

Voltammetric Characterization of Montmorillonite-Based Organo Derivatives

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Abstract: Organo derivatives of clay mineral montmorillonite were prepared by modification of montmorillonite (type SAz-1) with three alkylammonium cations – hexadecyltrimethylammonium (HDTM), benzyldimethylhexadecylammonium (BDH), and hexadecylpyridinium bromide (HDP). The prepared organo-montmorillonites were characterized by X-Ray diffraction and infrared spectroscopy to test the alkylammonium cations presence in the organo derivatives. Multisweep cyclic voltammetry of copper at carbon paste electrodes modified with the organo-montmorillonites used to study their sorption properties has proved the sorption decrease in comparison with the unmodified montmorillonite. The obtained results correlate with the study performed by means of sorption isotherms.

Keywords: Modified carbon paste electrode; Montmorillonite; Alkylammonium cations; Copper sorption;

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Introduction

Organo derivatives based on various types of clay minerals have been studied due to their improved mechanical properties as well as their ability to adsorb the anions or organic compounds [1-3]. Organo derivatives prepared by modification of clay minerals with quaternary ammonium cations exhibit organophilic nature of good sorption properties.

These clay composites can be used to removing various pollutants from the aqueous solutions [4]. Clay minerals of bentonite types, especially montmorillonite, are frequently modified for this purpose. According to a charge of montmorillonite and a length of alkyl chain of alkylammonium cation various types of arrangement of the organo-montmorillonite structure are formed (see Fig. 1).

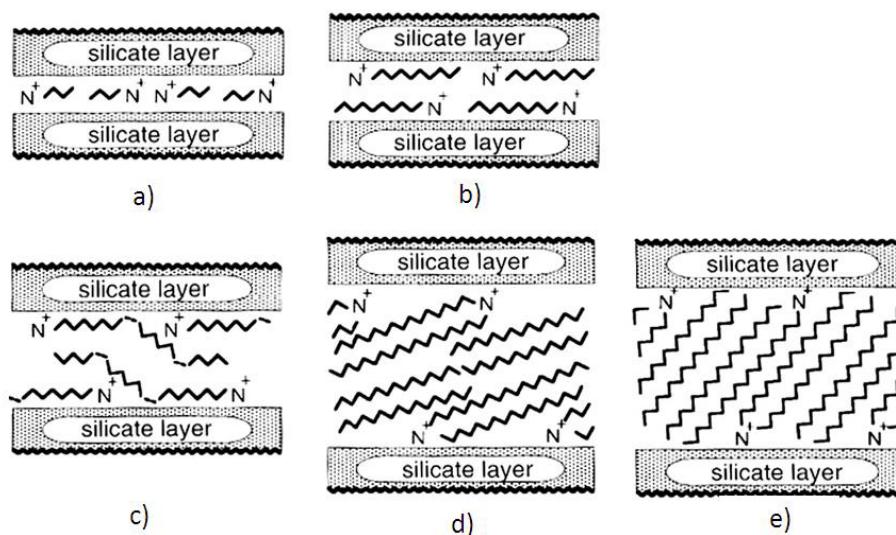


Fig. 1: Orientations of alkylammonium ions in the galleries of layered silicates (scheme)
 Legend: a) monolayer, b) bilayer, c) pseudotrimolecular layer, d) e) paraffin-type arrangements [5].

The sorption properties of organo-montmorillonites are influenced by the structural arrangement that can be assessed by means of X-ray diffraction (XRD) and infrared (IR) spectroscopy [5,6]; these methods suitably complement study of sorption mostly performed by means of batch technique.

However, as the modified carbon paste electrodes [7] have become an indisputable part of electrochemistry, those modified with clay minerals offer possibility to characterize clay minerals regarding their sorption properties [8]. Multisweep cyclic voltammetry on the clay modified electrodes has been already used as an additional method to other non-electrochemical methods. Its advantage is mainly in relatively fast performance providing information about sorption ability of the clay modifier and describing an influence of the sorption conditions such as composition of sorption medium (presence of other cations and anions), pH, and temperature. Of course, in comparison with non-electrochemical methods the electrochemical characterization of clay minerals enables a semi-quantitative evaluation of the sorption processes.

This work has followed from our former studies [9,10] dealing with influence of the hexadecyltrimethylammonium presence on the copper sorption on clay mineral montmorillonite. The study has been expanded to benzyldimethylhexadecylammonium and hexadecylpyridinium and some selected non-electrochemical methods were used to characterize the prepared organo-montmorillonites.

