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Cation and anion exchange on clay modified electrodes

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Abstract Carbon paste electrodes modified with clay minerals were used for the study of ion-exchange properties of these clay minerals. Cation exchange of Cu(II) was studied by the dependence on the pH, ionic strength and the form of the minerals. The highest anionic exchange of Hg(II) acetates and chlorides was found on montmorillonites. Anionic exchange of Au(III) chloro complexes was found on montmorillonite, but their sorption is strongly influenced by other anions such as chlorides and thiocyanates. The results found are important with regard to the study of the anion-exchange properties of clay minerals.

Key words Clay · Ionic exchange · Modified electrodes · Voltammetry

Introduction

Clay minerals belong to the class of phyllosilicates with a layered aluminosilicate structure, formed from one sheet of AlO_6 octahedra and either one sheet of SiO_4 tetrahedra (1:1 phyllosilicates) or two Si-tetrahedral sheets (2:1 phyllosilicates) [1, 2]. The 2:1 phyllosilicates as smectites exhibit cation exchange, intercalation and swelling properties.

The clay-modified electrodes have been exploited for the study of the ion-exchange properties of clay minerals. Great attention has been predominantly given to cationic species such as $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Os}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{NH}_6)_6^{3+}$, $\text{Fe}(\text{bpy})_3^{2+}$ and similar complexes sorbed into the mont-

morillonite film on the electrode [3–9]. The electroactivity of the sorbed cations depends on the soaking time of the film in the solution of the electroactive ion, on the ion concentration, on the mode of preparation of the film and its thickness and on the identity of the incorporated ion. Uptake of the cationic species is influenced by competitive exchange of different ions of the electrolyte, by the pH value of the medium and by swelling and the layer stacking order of the clay film. The electrochemical behaviour of the methyl viologen dication [3, 10], tetrathiafulvalenium [11] and of other organic cations [4, 12] adsorbed into the clay was also often studied.

Cationic species Me^{n+} were studied with regard to their determination by means of the clay modified carbon paste electrodes. The ion exchange during the preconcentration step involves a replacement of exchangeable cations in the clay. For example, Fe(III) is able to exchange Na^+ cations in montmorillonite [13]. The ion exchange is the dominating step for the preconcentration of Ag^+ and Cu^{2+} on the vermiculite-modified carbon paste electrode [14], and very high Cu(II) exchange was found on the montmorillonite-modified carbon paste electrode [15].

The cation exchange decreases with increasing ionic strength owing to replacement of exchangeable cations in the clay layer structure by the electrolyte cations. This competitive ion exchange is used to regenerate the electrode surface by washing the analyte from the clay layers [13, 16]. The presence of high valence cations also causes a decrease of the cation exchange process. For example, sorption of Cu(II) is disturbed by bivalent metal cations in 100-fold excess (Pb, Hg, Cd, Zn) [15, 16] and by the bi- and trivalent cations Fe(II, III), Co(II), Ni(II), Mn(II) and Bi(III) in 200-fold excess [16]. The influences of surfactants [16], humic ligands [15, 17] and selected pesticides [18] on the Cu(II) ion exchange on various clay minerals have also been studied by means of the clay-modified paste electrode.

Owing to the negative charge of the clay layers, anions are repelled. However, the diffusion transport of the electroactive anions is possible owing to their penetration

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through the clay film. It suggests the presence of channels between the clay particles. So, hydration and osmotic effects influence the electroactive anion migration within the clay film [19, 20]. Organo-clays with quarternary long-chain alkylammonium ions showed a great affinity for anionic species in comparison to the unmodified clays [21, 22]. Montmorillonite modified with cetyltrimethylammonium bromide [23] was suitable for strong electrostatic binding of anionic species such as $\text{Fe}(\text{CN})_6^{4-}$, $\text{Mo}(\text{CN})_8^{4-}$ and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$.

