Electrochemical Properties of Surfactants Modified Smectite Clays

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Article

Electrochemical Properties of Surfactants Modified Smectite Clays

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Abstract: The objective of the present paper is to get a better understanding of the electrochemical properties of organoclays, which were prepared via solid-state intercalation of three cationic surfactants, such as dodecyltrimethylammonium, tetradecyltrimethylammonium, and hexadecyltrimethylammonium, as bromide salts, at different loading levels into the interlayers of two natural smectite clays (AH and DI). The electrochemical properties of the prepared organoclays were investigated by cyclic voltammetry. The cyclic voltammetry response of the electrochemical probe, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, shows that the intensities of the anodic and cathodic peaks don't increase when the working electrode is based on carbon paste modified with the raw clays (AH or DI), whereas the peaks intensities increase significantly when the working electrode consists of carbon paste modified with organoclays. This increase in the intensity of the current indicates an improvement in the surface conductivity of the carbon paste electrode when they are modified with organoclays. When the working Electrode is based on organoclays modified carbon paste, the potential differences (ΔEp) are ranged between 140 and 170 mV, which are lower than those of the unmodified carbon paste electrode (330 mV) and those modified with raw clays (520 mV). This indicates an easy electron transfer process on the surface of the organoclays modified carbon paste electrodes.

Keywords: organoclays; carbon paste electrode; carbon paste modified electrode; surfactants; cyclic voltammetry

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1. Introduction

Clay modification is widely undertaken in aqueous solution via cation exchange or solid-state intercalation reactions. Organic molecules are inserted in dried clay interlayers by solid-state intercalation and washed with water, making the synthesis environmentally friendly and more favorable for industrialization [1]. Generally, literature results reported organoclays synthesis using various procedures and chemicals, numerous types of clays, and diverse surfactants as reviewed elsewhere [1]. To obtain organoclays with hydrophobic properties, quaternary alkylammonium salts are the most frequently used, but n-alkyl-pyrrolidones, biomolecules, polymeric quaternary alkylammonium, and phosphonium salts are also employed to the accomplishment of this outcome [1]. The obtained organoclays are usually characterized by using different techniques such as X-ray Powder Diffraction (XRPD), Fourier Transform Infrared spectroscopy (FT-IR), Transmission and Scanning Electron Microscopy (TEM and SEM, respectively), Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC), and electrochemical methods (cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS)). Whereas XRPD, FT-IR, Transmission and scanning electron microscopy analyses (TEM and SEM), and Thermogravimetric (TG) and differential scanning calorimetry (DSC) are used for the structural characterization of surfactant modified clays, electrochemical methods are involved to characterize their electrochemistry-related

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properties and analyze the redox state of the constituent elements. Among the electrochemical methods which are currently used, cyclic voltammetry has gained an important role and represents a very versatile tool for solid-state electrochemical characterization.

Cyclic voltammetry is used for the evaluation of the permeability and the ionic exchange properties of the organoclays and this is done by analyzing a thin layers of an organoclay deposited onto a glassy carbon electrode or an organoclay modified carbon paste electrode [2–4]. The cyclic voltammetry results indicated a best electrical conductivity of the organoclays modified carbon paste electrodes compared to the raw clay counterparts [4–6]. The electrochemical response using cyclic voltammetry depends mostly on the chemical interactions between the modifier of the working electrode and the probe redox in solution [6–9]. In the case of the carbon paste modified electrode using organoclays based on natural clays as modifier, the physicochemical properties should be considered due to the fact that the reproducibility of the measurement on the modified electrode can be affected by their heterogeneity. Carbon paste modified electrodes based on organically modified clays have a great interest because of the diversity of their applications. The principal advantage of this cyclic voltammetry is that the field of interesting potential can be swept during only one experiment.

