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**CARBON PASTE ELECTRODES MODIFIED
WITH CLAYS AND HUMIC ACIDS**

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Possibilities of modified carbon paste electrodes (CPEs) in "diagnosis" of the ion-exchange and complexation properties of complicated modifiers of natural origin are shown. The carbon paste electrodes were modified with clay minerals, humic acids and with clay-humates associates. Results of "diagnostic" measurements were used in the elaboration of the determination of Cu(II) by means of the CPE modified with montmorillonite and of Hg(II) by means of the CPE modified with humic acid.

Introduction

Chemically modified electrodes have become very attractive research area in electrochemistry during the previous two decades. Carbon paste modified electrodes (CPMEs) have been often preferred due to their easy and quick preparing, due to simple and effective surface regeneration [1,2]. Applications of the CPMEs are based on their broad potential range - especially in positive

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direction. It can be said, that CPMEs are still a subject of great interest, as a growth of the publications has been recorded till now. Recently, application of the CPME has been extended to the field of biosensors, as carbon paste can be modified with a variety of biological materials (enzymes, tissues, microbial cells, etc.).

There are two main purposes for use of the modified electrodes. Obviously, an improving of analytical performance of the modified electrodes has led to their analytical applications. Simultaneously, the electrochemical studies performed on the modified electrodes have tended to investigation of the modifiers themselves. Stripping analysis with mineral carbon paste electrode (CPE), solid state voltammetry, bulk stripping analysis, solid state voltammetry or contact voltammetry - these terms have designated the investigation of solid compounds by means of the electrodes modified with them during development of this technique [3]. Voltammetry on the CPEs modified with solid particles represents an electrochemical technique for direct electrochemical studies of solids, including natural minerals and oxides. Another electrochemical method used to study of solids is abrasive stripping voltammetry, although the compounds are deposited on the electrode surface mechanically. Regarding the minerals and oxides, this technique enables qualitative identification of metal constituents of minerals, identification of minerals with their voltammetric fingerprint and determination of thermodynamic data of minerals with a reversible electrochemistry behaviour [4,5]. Both the abrasive stripping voltammetry and voltammetry on the CPEs are suitable for study of the solid modifiers' properties, although there is some complication regarding the presence of plasticizer in the CPE. On the other hand, the CPEs are more suitable and more used as sensors in the analytical application.

Clays, zeolites, oxides and other inorganic crystalline-structured solids have been also used as carbon paste modifiers. These materials are still of great interest due to their ion-exchange, sorption and size exclusion properties as well as catalytic effects. Furthermore, these inorganic solids exhibit relatively high chemical and physical stability and they have well-defined microstructures. As clays and mainly zeolites have been long used as sorbents and catalysts, study of the electrochemical properties of electrodes modified with such materials became a desirable contribution to this research.

Various organic, organo-metallic and inorganic cation-exchanged zeolites and zeolite-encapsulated metal complexes have been used as electrodes' modifiers, and they have exhibited an electroactive behaviour [6,7]. Cyclic voltammetry is a simple, but powerful technique for the electrochemical characterizations of compounds based on high cation exchange capacity of zeolites [8]. Except electroanalytical applications, zeolite modified electrodes can be successfully used in molecular recognition, charge and mass transport characterization and electrocatalysis [6-8].

In 1983 Ghosh and Bard [9] described the first electrode modified with clay film and further studies of electrochemical behaviour of redox couples on

the clay electrodes have started since that moment. Sorption of metal ions onto the clay minerals can be investigated by means of open circuit accumulation [10,11] or by repetitive (multisweep) cyclic voltammetry [12] on the clay modified CPEs. These studies can give metals preconcentration model with concentration equilibrium constant [10] or can distinguish individual clay minerals [12]. Effects of ligands of environmental importance - pesticides [11] and humic substances [13] - on the metal ion uptake can be studied, too.

