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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 AlO₆ octahedra and either one sheet of SiO₄ 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 Ru(bpy)₂⁺, Os(bpy)₂⁺, Ru(NH₆)₆³⁺, Fe(bpy)₂⁺ and similar complexes sorbed into the montmorillonite 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], tetra-thiafulvalenium [11] and of other organic cations [4, 12] adsorbed into the clay was also often studied.

Cationic species Meⁿ⁺ 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 pre-concentration of Ag⁺ and Cu²⁺ 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 electreactive anions is possible owing to their penetration...
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 quaternary 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 Fe(CN)₆³⁻, Mo(CN)₆⁴⁻ and Fe(C₂O₄)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 – hydrotalcite, Mg₃Al₂(OH)₁₆CO₃·4H₂O – described incorporation of ammonium metatungstate in the clay film [24]. The layered double hydroxide Zn₂Cr(OH)₆·Cl·2H₂O 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 [Hg(ac)₄]²⁻ and [HgCl₄]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 (MMTₓₓ) (Wyoming deposit, USA), montmorillonite (MMTₓₚ) (Jelsový Potok deposit, Slovakia), vermiculite (Verₓₓ) (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 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 (Verₓₓ) (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 MMTₓₓₓ, MMTₓₚ and Verₓₓ 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 NaMMTWy, NaMMTₓₚ and NaVerₓₓ were air-dried and stored.

The cation exchange capacity of some minerals was determined by exchange of the minerals cations by [NH₄]⁺ 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: MMTₓₓₓ 22.9%, MMTₓₚ 19.8%, Verₓₓ 6.8%, Ka 15.9%, Verₓₓ 12.7%, NaMMTWy 21.7%, NaMMTWy 24.2% and NaVerₓₓ 14.7% (w/w).

**Table 1** The values of the cation exchange capacities (CEC) for MMTₓₓₓ, MMTₓₚ and Verₓₓ and their Na forms

<table>
<thead>
<tr>
<th>Clay</th>
<th>Na (mol/kg)</th>
<th>K (mol/kg)</th>
<th>Ca (mol/kg)</th>
<th>Ca (equiv/kg)</th>
<th>Mg (mol/kg)</th>
<th>Mg (equiv/kg)</th>
<th>CEC (equiv/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMTₓₓₓ</td>
<td>0.487</td>
<td>0.009</td>
<td>0.111</td>
<td>0.222</td>
<td>0.017</td>
<td>0.034</td>
<td>0.752</td>
</tr>
<tr>
<td>NaMMTWy</td>
<td>0.504</td>
<td>0.002</td>
<td>0.014</td>
<td>0.028</td>
<td>0.009</td>
<td>0.018</td>
<td>0.552</td>
</tr>
<tr>
<td>MMTₓₚ</td>
<td>0.003</td>
<td>0.013</td>
<td>0.316</td>
<td>0.632</td>
<td>0.125</td>
<td>0.250</td>
<td>0.898</td>
</tr>
<tr>
<td>NaMMTₓₚ</td>
<td>0.722</td>
<td>0.006</td>
<td>0.034</td>
<td>0.068</td>
<td>0.016</td>
<td>0.032</td>
<td>0.828</td>
</tr>
<tr>
<td>Verₓₓ</td>
<td>0.005</td>
<td>0.010</td>
<td>0.023</td>
<td>0.046</td>
<td>0.476</td>
<td>0.952</td>
<td>1.013</td>
</tr>
<tr>
<td>NaVerₓₓ</td>
<td>1.060</td>
<td>0.006</td>
<td>0.023</td>
<td>0.046</td>
<td>0.033</td>
<td>0.066</td>
<td>1.178</td>
</tr>
</tbody>
</table>