Layered double hydroxides ("anionic clays") consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules offer further possibilities for the electrochemical study of anionic species. The first report on the modification of electrodes with one of the naturally occurring anionic clay minerals – hydroxalite, $\text{Mg}_2\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ – described incorporation of ammonium metatungstate in the clay film [24]. The layered double hydroxide $\text{Zn}_2\text{Cr}(\text{OH})_6 \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$ also represents an anion-exchanging clay. It was used for the modification of various electrodes, and the electrochemical behaviour of organic sulfonate anions was also studied [25–28].

The anion exchange capacity of the clay minerals is about 4–5 times lower than the cation exchange capacity [30]. In spite of this fact, an anion exchange of the two complex anions $[\text{Hg}(\text{ac})_4]^{2-}$ and $[\text{HgCl}_4]^{2-}$ was found on carbon paste modified with montmorillonite and mica (biotite) [29]. This work follows up previous investigations of the sorption of the cations Cu(II) [15, 17] and Hg(II) [29] by expanding to other clay minerals. The paper also deals with an exchange of Au(III) anionic complexes studied by means of the clay-modified carbon paste electrodes.

Experimental

Materials and chemicals

The clay minerals montmorillonite (MMT_{Wy}) (Wyoming deposit, USA), montmorillonite (MMT_{JP}) (Jeľšový Potok deposit, Slovakia), vermiculite (Ver_{Let}) (Letovice deposit, Czech Republic) and kaolinite (Ka) (Sedlec deposit, Czech Republic) were treated as follows. Ground and swollen clay samples were elutriated with distilled water to remove fractions with higher specific gravity (especially quartz) and particles with diameter higher than approximately 0.5 mm (clay aggregates, etc.). The resulting slurry of fine clay particles was diluted with distilled water to obtain a 2% (w/w) suspension. Particles with diameter below 5 μm were isolated

by sedimentation and subsequent centrifugation (3000 rev/min) for 45 min. The product was air-dried and stored.

Vermiculite (Ver_Z) (Zimbabwe deposit) was treated and prepared for further experiments in a different way. A fraction with a grain size of 0.080 mm was disintegrated by means of a high-energy abrasive water jet at operational pressure 350 MPa. Other parameters were: water jet diameter 0.25 mm, abrasive jet diameter 1.0 mm, density flow rate of the abrasive material 0.15 kg/min; all process was performed with distilled water in order to eliminate any contamination of the mineral. The clay suspension produced was diluted with distilled water to obtain a 2% (w/w) suspension. Particles with diameter below 5 μm were isolated by sedimentation and subsequent centrifugation (3000 rev/min) for 45 min. The product was air-dried and stored.

Sodium forms of the minerals MMT_{Wy} , MMT_{JP} and Ver_Z were prepared by exchange of the minerals' cations by Na^+ ions. An amount of 2 g of the fraction <5 μm was added to 100 ml of 1 M sodium chloride solution. The suspension was thoroughly shaken by a laboratory shaker for about 10 h and then centrifuged at 3000 rev/min for 45 min. The sediments of the Na-exchanged clays were thoroughly washed with redistilled water to remove Cl^- ions. The products NaMMT_{Wy} , NaMMT_{JP} and NaVer_Z were air-dried and stored.

The cation exchange capacity of some minerals was determined by exchange of the minerals cations by $[\text{NH}_4]^+$ ions. An amount of 2 g of the fraction <5 μm was added to 100 ml of 1 M solution of ammonium acetate. The suspension was thoroughly shaken for about 10 h and then centrifuged at 3000 rev/min for 45 min. The concentration of Na, K, Ca and Mg ions in the supernatant were determined by atomic absorption spectroscopy. The cation exchange capacities for the montmorillonites and vermiculite are stated in Table 1.

Nitric acid, hydrochloric acid, potassium chloride, sodium acetate and acetic acid (all analysis grade, Merck) were used to prepare the background electrolytes. Stock standard solutions of all metals used were prepared from Titrisol standards (Merck). Redistilled water (glass apparatus) was used throughout. The glassware was cleaned as described previously [15].