Carbon paste electrodes modified with humic acids, clays and oxides can serve to model studies of some soil processes connected with behaviour and fate of anthropogenic compounds in the soil ecosystem. Just this investigation is a promising domain of the carbon paste electrodes modified with solids. This work stated some examples of such application of the CPME.

Complexation of Metals with Humic Substances

Humic acid HA1 (Serva), HA2 (Aldrich) and HA3—a home-made preparation from naturally oxidised North Bohemia lignite ("kapucín") were used for the preparation of modified carbon paste electrode CPE(HA) (14). Differential pulse voltammetry of Cu(II), Zn(II) and Hg(II) exhibited potential $E_p^{CPE(HA)}$ shifted to more negative values in comparison with $E_p^{CPE(0)}$ on the unmodified CPE.

The potential shifts $\Delta E = E_p^{CPE(0)} - E_p^{CPE(HA)}$ and courses of current responses were studied in the dependence on pH. The curves $\Delta E = f(\text{pH})$ show a maximum pH at which an apparent release of humic substances from the electrode surface takes place. At the same pH a decrease of the current responses of the CPE(HA) was found to occur (Fig. 1). In general, the current decrease is associated with the release of humic substances from the electrode surface. It was supported by the fact that no rapid current decrease was found on the CPE(0) as well as on the CPE modified with Ba(II) salts of humic acid, and those salts did not release from the electrode due to their solubility.

Seemingly the metal complexes with humic acids are formed after the dissolution of humic substances in solution, however, the potential shifts were also found on the modified CPEs under conditions of no dissolution of humic substances into the solution. This conclusion is important because it confirms the earlier presumption about metal complexations with solid humic acids present on the electrode surface [15]. The complex-forming reactions are probably connected with the dissociation of humic substances on the electrode surface.

Quite different dependences of ΔE and current on the pH were obtained by voltammetry of Cu(II) on CPE(0) in the presence of humic ligands in the solution. The current response decreased uniformly over the whole pH range in the presence of humic ligand (Fig. 1), and potential shift dependence did not exhibit any maximum.

The idea about complexation in the electrode/solution interface was sup-

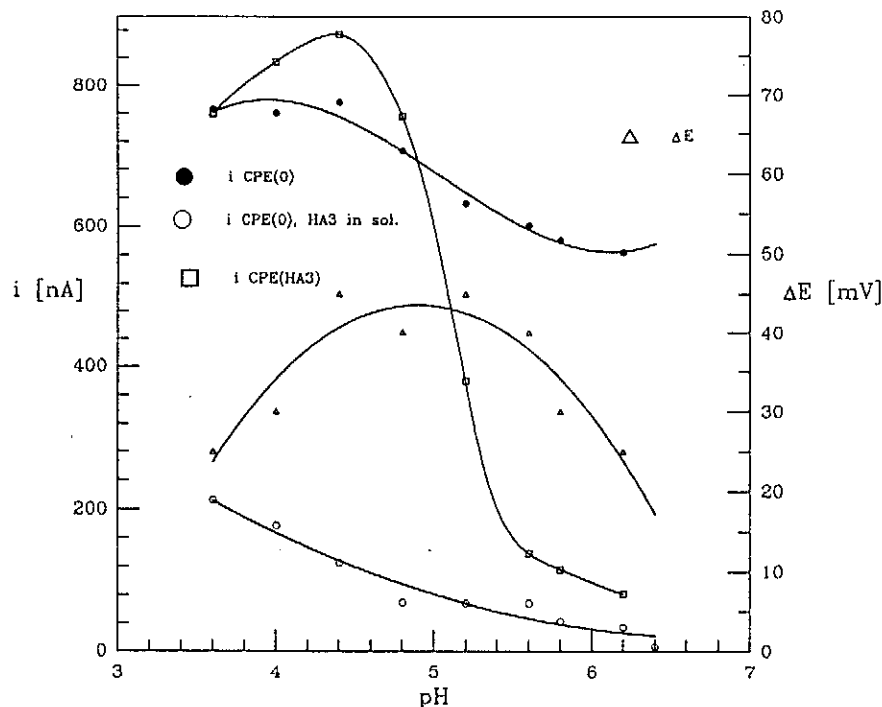


Fig. 1 Influence of pH on the voltammetry of $1.6 \mu\text{M}$ Cu(II) on the CPE(0) in the absence and in the presence of 16 mg HA3-Na and on the CPE(HA3), acetate buffers, non-constant ionic strength

