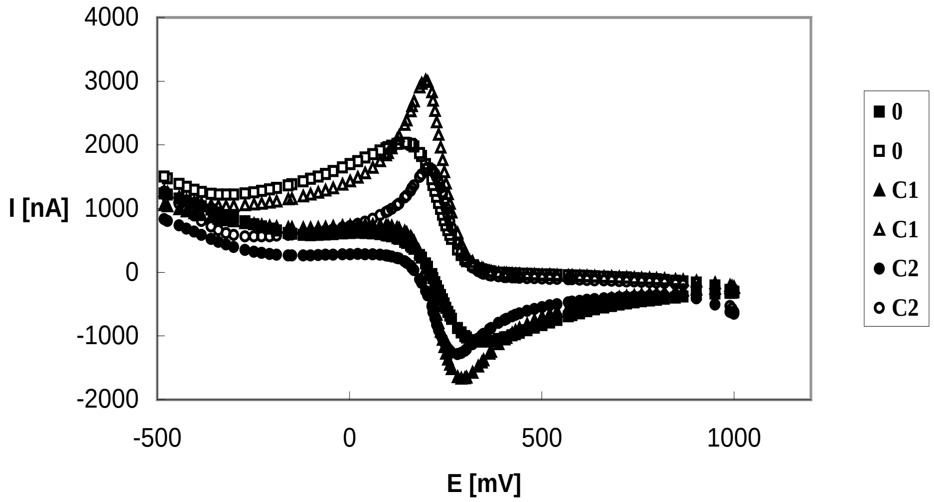

Figure 2. *Cyclic voltammetry of 0.001 M* $[Fe(CN)_6]^{3-/4-}$ *in 1 M KCl on CPE(MMT,SAz-1) in the presence of HDTM* (C1 = 4.76×10^{-5} mol l^{-1}, C2 = 1.19×10^{-3} mol l^{-1})

The values ΔE suggested more reversible behavior in the presence of HDTM for both CPE(0) and CPE(MMT,SAz-1) electrode (Table 1). These findings correspond to other studies revealing the excellent electrochemical reversibility in the presence of surfactants, especially HDTM [13].

Table 1. *The cyclic voltammetric characteristics of the redox pair* $[Fe(CN)_6]^{3-/4-}$ *with or without HDTM presence*

Electrode / HDTM conc. [mol l^{-1}]	ΔE_p [V]	I_a / I_c
CPE(0) 0	0.250	0.955
CPE(0) 4.76×10^{-5}	0.090	0.815
CPE(0) 2.38×10^{-4}	0.080	0.830
CPE(0) 1.19×10^{-3}	0.066	0.850
CPE(MMT,SAz) 0	0.193	0.840
CPE(MMT,SAz-1) 4.76×10^{-5}	0.096	0.820
CPE(MMT,SAz-1) 2.38×10^{-4}	0.082	0.790
CPE(MMT,SAz-1) 1.19E x 10^{-3}	0.076	0.885
CPE(MMT,SAz- HDTM) 0	0.186	0.890

Note: The characteristics ΔE_p and I_a/I_c suggest that the HDTM presence in the solution influences the electrochemical behaviour of the redox system substantially compared to HDTM incorporated into the MMT modifier.

Multisweep Cyclic Voltammetry of the Cu^{2+} Ion

Study of the Cu^{2+} sorption on the montmorillonite performed by multisweep cyclic voltammetry (MCV) has already demonstrated that MMT,SAz-1-HDTM exhibited the lower steady current due to a lower sorption of Cu^{2+}. The cation exchange sites of the HDTM derivative of montmorillonite are occupied with the cations, which inhibits sorption of the cationic forms Cu^{2+} and $[Cu(ac)]^+$ (ac – acetate) in comparison with the unmodified montmorillonite. HDTM incorporated into the interlayer of MMT,SAz-1 decreased the sorption approximately to 82 %. The sorption kinetics was the same on both MMT,SAz-1 and MMT,SAz-1-HDTM (the second order) [14].

In order to evaluate the HDTM influence, in this study MCV was performed on CPE(MMT,SAz-1) in the HDTM presence in the solution. The HDTM presence in the sorption solution showed to be more considerable inhibiting factors of the Cu^{2+} sorption. The steady current of MCV corresponding to the adsorption equilibrium on the MMT,SAz-1 is achieved after the 5th cycle at the lower HDTM concentration and after the 3rd cycle at the higher HDTM concentration. The subsequent cycling showed the current decrease (Fig. 3 and 4). This fact suggests the different sorption course in comparison with MMT,SAz-1 and MMT,SAz-1-HDTM in the HDTM absence (Fig. 5). In addition, the maximum steady current rapidly decreases with increasing HDTM concentration, the Cu^{2+} sorption is lower in comparison with MMT,SAz-1-HDTM – 98 %, 61 % and 42 % for 4.76×10^{-5}, 2.38×10^{-4}, and 1.19×10^{-3} mol l^{-1}, respectively.