Apparatus

An EKO-TRIBO-Polarograph (ETP, Polaro Sensors, Prague) was employed for the measurements of Cu(II) and Hg(II). An electrochemical analyzer Autolab with PGSTAT10 (Eco Chemie, The Netherlands) was employed to study the Au(III) sorption. A three-electrode cell equipped with a carbon paste electrode as the working electrode, an Ag/AgCl (sat. KCl) reference electrode and a Pt wire (BAS) counter electrode was used for all measurements. All measurements were performed on a freshly renewed surface of the carbon paste electrode. Regeneration was done by cutting of small portion of the paste and by polishing the surface on a coated paper.

The carbon paste electrode used of inner diameter 1.7 mm has already been described [15]. The preparation of the carbon paste modified with clay minerals by mixing carbon powder, nujol and wetted mineral has also already been reported [15]. The content of water in the clay modifiers was: MMT_{Wy} 22.9%, MMT_{JP} 19.8%, Ver_{Let} 6.8%, Ka 15.9%, Ver_Z 12.7%, NaMMT_{Wy} 21.7%, NaMMT_{JP} 24.2% and NaVer_Z 14.7% (w/w).

Table 1 The values of the cation exchange capacities (CEC) for MMT_{Wy} , MMT_{JP} and Ver_Z and their Na forms

Clay	Na (mol/kg)	K (mol/kg)	Ca (mol/kg)	Ca (equiv/kg)	Mg (mol/kg)	Mg (equiv/kg)	CEC (equiv/kg)
MMT_{Wy}	0.487	0.009	0.111	0.222	0.017	0.034	0.752
NaMMT_{Wy}	0.504	0.002	0.014	0.028	0.009	0.018	0.552
MMT_{JP}	0.003	0.013	0.316	0.632	0.125	0.250	0.898
NaMMT_{JP}	0.722	0.006	0.034	0.068	0.016	0.032	0.828
Ver_Z	0.005	0.010	0.023	0.046	0.476	0.952	1.013
NaVer_Z	1.060	0.006	0.023	0.046	0.033	0.066	1.178

The modified carbon paste electrodes, CPE(MMT_{Wy}), CPE(MMT_{Jp}), CPE(NaMMT_{Wy}), etc., were all prepared with 10% (w/w) of the wetted clay minerals.

Results

Cation exchange

Multisweep cyclic voltammetry on the clay-modified CPEs was used to study the Cu(II) exchange on the clay minerals in acetate buffers (pH range of 3.6–5.6). The two natural montmorillonites (MMT_{Wy} and MMT_{Jp}) exhibited the highest Cu(II) exchange capacity at pH 3.6, when about 90% of the copper is in the cationic forms Cu²⁺ and [Cu(ac)]⁺ (ac = acetate). The remaining 10% of the copper is in the form of the uncharged Cu(ac)₂. The exchange of the cationic forms of Cu was also found on the vermiculite; however, it was lower in comparison to the montmorillonites. The Cu(II) exchange on the montmorillonites is more affected by the increasing pH and simultaneously with the increasing ionic strength of the buffers (Fig. 1). It suggests that, except for competitive exchange of the electrolyte cations, the structure of the clay minerals can play a significant role in the Cu(II) exchange reaction. Table 2 gives the values of the enrichment factor *f* calculated as:

$$f = \frac{[i_{\max}]^{\text{clay}} - [i_{\max}]^0}{[i_{\max}]^0} \quad (1)$$

where $[i_{\max}]^{\text{clay}}$ and $[i_{\max}]^0$ are the constant maximum current achieved on the clay-modified and the unmodified paste electrodes, respectively. The constant maxi-