ported by the dependences of ΔE and $\Delta E'$ on pH. The $\Delta E'$ value represents the corrected value of ΔE according to equation $\Delta E' = \Delta E + 0.03 \log(i/i_L)$ (i_L denotes the current i measured in the presence of ligand) [16]. The dependence of $\Delta E'$ on pH is identical with the dependence of ΔE in the pH range with no release of humic acid ligand from the electrode surface (Fig. 2). It is the pH range where the complexation was supposed to take place at the electrode/solution interface. The values $\Delta E'$ are higher than ΔE in the pH range where humic ligand is released from the electrode surface, which is equal to the complexation in the solution (Fig. 3). In this pH range complexes are probably formed both near the electrode surface and in the solution. The course of the current corresponds to this idea as the current decreases in this pH range (Fig. 1). The complexes formed in the solution do not contribute to the current response that is caused by insufficiently rapid attainment of equilibrium between the metal and complex in the diffusion layer of the electrode, so that the metal-humic substances' complexes formed in the solution dissociate slowly. The complexes formed at the interface contribute to the rapid attainment of equilibrium between the metal and complex in the diffusion layer of the electrode, so these complexes behave as labile, rapidly dissociating species.

The voltammetric study of the Cu(II) complexes with humic ligand in the

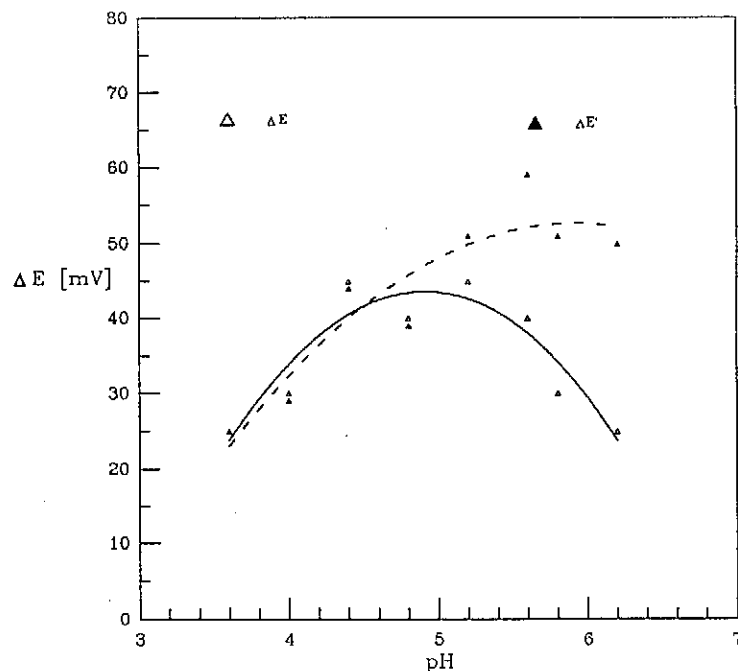


Fig. 2 Dependences of ΔE and $\Delta E'$ on pH on the CPE(HA3) electrode in solutions with non-constant ionic strength, 1.6 μM Cu(II)

solution was performed by means of DPV on CPE(0) and by cyclic voltammetry on the HMDE. DPV on the CPE(0) showed slowly dissociating complexes of Cu(II) with humic acid in the pH range 3.6–6.4. Cyclic voltammetry on the HMDE confirmed these results. The complexes of copper with humic substances are slowly dissociating when they are formed in the solution.

The influence of ionic strength on the complexation presented in changes of the release of humic ligands from the electrode surface, in their dissolution and in lowering of potential shifts. The influence of the ionic strength is different for various types of humic substances, as it was already stated [17].