Experimental

Materials and Chemicals

Montmorillonite SAz-1 (MMT,SAz-1) (Apache County, USA) was provided from The Clay Minerals Society, Source Clays Repository (USA). The fraction used for all experiments consisted of 80 % of particles below 5 μm (Fritsch Particle Sizer Analysette 22, Fritsch GmbH, Idar-Oberstein, Germany). The montmorillonite was classified (via X-ray diffraction and IR spectroscopy) as pure montmorillonites without any admixture of other minerals including quartz [11]. Organo-montmorillonites were prepared by intercalation of three alkylammonium cations. Hexadecyltrimethylammonium bromide (HDTMABr) (Sigma-Aldrich), benzyldimethylhexadecylammonium chloride (BDHDACl) (Fluka), and hexadecylpyridinium bromide (HDPBr) (Sigma-Aldrich) of analytical reagent grade were used to prepare the modified montmorillonites MMT,SAz-1-HDTM, MMT,SAz-1-BDH, and MMT,SAz-1-HDP).

All the chemicals used (sodium acetate and acetic acid for preparation of the background electrolytes were of analytical grade (Merck, Darmstadt, Germany). Stock standard solution of Cu for voltammetry was prepared from Titrisol standards (Merck, Darmstadt, Germany).

Preparation and Characterization of Organo Derivatives

An amount of 1 g of montmorillonite and 100 ml 7.5×10^{-3} M solution of alkylammonium cation was shaken at laboratory temperature for 2.5 h; subsequently, the suspension was centrifuged (9000 rpm) for 10 min. The supernatant was removed, the solid was washed out with 5 ml solution of ethanol : water = 2 : 1 and the suspension was again centrifuged at the same rate. The washing out was repeated with 5 ml of ethanol and the preparative of organo-montmorillonite was air dried after centrifugation.

X-ray Diffraction

X-Ray diffraction (XRD) was carried out at Nanotechnology Centre, VSB-Technical University Ostrava. XRD patterns of the tested samples were measured by diffractometer (model INEL) equipped with Cu anode, generator (2000 sec, 35 kV, 20 mA) and detector CPSD 120, samples were measured in a flat rotation holder.

Infrared spectroscopy

Infrared spectra were recorded on Nicolet Avatar 320 FTIR spectrometer (ThermoNicolet, USA) equipped with the DTGS/KBr detector for the middle IR range. The KBr pressed-disc (13 mm diameter) technique (1 mg of sample and 200 mg of KBr) was used. The spectra were measured in the spectral range from 4000 to 400 cm^{-1} (64 scans, 4 cm^{-1} resolutions).

Electrochemical Apparatus

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) (the working electrode), an Ag/AgCl/3M KCl reference electrode and a Pt-wire counter electrode. Multisweep cyclic voltammetry (MCV) at a scan rate of 20 mV s^{-1} was applied within the potential range of -1.3 V to $+0.2 \text{ V}$ vs. ref.

Carbon Paste Electrode

Preparation of the carbon paste electrodes and the measurement techniques were performed as they were already described [12]. The following carbon paste electrodes (CPEs) were prepared:

- (i) CPE(MMT,SAz-1) CPE modified with 10 wt. % of montmorillonite SAz-1
- (ii) CPE(MMT,SAz-1-HDTM) CPE modified with 10 % (w/w) of MMT,SAz-1-HDTM
- (iii) CPE(MMT,SAz-1-BDH) CPE modified with 10 % of MMT,SAz-1-BDH
- (iv) CPE(MMT,SAz-1-HDP) CPE modified with 10 % of MMT,SAz-1-HDP.

Results and Discussion

Characterization of Organo Derivatives by Non-voltammetric Methods

The XRD patterns of the prepared organo-montmorillonites exhibited an evident increase of the basal spacing ($d(001)$) compared to the original montmorillonite (see Table I overleaf). The increase of the $d(001)$ values proves an intercalation of alkyl-ammonium cations into the montmorillonite interlayer [6]. The value about 1.7 nm indicates bilayer arrangement of cations, the values 2.2 and 2.4 are supposed to indicate a paraffin-type of arrangement [5,13].

The infrared spectra of MM,SAz-1, as well as those of the organo-montmorillonites have been interpreted according to [14]. The characteristic absorption bands of the intercalated alkylammonium cations were present in the infrared spectra of all organo-montmorillonites in comparison with the original MMT,SAz-1.