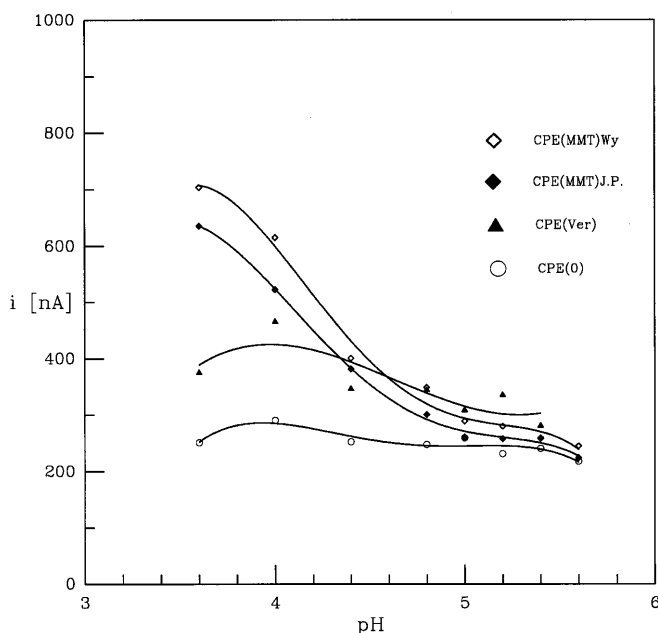


Fig. 1 The influence of pH on Cu(II) sorption for various clay-modified electrodes. Repetitive cyclic voltammetry in the acetate buffers, pH 3.6–5.6; scan rate 20 mV · s⁻¹; potential range from -600 mV to +600 mV; C_{Cu(II)} = 2.55 × 10⁻⁵ M

Table 2 The enrichment factors of various clay minerals for Cu(II) with the dependence on pH of the acetate buffer

pH	<i>f</i>					
	MMT _{Wy}	NaMMT _{Wy}	MMT _{Jp}	NaMMT _{Jp}	Ver _Z	NaVer _Z
3.6	1.81	0.99	1.57	1.30	0.50	0.00
4.0	1.12	0.77	0.89	2.00	0.61	0.00
4.4	0.59	0.74	0.79	1.19	0.38	0.00
4.8	0.39	0.44	0.39	0.49	0.40	0.00
5.0	0.12	0.36	0.18	0.43	0.20	0.00
5.2	0.21	0.27	0.41	0.62	0.46	0.00
5.4	0.08	0.22	0.48	0.56	0.17	0.03
5.6	0.12	0.03	0.37	0.39	–	0.07

imum current i_{\max} was obtained after the 8th to 10th scans of the cyclic voltammetry in the Cu(II) solution. The enrichment factor was not calculated as common ratio of $i_{\text{CME}}/i_{\text{bare}}$ in order to subtract the contribution of the bare electrode to the cation sorption on the electrode. The enrichment factor expresses an enhancement of the analytical response due to an enrichment achieved on the clay electrode. The decrease of the value *f* with increasing pH is caused by an increasing concentration of Na⁺ ions competing with the ion exchange of Cu(II) and by a decrease of the concentration of the exchangeable cations Cu²⁺ and [Cu(ac)]⁺. The decrease of *f* for NaMMT_{Wy} in comparison with MMT_{Wy} at pH 3.6 and 4.0 correlates with a decrease of the cation exchange capacity (Table 1). However, *f* increases for NaMMT_{Wy} at pH 4.4 and higher. Although the cation exchange capacity did not change in the case of MMT_{Jp} and its Na form, *f* increased at pH 4.0 and higher. The different course of the *f* dependence on pH for the natural and sodium forms MMT is probably connected with a replacement of the divalent cations Ca²⁺ and Mg²⁺ in the ion-exchange sites with Na⁺. The course of the Cu²⁺ and [Cu(Ac)]⁺ distribution in the medium also influences this dependence. The enrichment factor achieved on Na-vermiculite decreased to zero, although the cation exchange capacity did not change in comparison to Ver_Z. However, the Mg²⁺ content corresponds to 93.9% of the Ver_Z cation exchange capacity in comparison to only 5.6% for Na-Ver_Z. The Cu(II) exchange on the vermiculite is significantly dependent on the Mg content in the interlayer space, which corresponds with data stated in the literature [2].