Ngameni et al. 2006 [4] have studied the ion exchange properties of smectite clay, before and after intercalation of hexadecyltrimethylammoniumn cations (C_{16}) by using cyclic voltammetry analysis. The authors reported that the C_{16}-organoclays coated onto glassy carbon electrode can be used as $Fe(CN)_6^{3-}$ sensor [4]. Tonle et al. 2004 [6] reported a selective behavior of clay and organoclay-films coated onto glassy carbon electrode toward $Fe(CN)_6^{3-}$ and $Ru(NH_3)_6^{3+}$species due to favorable or unfavorable electrostatic interactions. The clay-film coated onto glassy carbon electrode accumulated $Ru(NH_3)_6^{3+}$ and rejected $Fe(CN)_6^{3-}$, whereas γ-aminopropyltriethoxysilane-organoclay coated onto glassy carbon electrode attracted $Fe(CN)_6^{3-}$ and rejected $Ru(NH_3)_6^{3+}$ [6]. Falaras and Petridis (1992) reported that cyclic voltammetry methodology indicated an interesting affinity of $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $Fe(C_2O_4)_3^{3-}$anions toward clay-modified electrodes coated with cetyltrimethylammonium bromide (C_{16}) [10]. Mojović et al. (2011) reported the effectiveness of the electrooxidation of phenol in aqueous solution onto C_{16}-bentonite thin layer coated onto glassy carbon electrodes by using multisweep cyclic voltammetry [11]. Mojović et al. (2011) also reported that carbon paste modified electrodes based on $(CH_3)_3N^+$-, $(n\text{-}C_{12}H_{25})_2(CH_3)_2N^+$-, $n\text{-}C_{16}H_{33}(CH_3)_3N^+$-bentonites exhibited similar electrochemical behavior toward phenol by using multisweep cyclic voltammetry analysis, but the current intensities of the electrochemical response and Tafel slopes were different [5]. Cubuk et al. (2015) reported that an electrode based on C_{16}-smectite exhibited high selectivity potentiometric response toward thiocyanate compared to other anions, and this was explained by the appearance of positive charges onto the organosmectite surfaces due to the excess of the surfactants loaded [12]. Zuzana and Martin have reported that carbon paste electrodes modified with montmorillonite showed high affinity for Cu^{2+} sorption than those modified with $n\text{-}C_{16}H_{33}(CH_3)_3N^+$-, $n\text{-}C_{16}H_{33}((Ph)(CH_3)_2)N^+$-, and $n\text{-}C_{16}H_{33}$-(pyridinium)-montmorillonite [13].

According to the literature, cyclic voltammetry analysis using working electrodes based on organoclays, obtained by intercalation of $n\text{-}C_{16}H_{33}(CH_3)_3N^+$ cation, have been more studied [4–6,10,14], but few investigations have been conducted using clays modified with $n\text{-}C_{12}H_{25}(CH_3)_3N^+$ [5] and $n\text{-}C_{14}H_{29}(CH_3)_3N^+$ cations. In addition, to the best of our knowledge, organoclays, which were prepared via solid-state intercalation of cationic surfactants ($n\text{-}C_{12}H_{25}(CH_3)_3NBr$, tetradecyltrimethylammonium, $C_{16}H_{33}(CH_3)_3NBr$), have not yet been used as modifier of carbon paste modified electrodes and the present study should allow us to check the electrochemical properties of those organoclays modified carbon paste electrodes.

The present study is devoted to the electrochemical characterization of organoclays modified carbon paste electrodes, based on three surfactants such as dodecyltrimethylammonium ($n\text{-}C_{12}H_{25}(CH_3)_3NBr$ denoted (C_{12})), tetradecyltrimethylammonium ($n\text{-}C_{14}H_{25}(CH_3)_3NBr$ denoted (C_{14})), and hexadecyltrimethylammonium ($n\text{-}C_{16}H_{33}(CH_3)_3NBr$ denoted C_{16}) intercalated into two natural smectite clays from Siétougou (denoted AH) and Diabari (denoted DI) samples collected in the Eastern part of Burkina Faso. The organoclays (C_{12}-AH, C_{12}-DI, C_{14}-AH, C_{14}-DI, C_{16}-AH, and C_{16}-DI) used in the present work have been successfully synthesized via solid-state intercalation and characterized by using XRPD, FT-IR, and SEM, as reported in our previous studies [15,16].