The complexation of Zn(II) and Hg(II) with humic acids was found, too, the highest potential shifts were obtained in the pH range where no release of humic substances was observed. The complexation of Hg(II) with humic acid HA1 in the acid medium was successfully used in the development of the determination of low concentration of Hg(II) on the CPE(HA1) [15].

Carbon Paste Electrode Modified with Clay Minerals

Clay minerals montmorillonite Wyoming (USA) (MMT_{Wy}), montmorillonite Jelšův Potok (SK) (MMT_{JP}), kaolinite KA (Sedlec, CR) and vermiculite VER

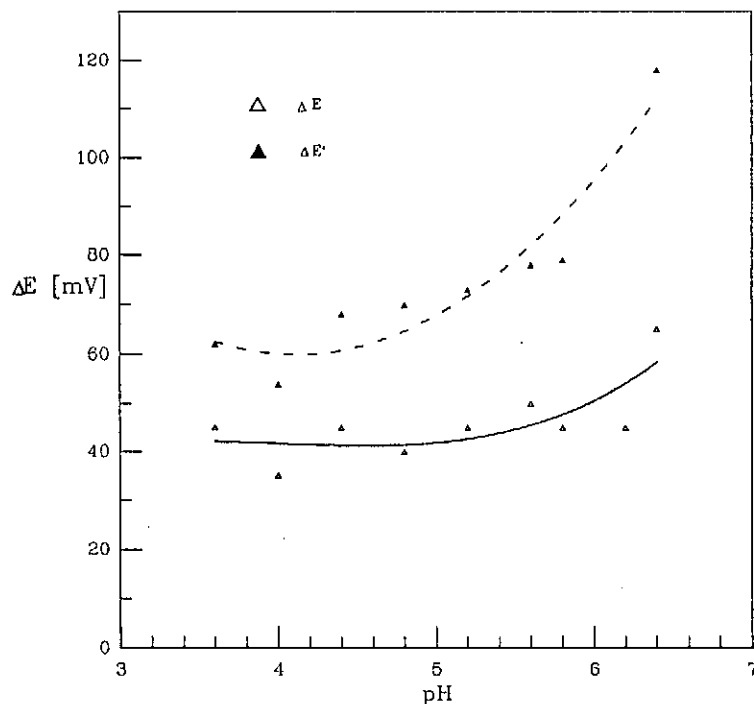


Fig. 3 Dependences of ΔE and $\Delta E'$ on pH on the CPE(0) in the presence of 16 mg of HA3-Na in solutions with non-constant ionic strength, 1.6 μM Cu(II)

(Letovice, CR), all with particle size below 5 μm , were used to the modification of CPE. A novel modification by minerals wetted in an atmosphere saturated with water vapour showed to be optimum both for study of metals sorption [12] and for analytical purposes [18]. This procedure is advantageous in comparison with formerly used wetting methods [19] as the clay modifier is sufficiently wet and it is not too moist, which could cause complications during the carbon paste preparation. In addition, the water content in the clay is known. This novel method was worked out on the basis of work describing the swelling of the clay film in humidified air for a minimum of 12 hours before use [20]. The clay modifier saturated with water exhibited swollen structure with increased interlayer distances, thus ion-exchange and sorption processes take place easier. No activation and regeneration of such prepared clay CPE are necessary.

Repetitive cyclic voltammetry (RCV) on the clay carbon paste electrodes can be used to study clay minerals and their sorption properties [12]. RC voltammogram on the clay CPE shows the current increase caused by metal sorption into the clay during the cycling of the potential in appropriate potential range. When the current reaches a maximum value, saturation of the ion-exchange sites of the clay is completed. The maximum current response i^{max} indicates the maximum occupation of available ion-exchange sites of the clay by metals ions at the given conditions. This i^{max} value is supposed to be pro-