Structural changes of the clay minerals also represent an important factor influencing the cation exchange. It has already been found [17] that Cu(II) exchange on the acid-treated montmorillonite was about four times lower in comparison to untreated MMT_{Wy}. This fact corresponded to results from X-ray diffraction, which found structural changes for acid-treated MMT_{Wy}. The structural changes were caused by the partial formation of the Al- or hydroxy-Al montmorillonite during the acidic treatment [17]. Thus, a large part of the cation-exchange sites of such acid-treated clay is not available for Cu(II). When MMT_{Wy} was acidically treated in the presence of humic ligands, its cation exchange capacity

also decreased owing to formation of montmorillonite humate. The humate is an associate of the folded and aggregated molecules of the humic acid [31] with a part of the surface of the Al- or hydroxy-Al montmorillonite. As the Cu(II) exchange on the montmorillonite humate was higher in comparison with acid-treated montmorillonite, it is probable that the ion exchange takes place via humic acid bound on the clay surface [17]. Cation exchange on the clay minerals studied was also found in the case of Cd^{2+} and Pb^{2+} . No cation exchange was found in the case of Hg^{2+} in the acid electrolytes. Probably the affinity of the clays to Hg^{2+} cations is very low. In addition, the cation-exchange sites can be occupied by Al^{3+} ions released from the clay structure, owing to the high concentration of H^+ ions in this electrolyte [17, 32].

Anion exchange of Hg(II) complexes

Anion exchange of the complex anions of Hg(II) – $[\text{Hg}(\text{ac})_4]^{2-}$, $[\text{HgCl}_4]^{2-}$ and $[\text{HgCl}_3]^-$ – was found on the paste electrode modified with montmorillonite and vermiculite. Anion exchange of the chloro complexes was used for the determination of Hg(II) in chloride medium by means of anodic stripping voltammetry on the CPE(MMT_{Wy}) [29].

The study of the exchange of Hg(II) anionic complexes was extended to other clay minerals; the exchange was also studied by means of cyclic voltammetry on the clay modified CPEs. In the case of acetates, the highest exchange was found in the acetate buffer at pH 3.6, where approximately 98% of Hg(II) ions are present as the complex anion $[\text{Hg}(\text{ac})_4]^{2-}$. The $[\text{Hg}(\text{ac})_4]^{2-}$ exchange decreased with increasing pH and increasing ionic strength. The anion exchange of Hg(II) chloro complexes was studied in 1 M KCl, pH 2, where approximately 99% of Hg(II) is present as $[\text{HgCl}_4]^{2-}$ and $[\text{HgCl}_3]^-$ with predominance of the former (about 90%). The enrichment factors are shown in Table 3.

Among minerals tested MMT_{Wy} exhibited the highest anion exchange capacity for Hg(II) acetates and for Hg(II) chlorides. Surprisingly, MMT_{JP} exhibited no exchange capacity for acetates and a very low capacity

Table 3 The enrichment factors for Hg(II) in acetate buffer (pH 3.6) (f_{ac}) calculated from maximal currents of the repetitive cyclic voltammetry (RCV) and in 1 M KCl (pH 2) (f_{Cl}) calculated for the 10th scan of the RCV

Clay	f_{ac}	f_{Cl}
MMT _{Wy}	1.04	0.80
NaMMT _{Wy}	1.04	0.87
MMT _{JP}	0.00	0.25
NaMMT _{JP}	0.71	0.76
Ver _Z	0.05	0.45
NaVer _Z	0.65	0.50
Ver _{Let}	0.11	0.27
Ka	0.45	0.70

for chlorides. The Na^+ cation is an exchangeable cation in natural MMT_{Wy}, but in the case of MMT_{JP} the bivalent Ca^{2+} and Mg^{2+} are the exchangeable cations (Table 1). When MMT_{JP} is modified to the Na form, its anion exchange capacity significantly increases. A similar effect takes place in the case of Ver_Z. Thus, the bivalent exchangeable cations Ca and Mg probably prevent the exchange of the exchangeable anions. Higher chloride exchange was found on the kaolinite which is also mentioned as a mineral with anion exchange capacity [30].