2. Materials and Experimental Methods

2.1. Materials

The natural smectite clays used in this study are from the villages Siétougou and Diabari, denoted AH and DI, respectively, and located in the eastern part of Burkina Faso at the following coordinates, AH: latitude = 11°54′43.2″, longitude = 00°38′22.7″, and DI: latitude = 11°51′19.9″, longitude = 00°25′08.07″. The surfactants n-dodecyltrimethylammonium bromide (n-$C_{12}H_{25}(CH_3)_3NBr$, (C_{12}) n-tetradecyltrimethylammonium bromide (n-$C_{14}H_{29}(CH_3)_3NBr$, (C_{14})), n-hexadecyltrimethylammonium bromide (n-$C_{16}H_{33}(CH_3)_3NBr$, (C_{16})) were purchased from Sigma-Aldrich, and used without any further purification. Potassium ferricyanide ($K_3[Fe(CN)_6]$) was purchased from Sigma-Aldrich and used as probe redox for the cyclic voltammetry experiences.

2.2. Experimental Methods

2.2.1. Organoclays Synthesis

Organoclays synthesis: 4 g of dried smectite clay (powder size < 80 µm) and a well-defined amount of surfactant, which represents a level of 0.5, 1.0, 1.5, and 2.0 CEC of the used clay, were placed in an agate mortar. The whole was mixed for 10-15 minutes to get a homogeneous powder. All organoclay products were washed with distilled water to get rid of bromide ions as checked by the addition of an aqueous solution of silver nitrate, dried at room temperature, and dried further in an oven at 105 °C for 24 hours. The dried organoclays were ground in an agate mortar, and stored in bottles. The organoclays were labeled as surfactant loading-type of the surfactant-original location of clay, e.g., 0.5 CEC-C_{12}-AH.

Organoclays modified carbon paste electrode preparation: The electrodes with carbon paste not modified (CPE (0)) or modified by using raw clays (CPME (AH) and CPME (DI)) and organoclays (CPME (1.0 CEC-C_{12}-AH), CPME (1.0 CEC-C_{12}-DI), CPME (2.0 CEC-C_{12}-AH), CPME (2.0 CEC-C_{12}-DI), CPME (1.0 CEC-C_{14}-AH), CPME (1.0 CEC-C_{14}-DI), CPME (2.0 CEC-C_{14}-AH), CPME (2.0 CEC-C_{14}-DI), CPME (1.0 CEC-C_{16}-AH) CPME (1.0 CEC-C_{16}-DI), CPME (2.0 CEC-C_{16}-AH) and CPME (2.0 CEC-C_{16}-DI)) were prepared by a standard process [17]. The electrode with carbon paste (CPE (0)) was prepared by adding 0.5 mL of paraffin oil to 1 g of graphite powder, and the whole was mixed manually in an agate mortar until we obtained a homogeneous paste. In the case of the CPME, the mass ratio of the modifier in the modified carbon pastes is 20 %. 0.2 g of the modifier (clays or organoclays) was added to 0.8 g of graphite powder and the whole was mixed in an agate mortar until we obtained a homogeneous material. Then, 0.5 mL of paraffin oil is added to the homogeneous material obtained and the mixture is mixed until obtaining the modified carbon paste. Part of the carbon paste modified or not modified is then introduced manually into the cylindrical stem of the work electrode (diameter: 2 mm, depth: 5 mm) and then smoothed on a clean and smooth paper for analyses [18,19].

2.2.2. Cyclic Voltammetry Characterization

The cyclic voltammetry was carried out using a mini potentiostat of mark 910 MINI PSTAT controlled by a computer using software PSTAT software version 1.1. The voltammetry cell with three electrodes consists of a working electrode electrode, based on a carbon paste electrode, CPE, or a carbon paste modified electrode, CPME, the reference electrode (Ag/AgCl saturated in KCl), and an auxiliary platinum electrode. The three electrodes plunge in a solution of KCl (0.1 M) containing $K_3[Fe(CN)_6]$ at 8.10^{-3} mol/L as concentration. Sweeping was carried out in the range of going potential from −0.3 to 0.7 V with a scanning rate of 50 mV/s. The diagnosis of the fast character, quasi-fast, or slow of the system was carried out while varying the scanning rate from 0.025 to 0.150 V/s. The reducer $[Fe(CN)_6]^{3-}$ is used like probe redox in solution.

The kinetics associated with the process is usually governed by the transport of mass in film and/or by the transfer of charges at the interface [3]. In general, one distinguishes three means of transport from matter:

- The diffusion is the movement of the electro-active species caused by a gradient of concentration created following the reactions of oxidation-reduction of the species at the surface of the electrode;
- The migration is the movement of the species caused by a gradient of the potential applied to the electrode;
- Convection is the movement of the species in solution caused by mechanical forces.