Table I: Basal spacing values $d(001)$

Montmorillonite	$d(001)$ [nm]
MMT,SAz-1	1.47
MMT,SAz-1-HDTM	1.65
MMT,SAz-1-BDH	1.78 – 2.40
MMT,SAz-1-HDP	1.69 – 2.20

The absorption bands at 2920 cm^{-1} (antisymmetric stretching vibrations) and at 2850 cm^{-1} (symmetric stretching vibrations) of C–H bounds reflect alkyl chains of the alkylammonium cations. The band at 3050 cm^{-1} (symmetric stretching vibration of C–H bounds in aromates) and at 1620 and 1471 cm^{-1} (symmetric stretching vibration of C–C bounds in conjugated system) confirm the presence of benzene ring in BDH and HDP intercalated into the organo-montmorillonites. The absorption band at 1487 cm^{-1} corresponds to the bending vibration of the N–H bounds in ammonium groups.

Voltammetry with Carbon Paste Electrode Modified with Organo Derivatives

Multisweep cyclic voltammetry (MCV) on the clay modified CPEs represents a suitable method to distinguish the sorption properties of organo-montmorillonites and montmorillonite. The MCV current responses of metals on the cycling time exhibit a characteristic feature of the metals sorption on various types of clays. As already described, MCV on CPE(MMT,SAz-1) and on CPE(MMT,SAz-1–HDTM) proved the decrease of the Cu^{2+} adsorption on MMT,SAz-1-HDTM in comparison with MMT,SAz-1 [8, 9]. The current – time dependences illustrating the Cu^{2+} sorption on the other types of organo-montmorillonites (see Fig. 2 and 3, overleaf) prove an inhibiting influence of BDH and HDP in comparison with the unmodified MMT,SAz-1.

It is evident, that all alkylammonium cations intercalated into the MMT, SAz-1 cause the significant decrease of the Cu^{2+} sorption. This fact correlates with the sorption isotherms obtained by sorption experiments performed by means of batch technique [8]. The maximum sorption capacity a_{Cu} calculated from the linearized forms of the adsorption isotherms was $0.34\text{ mmol} \times \text{g}^{-1}$ (MMT,SAz-1) and 0.17 or $0.18\text{ mmol} \times \text{g}^{-1}$ for the organo-montmorillonites. The decrease of the Cu^{2+} sorption was nearly the same for all organoderivatives of MMT,SAz-1 – about 50 % - on the contrary to the sorption decrease found by MCV.

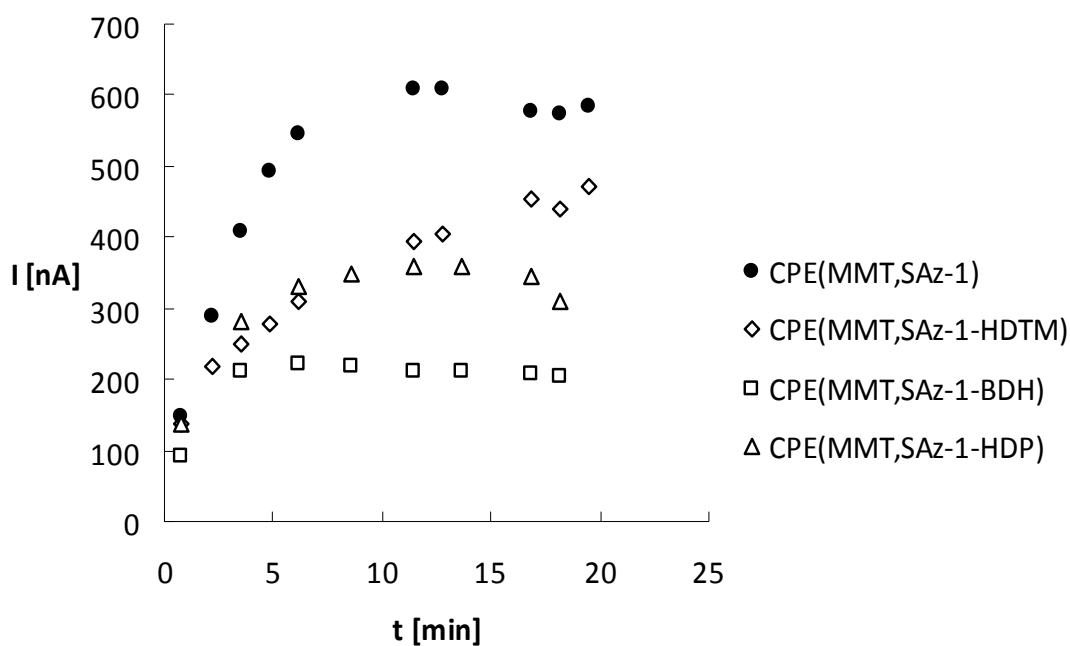


Fig. 2: Current vs. time dependences for various modified CPEs. Experimental conditions: supporting electrolyte / acetate buffer, pH 3.6; $c(\text{Cu}^{2+}) 2.5 \times 10^{-5}$ M (for other details, see *Experimental*).