Anion exchange of Au(III) chloro complexes

An open circuit sorption was performed in 0.001 M HCl on the CPE(MMT_{Wy}). The current response of the Au(II) chloro complexes sorbed onto the MMT_{Wy} was measured after medium exchange by differential pulse voltammetry (DPV) in 0.1 M KCl (pH = 4.7). The minimum sorption was found on the unmodified electrode (Fig. 2). The following mechanism is assumed for anion exchange of the gold chloro complexes on the montmorillonite:

1. Anion exchange of the Au(III) chloro complexes on the clay modifier in the sorption medium with very low ionic strength:

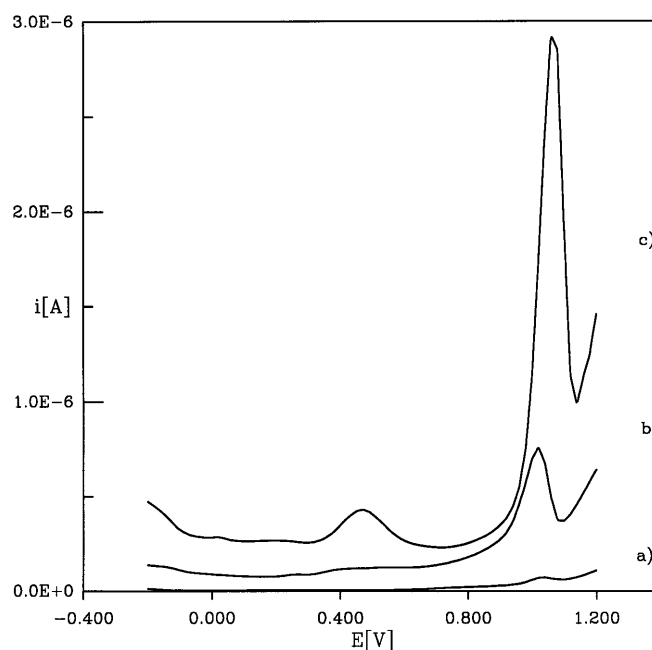
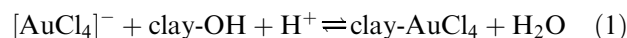
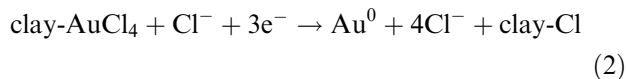


Fig. 2 Differential pulse voltammetry (DPV) in 0.1 M KCl (pH 4.7); scan rate $20 \text{ mV} \cdot \text{s}^{-1}$; pulse height 50 mV; a after 300 s open circuit sorption in $2 \times 10^{-5} \text{ M Au(III)}$ in 0.001 M HCl, unmodified electrode; b DPV of $2 \times 10^{-5} \text{ M Au(III)}$ in 0.1 M KCl (pH 4.7), CPE(MMT_{Wy}); c after 300 s open circuit sorption in $2 \times 10^{-5} \text{ M Au(III)}$ in 0.001 M HCl, CPE(MMT_{Wy})

2. Reduction by the negative potential after the medium exchange, in the electrolyte with significantly higher ionic strength:



3. Oxidation (anodic stripping) in the electrolyte:



The anodic stripping peak with $E_p = +1.059$ V results from step (3).

The anion exchange of the Au(III) chlorocomplexes was found to be significantly dependent on the presence of other cations and anions. The competitive anion exchange of the excess of chloride in the sorption media decreased the anion exchange of the anionic chloro complexes of Au(III) (Fig. 3). Although the amount of the chloro complexes increased with increasing concentration of chloride ion, the anion exchange decreased to 6% in 0.1 M KCl (pH 3) and disappeared altogether in 1 M KCl (pH 3). The anion exchange of the chloride ions on the montmorillonite predominated completely in this sorption medium.

No anion exchange was found in 0.001 and 0.01 M KCl (pH 4.7); the highest anion exchange was found in 0.1 M KCl at the same pH value. However, the anion exchange is 38 times higher in 0.001 M HCl in comparison to 0.1 M KCl. The competitive anion exchange of Cl^- again predominated and the anion exchange of

the Au(III) chloro complexes again decreased. In addition, the formation of the gold chloro complexes can be influenced by hydrolysis at this pH value.