According to the kinetics of the transfer of charge at the electrode, a given system can appear fast (reversible), quasi-slow (quasi-reversible), or very slow (irreversible). From an experimental point of view, it is useful to record the curve's intensity-potential (voltammogram) at various scanning rates to highlight the criteria making it possible to distinguish the nature of the system. These criteria are summarized in Table 1.

Table 1. Criteria of diagnosis of a system studied by cyclic voltammetry.

Fast system (reversible)	Quasi-slow system (quasi reversible)	Very slow system (irreversible)
ΔEp = Epa−Epc = 59/n (mV at 25 °C) is independent of ν	ΔEp = Epa−Epc is higher than 59/n (mV at 25 °C) and increases with ν	ΔEp = Epa−Epc increases with ν ; Ep-Ep/2 = 47.7/αn
Epa and Epc are independent of ν	Epc moves towards the negative values when ν increases	Epa and Epc are related to ν
Ipa/Ipc = 1	Ipa/Ipc = 1 for α = 0,5	Ipa/Ipc ≠ 1 or not of return
Ipa and Ipc vary with $\nu^{1/2}$	Ip increases with ν, but is not proportional to $\nu^{1/2}$	Ip varies with $\nu^{1/2}$

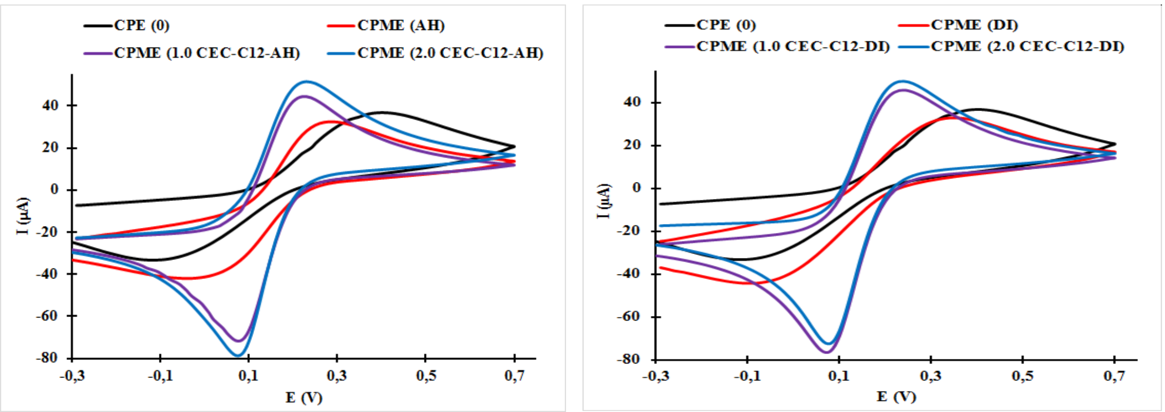
ν indicates the scanning rate of the cyclic voltammetry.

3. Results and Discussion

3.1. Effect of Surfactant Loading on the Cyclic Voltammogram Response of the Carbon Paste Electrode and Carbon Paste Modified Electrodes