An apparent gradual decrease of the cathodic (reverse) Cu^{2+} responses resulting in a definitive disappearing is worth to mention (Fig. 3 and 4). Such behavior of Cu^{2+} was already observed on CPE(MMT,SAz-1-HDTM) in comparison with CPE(MMT,SAz-1) [14]. This phenomenon can be explained by the lower content of Cu^{2+} adsorbed onto the MMT,SAz-1-HDTM during the anodic (forward) scan.

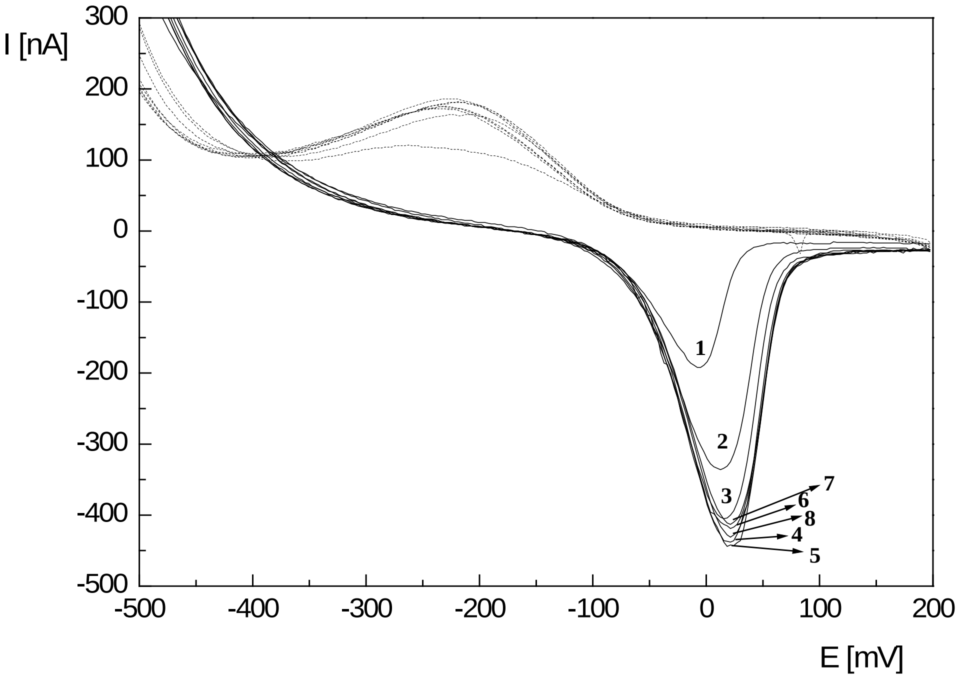

Figure 3. *Multisweep cyclic voltammetry of Cu^{2+} (2.5×10^{-5} M) in acetate buffer* (pH 3.6) on CPE(MMT-SAz-1) in the presence of HDTM (C = 4.76×10^{-5} mol l^{-1})

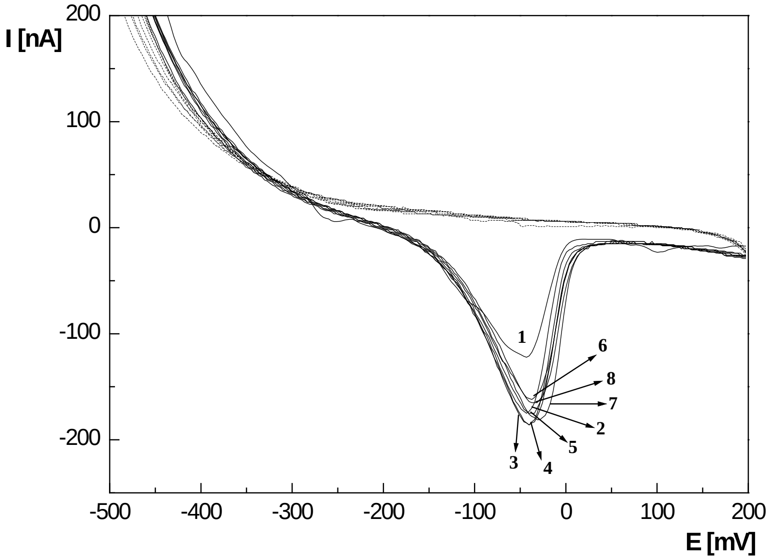

Figure 4. *Multisweep cyclic voltammetry of* Cu^{2+} *(2.5 x* 10^{-5} *M) in acetate buffer* (pH 3.6) on CPE(MMT,SAz-1) in the presence of HDTM (C = 1.19 × 10^{-3} mol l^{-1})