Interesting results were found in the case of Au(III) sorption without any applied potential in 0.1 M KSCN with subsequent DPV measurements in 0.1 M HCl. The resulting very broad anodic response of the sorbed species exhibited two unseparated peaks (Fig. 4). The 30 s open circuit sorption performed in 0.1 M KSCN [with no Au(III) ions] exhibited a current response of sorbed SCN^- ions of $1.43 \mu\text{A}$ at $E_a = +1.159$ V (curve a of Fig. 5). On the contrary, very low SCN^- sorption was found on the unmodified electrode after 5 min of open circuit in 0.1 M KSCN (curve c). The voltammogram b of Fig. 5 proves that the peak at $+1.159$ V represents the oxidation of SCN^- ions. These results lead to the conclusion that thiocyanate anions are also sorbed on the montmorillonite.

The sorption of anionic chloro complexes $[\text{HgCl}_4]^{2-}$ has been already found on montmorillonite [29]. Under the conditions of an open circuit sorption in 0.001 M HCl the anodic peak of sorbed Hg(II) chloro complexes occurred at $E_p = 0.140$ V in the case of Hg(II) with concentrations comparable to Au(III) and higher. The exchange of Au(III) chloro complexes decreased and the current response decreased to 75% at 10-molar excess of Hg(II). In the case of 100-molar excess of Hg(II), the exchange of Au(III) decreased to zero.

The anion exchange processes of the clay minerals can also be influenced by trivalent Al(III) and Fe(III). Generally, the high valence cations are able to replace exchangeable cations in the clays [2]. A 10-fold molar

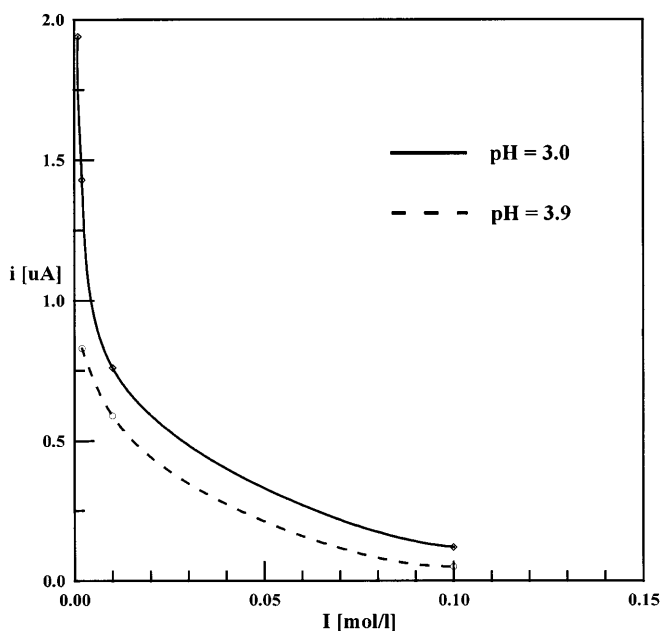


Fig. 3 Influence of ionic strength on the Au(III) chloro complexes sorption. DPV at a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$ with pulse height 50 mV in 0.1 M KCl (pH 4.7) after 300 s open circuit sorption in $0.001\text{--}0.1$ M KCl on the CPE(MMT_{wy}); $C_{\text{Au(III)}} = 2 \times 10^{-5} \text{ mol/l}$

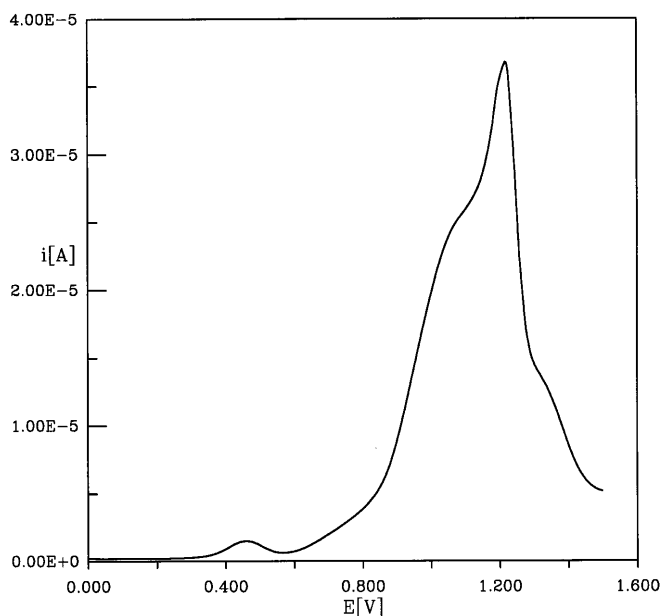


Fig. 4 DPV at a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$ with pulse height 50 mV in 0.1 M HCl after 120 s open circuit sorption in $2 \times 10^{-5} \text{ M Au(III)}$ in 0.1 M KSCN