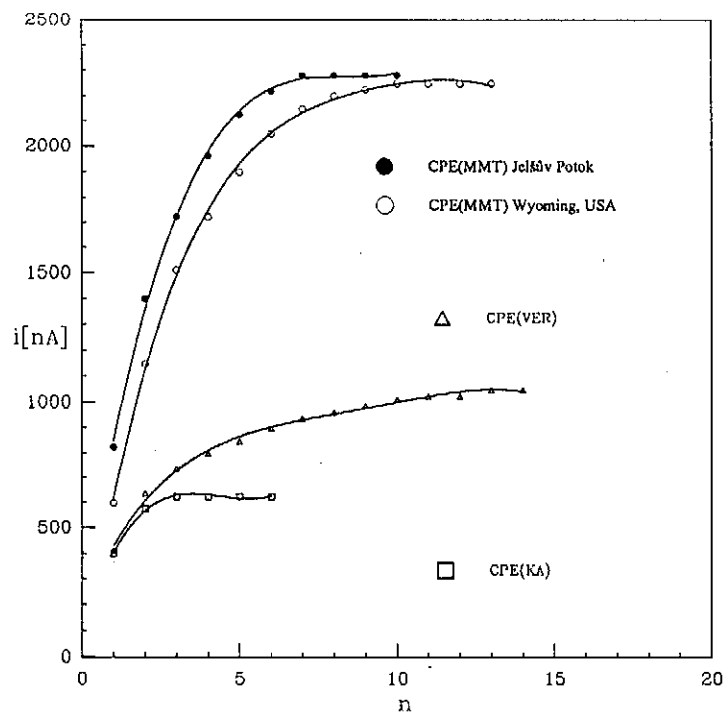


Fig. 4 Dependences of current response on number of scans, repetitive cyclic voltammetry. Acetate buffer pH 3.6, I 0.015, 1.6 μM Cu(II)

portional to the ion-exchange capacity (IEC) of the clay for some metal [12].

Some dependences characteristic of particular clay minerals and particular metal ions can be obtained from RCV measurement. The dependence of current response on time of the cycling gives a curve typical of Cu sorption on the clay in the CPE (Fig. 4). It is seen that two types of montmorillonites exhibited practically the same course of this dependence. Different dependences were also obtained for various metals (Fig. 5). Influence of the medium composition can also be evaluated by means of this method (Fig. 6). Again, two various types of montmorillonite exhibited similar pH dependences of Cu sorption. This dependence is quite different from those obtained on vermiculite and kaolinite. As the highest sorption of Cu(II) was found on the CPE(MMT), this electrode was used for the determination of Cu(II) [18].

The influence of humic acids on Cu sorption was also studied. The Cu incorporation into the MMT decreased considerably in the presence of humic ligand due to Cu - humic complexations. As humic substances form organic coatings of the clay minerals' particles in the soil, a study of clay - humate complexes (or clay - humates) is important for closer knowledge of soil system. The carbon paste electrodes modified with clay - humate systems have been shown to be suitable for this study.