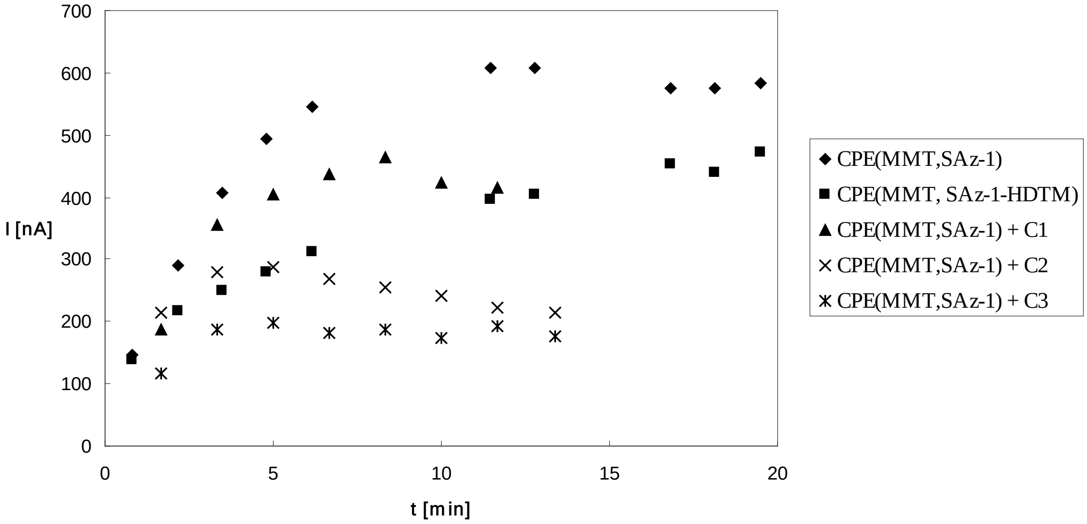

Figure 5. *Current vs. t- dependences for CPE(MMT,SAz-1-HDTM) and for CPE(MMT,SAz-1)* without and with various concentration of HDTM in acetate buffer (pH 3.6), $C_{Cu}{}^{2+}$ = 2.5×10^{-5} M (C1 = 4.76 × 10^{-5} mol l^{-1}, C2 = 2.38 x 10^{-4} mol l^{-1}, C3 = 1.19 x 10^{-3} mol l^{-1})

Conclusions

Multisweep cyclic voltammetry on the CPE(MMT,SAz-1) in the absence or presence of HDTM proved the considerable inhibition of HDTM on the Cu^{2+} adsorption on montmorillonite. In the case of the lower HDTM concentration (on a level 10^{-5} M comparable with the Cu^{2+} concentration) the inhibiton has nearly the same effect as HDTM incorporated into the montmorillonite. With increasing HDTM concentration the Cu^{2+} sorption decreases much more intensively in comparison with the MMT,SAz-1-HDTM.

As no enormous decrease of the current was found for the redox pair $[Fe(CN)_6]^{3-/4-}$ at increasing concentrations of HDTM, it can be supposed that the decrease obtained in the case of Cu^{2+} is connected rather with the competitive sorption of HDTM and Cu^{2+} than with the electrochemical behavior (for example “contamination” of the electrode surface with HDTM due to its active surface properties). However, this hypothesis is to be proved by complementary sorption experiments by means of batch technique in order to propose the multisweep cyclic voltammetric methods of the sorption study.

Acknowledgement

The work was supported by the project IAA 301870801, from the Grant Agency of Academy of Sciences of the Czech Republic.

References

1. K. Barabaszová: *Nanotechnology and Nanomaterials*. VŠB-TU Ostrava, 2006.
2. S. S. Ray, M. Okamoto: *Prog. Polym. Sci*. **28** (2003) 1539.
3. G. Centi, S. Perathoner: *Microporous Mesoporous Mater.* **107** (2008) 3.
4. F. Arabi Bergaya: *Microporous Mesoporous Mater.* **107** (2008) 141.
5. L. B. de Paiva, A. R.Morales, F. R. V. Díaz: *Applied Clay Sci.* **42** (2008) 8.
6. K. G. Bhattacharyya, S. S.Gupta: *Sep. Pur. Technol.* **50** (2006) 388.
7. Z. Navrátilová, P. Kula: *J. Solid State Electrochem.* **4** (2000) 342.
8. R. Vittal, H. Gomathi, K.-J. Kim: *Advances Colloid Interface Sci.* **119** (2006) 55.
9. R. Maršálek, Z. Navrátilová: *Chem. Papers* **4** (2010) in print.
10. http://www.agry.purdue.edu/cjohnston/sourceclays/chem.htm ; Nov. 10, 2010.
11. Z. Navrátilová, L. Vaculíková: *Chem. Pap.* **60** (2006) 348.
12. Z. Navrátilová, P. Wojtowicz, L.Vaculíková, V. Šugárková: *Acta Geodyn. Geomater.* **4** (2007) 1.
13. R. Vittal, J.H. Gomathi, G. P. Rao: *J. Electrochem. Soc. Volume* **146** (1999) 786.
14. Z. Navrátilová, Z. Hranická; in: *Sensing in Electroanalysis,* Vol. 4 (Vytřas K., Kalcher K.; Eds.), pp. 39-46. University Press Centre, Pardubice, 2009.