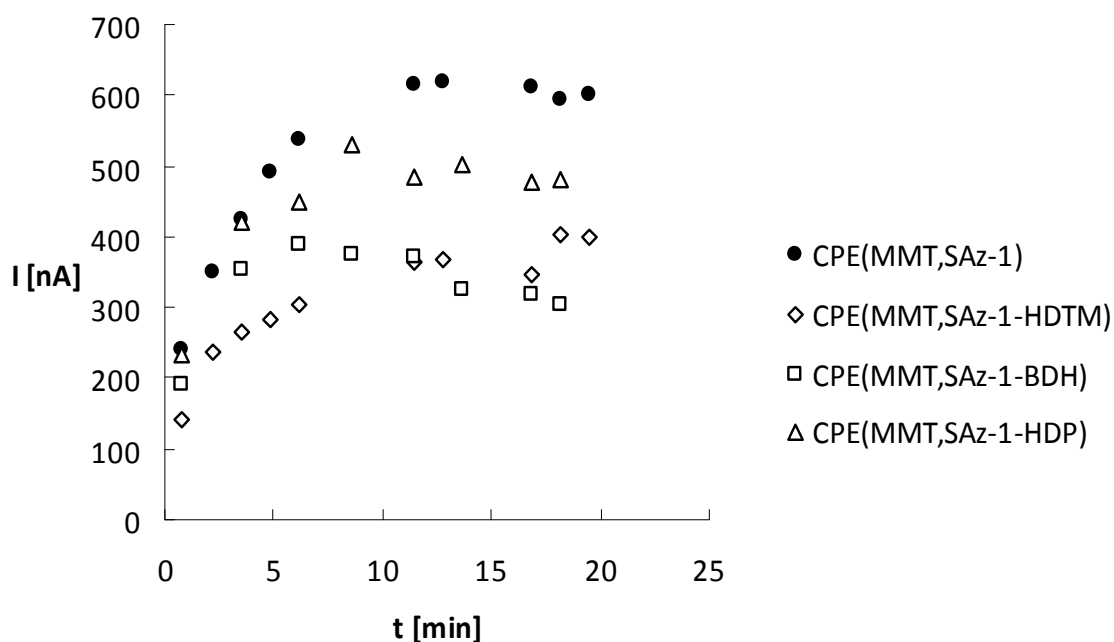


Fig. 3: Current vs. time dependences for various modified CPEs. Experimental conditions: supporting electrolyte / acetate buffer pH 4.0; $c(\text{Cu}^{2+}) 2.5 \times 10^{-5}$ M (for other details, see *Experimental*).

As it is seen in Fig. 2 and 3, the sorption decrease differs according to a type of alkylammonium and depends upon the pH value. Thus, it can be supposed that the used alkylammonium cations are variously protonized by the pH value, which can influence their hydrophilicity and subsequently their sorption abilities. This idea is supported by a course of the current – time dependences for various pH values. The MMT,SAz-1 intercalated with HDP exhibited the highest sorption at pH 4.0 while the sorption was nearly the same at pH 3.6; 4.4; 4.8; 5.0 and 5.2. The MMT, Saz-1 intercalated with HDTM and BDH exhibited the sorption decrease with increasing pH and the highest sorption was found at pH 3.6 and 4.0. Generally, aromaticity of the alkylammonium cations influences the sorption decrease only a little, which corresponds to the parameter " a_{Cu} " indicating no significant differences, too. However, the batch sorption experiments were performed in the non-buffered media.

Conclusions

Multisweep cyclic voltammetry on the carbon paste electrodes modified with montmorillonite and its organo derivatives provided the following results. The current – time dependences indicated the higher sorption capacity of the unmodified MMT,SAz-1, which corresponds to the batch sorption results. MMT,SAz-1 intercalated with alkylammonium cations exhibited the lower sorption capacity as it was also calculated from the adsorption isotherms. However, as the copper sorption on the organo-montmorillonites is partly influenced by pH, it can be supposed that sorption onto organo-derivatives of montmorillonite can be enhanced by pH.

Acknowledgements

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