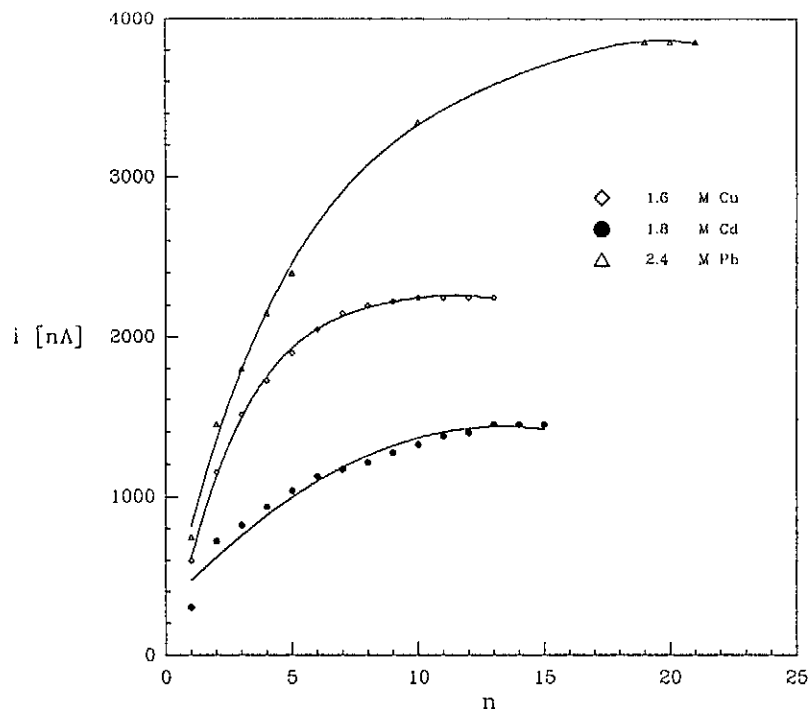


Fig. 5 Dependences of current response on number of scans, repetitive cyclic voltammetry. Acetate buffer pH 3.6, I 0.015, CPE(MMT)

Carbon Paste Electrode Modified with Montmorillonite-Humates

Two types of montmorillonite-humates were prepared for use as model systems in studies of humic acid influence on Cu(II) sorption on montmorillonite. C-humates (c-MMT.HA) were prepared by co-coagulation of montmorillonite (MMT Wyoming, USA) suspension with an appropriate amount of Na salt of humic acid (Serva) by acidification with HCl. After 24 hours, the MMT.HA coagulate was centrifuged (3 000 rpm, 15 min) and air-dried. Of course, "blank c-humate" (c-MMT.HA,0%) with zero content of HA was prepared by the same procedure. M-humates (m-MMT.HA) were prepared by thorough mixing of the dry MMT with dry solid HA in the appropriate amount ratio. This mixture was hydrated in an atmosphere saturated with water vapour till constant weight and then air-dried. The detailed procedure of preparation of the humates including their X-ray characterisation has been already described [13]. The c- and m-humates thus prepared were used as electrode modifiers by the formerly developed method [12] with the above-mentioned wetting procedure.

The repetitive cyclic voltammetry (RCV) of Cu(II) on the CPE modified with c-humates and m-humates was measured to obtain the i^{max} proportional to the ion-exchange capacity (IEC). The resulting dependences of i^{max} on pH

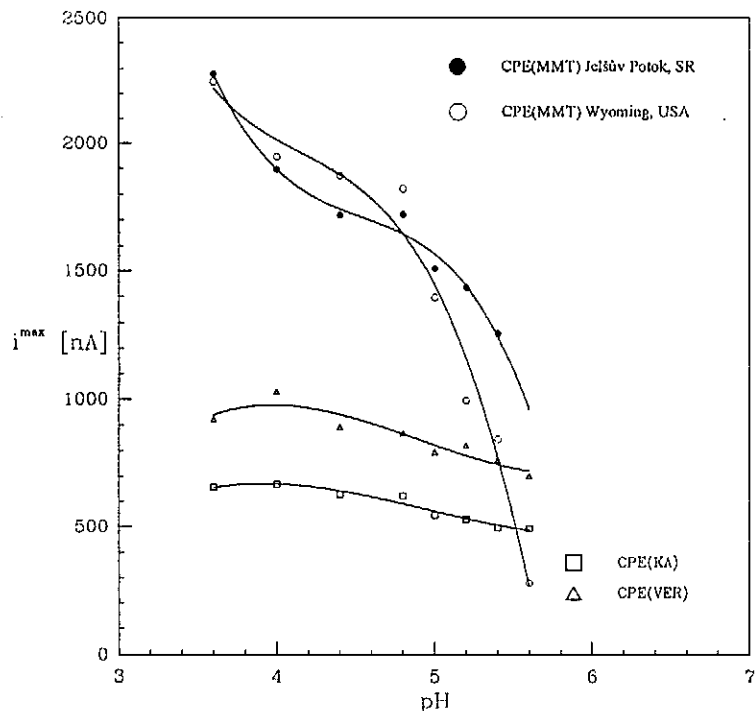


Fig. 6 Influence of pH on Cu(II) sorption on various clay electrodes. Acetate buffers pH 3.6–5.6, 1.6 μM Cu(II)

were compared with those obtained on the CPE(HA), CPE(MMT) and CPE(0) as well as on the CPE modified with c-MMT.HA,0% (i.e. acid-treated MMT).