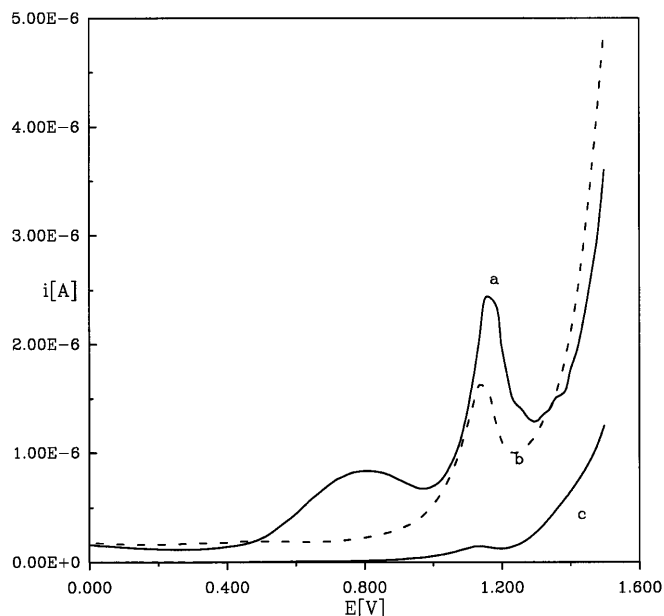


Fig. 5 DPV at a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$ with pulse height 50 mV in 0.1 M KCl (pH 4.7): *a* after 30 s open circuit sorption in 0.1 M KSCN on the CPE(MMT_{Wy}); *b* DPV in $4.8 \times 10^{-5} \text{ M SCN}^-$ in 0.1 M KCl , unmodified electrode; *c* after 300 s open circuit sorption in 0.1 M KSCN , unmodified electrode

excess of Al(III) in the sorption medium caused a 35% decrease of the current; in the case of 100-fold molar excess, the current decrease was about 79%. The exchange of the Au(III) chloro complexes was improved by Fe(III) present in the sorption medium. The current increased with increasing amounts of Fe(III) in the sorption medium and it achieved a maximum at the 10-molar excess of Fe(III) (about 78% increase). The peak potential shifted toward positive values corresponding to a strong sorption. However, almost no Au(III) current response was found in the case of a 100-molar excess of Fe(III).

The influence of Cu(II) was also studied as the high sorption of Cu(II) on the Wyoming montmorillonite has already been found [15]. It was found that Cu(II), as well as Au(III) chloro complexes, are sorbed in 0.001 M HCl under open circuit conditions. In the case of sorbed Cu(II), an anodic peak ($E_p = 0.010 \text{ V}$) appeared and the exchange of the Au(III) chloro complexes decreased. However, the current response of the sorbed Au(III) chloro complexes is sufficient (80%) even at 10-molar excess of Cu(II).

Apart from MMT_{Wy}, only the montmorillonite from Jelšovský Potok was used to study the anion exchange of the Au(III) chloro complexes. The anodic current response of the sorbed Au chloro complexes was about 5 times lower on the CPE(MMT_{JP}) in comparison to MMT_{Wy}. The MMT_{JP} exhibited lower anion exchange capacity as well as in the case of Hg(II) chloro complexes (Table 3).

Conclusion

Cyclic voltammetry on clay-modified carbon paste electrodes enables a relative comparison of the ion exchange capacities of clay minerals. The structural changes of the minerals caused by formation of clay humates can also be evaluated by these experiments.

The sorption found for gold and mercury chloro complexes and Hg(II) acetates has proved the anion exchange properties of the studied clay minerals.

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