The i^{max} of the acid-treated MMT—its IEC—is four times lower than the IEC of the acid-untreated MMT alone in the pH range of 3.6–4.4 (Fig. 7). This corresponds to the results of X-ray diffraction, which has found some structural changes in the case of c-MMT.HA caused by the partial formation of the Al- or hydroxy-Al montmorillonite during the acidic treatment (during the coagulation) [13]. Thus, a larger part of the ion-exchange sites of the acidic-treated MMT is not available for Cu ions. However, the c-MMT.HA,0% exhibited quite significant IEC in comparison with CPE(0). The course of the i^{max} - pH dependence for the c-MMT.HA,10% is similar to the dependence for the HA alone (Fig. 8), which indicates to the complexation of Cu with HA, as it was described above. The IEC of the c-humate is slightly higher in comparison with IEC of the HA alone and with the “blank c-humate” in the pH range of 3.6–4.4. This fact suggests that both surfaces of the Al- or hydroxy-Al MMT and HA contribute to the ion-exchange of Cu(II).

As the IEC dependence on pH for c-MMT.HA,10% is not a simple sum of the dependences for the “blank c-humate” and for the HA, c-MMT.HA,10% is no mere mixture of MMT and HA. It can be supposed that the c-humate complex is an associate of the folded and aggregated molecules of the HA [17]

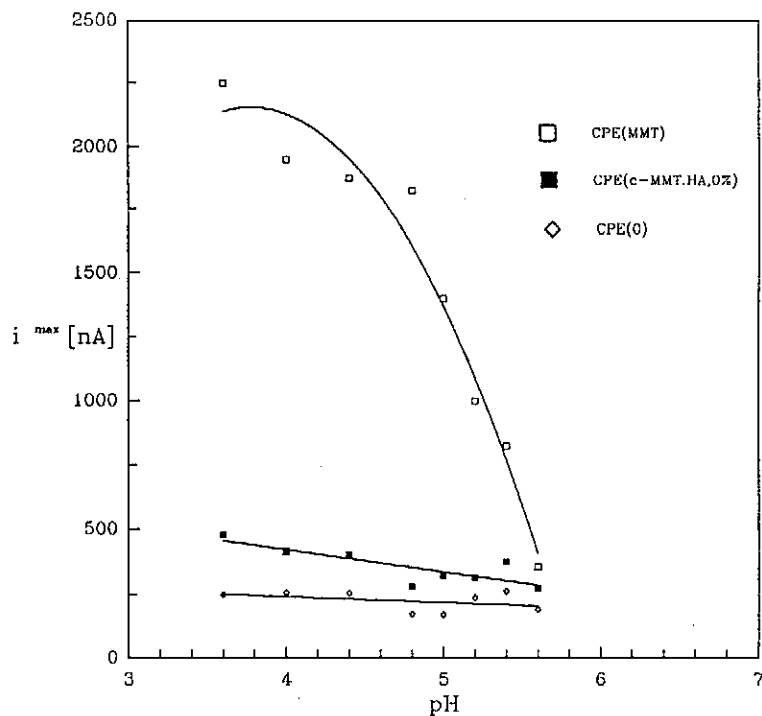


Fig. 7 Dependences of current maximum on pH for RCV of $1.6 \mu\text{M}$ Cu(II) on unmodified and various modified CPEs, acetate buffers pH 3.6–5.6, non-constant ionic strength

with a part of the surface of the Al- or hydroxy-Al montmorillonite. A part of the complexation sites of the HA is retained due to folding of the HA molecules during the acid co-coagulation. This idea corresponds to the former idea of Chassin [21].

Quite different results were obtained in the case of simple mixed humates, m-MMT.HA. X-ray diffraction has shown no structural changes of this humate, only moderate changes on its surface can be supposed. However, its IEC is significantly decreased in comparison with the MMT alone. Probably the ion-exchange sites of the MMT are not available due to nearly complete coating of the MMT surface by the HA molecules. The ion-exchange sites of the folded HA are exhausted due to their interactions with the MMT surface and probably with migrating Al(III) ions. A dissociation of the HA functional groups during the hydration of the solid mixture of the MMT and the HA and subsequent bounding with the MMT surface (maybe with Al atoms) can be supposed.

As it was shown, the carbon paste electrodes modified with two types of the MMT humates are able to distinguish humates prepared by two procedures. The supposed structural changes of MMT during acid co-coagulation with the humic acid are closely connected as with effect of Al(III) ions as with blocking of complexation sites in the case of m-humates.

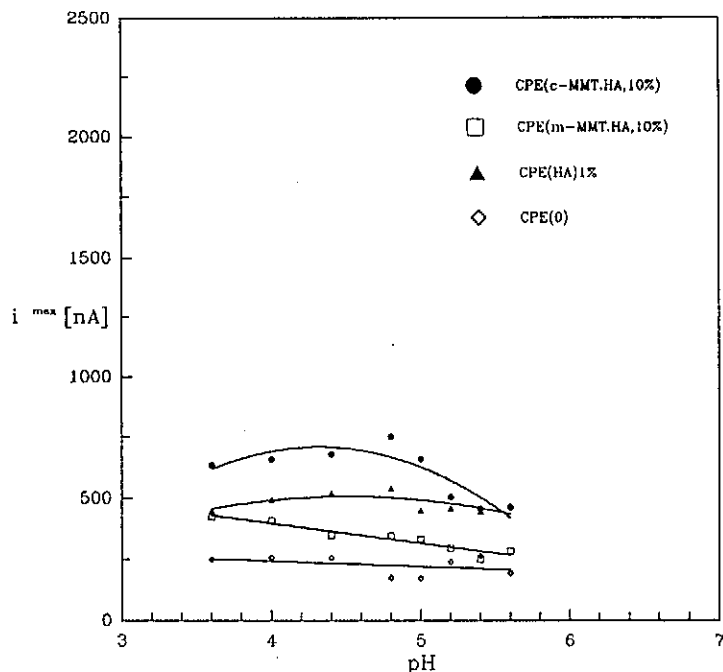


Fig. 8 Dependences of current maximum on pH for RCV of $1.6 \mu\text{mol Cu(II)}$ on various modified CPEs, acetate buffers pH 3.6 - 5.6, non-constant ionic strength. CPE(c-MMT.HA,10%) - 10 % of HA in MMT, CPE(HA)1%-1% of HA in paste

Conclusion

Evidently, the carbon paste electrode as a complicated, heterogeneous system does not provide too many possibilities for quantitative measurement of physico-chemical parameters, e.g. stability constant, sorption capacity, etc.

Because of easy modification and good reproducibility of the surface regeneration, modified CPEs can be used for relatively quick and simple "diagnosis" of the properties of complicated modifiers of natural origin.

As it was shown, for example, an assessment and comparison of complexation properties of natural polyelectrolytes—humic acids—can be performed in the dependence on type of the metal ion and on medium composition. The complexes formed can also be characterized from the point of view of their kinetic stability. A relative comparison of the ion exchange capacities of clay minerals to one another and for various metal ions is available by means of the modified electrodes.

The possibility of assessment of the complexation properties of clay - humate associates in the dependence on their origin represents an interesting approach to their study. These associates play an important role in the retention

and leaching of metals in the soils.

Such "diagnostic" measurements can lead, as authors have already shown, to the analytical utilisation of the carbon paste electrodes modified with natural materials - CPE(HA) for the Hg(II) determination in strongly acid solution after mineralisation of samples [15] and CPE(MMT) for the Cu(II) determination [18] in river sediments [22].

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