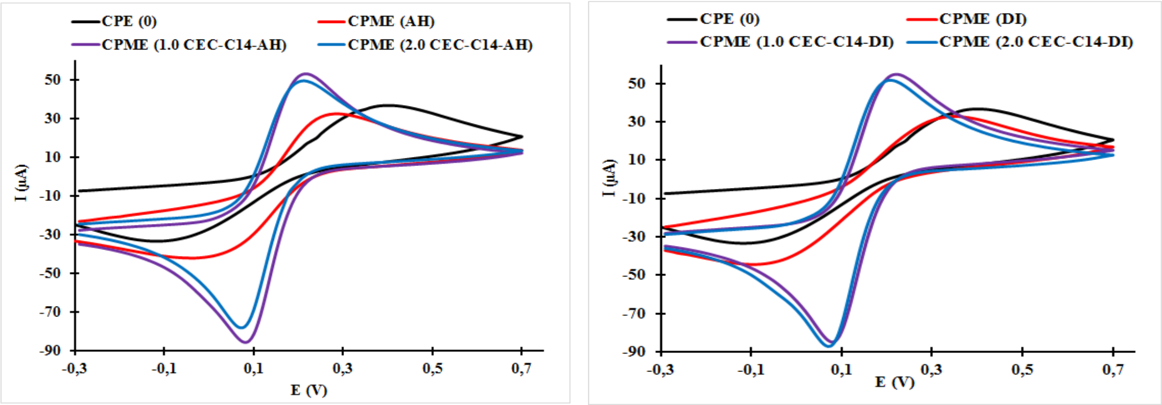
The electrochemical behaviors of the carbon paste electrode (CPE) and those of the carbon paste modified electrode (CPME), with AH and DI raw clays or organoclays (C_{12}-AH, C_{12}-DI, C_{14}-AH, C_{14}-DI, and C_{16}-AH, C_{16}-DI) as modifiers, was studied by cyclic voltammetry using the reducer $[Fe(CN)_6]^{3-}$ like probe redox in solution.

Figures 1–3 represent the cyclic voltammograms of the carbon paste electrode (CPE) and those of the carbon paste modified electrodes (CPME). Figures 1–3 show that the intensities of the two anodic and cathodic peaks do not increase when the carbon paste is modified with the raw clays (AH or DI), but increase when the carbon paste is modified with the organoclays [20,21]. This increase in the intensity of the current with the scan rate indicates an improvement in the surface conductivity of the organoclays modified carbon paste electrodes. This improvement of surface conductivity could be related to the presence of cationic surfactants in the organoclays used as modifiers of the carbon paste electrode, thus causing an improvement in the process of electron transfer [9,22]. It is also noted that the two anodic and cathodic peaks are better defined in the case of the organoclays modified carbon paste electrodes than in the case of the raw clays modified carbon paste electrodes. This result suggests that favorable chemical interactions occur between the organoclays present in the CPME and the probe ($[Fe(CN)_6]^{3-}$) in solution [9,22]. Figures 1–3 also indicate that the magnitudes of the peaks in the voltammograms obtained with ($[Fe(CN)_6]^{3-}$) are influenced by the amount of the surfactant loading into the modifier and this result is similar to those reported by Ngameni et al. 2006 [4].



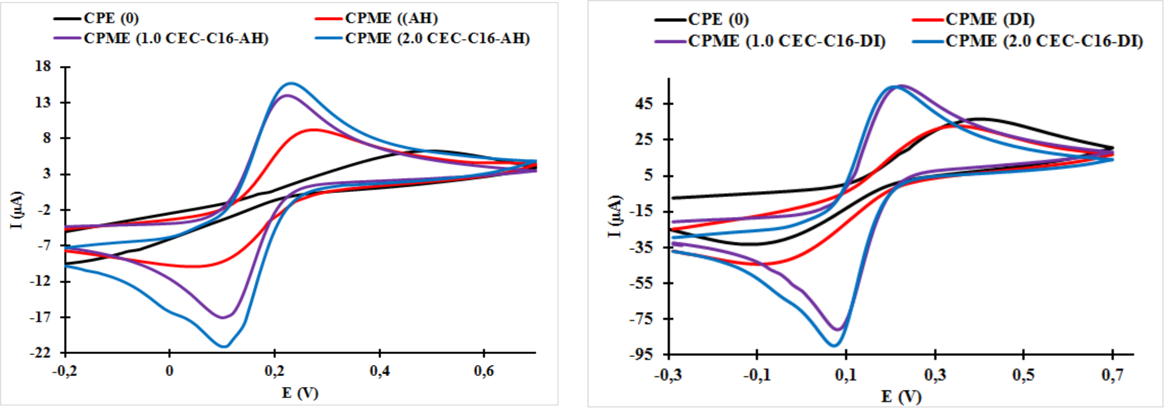
(**a**) (**b**)

Figure 1. Cyclic voltammogram of the CPE and CPME (a: with AH raw clay and C_{12}-AH organoclays; b: with DI raw clay and C_{12}-DI organoclays). Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; Ag/AgCl reference electrode saturated with KCl 0.1 mol/L; scanning rate ν=50 mV/s.



(**a**) (**b**)

Figure 2. Cyclic voltammogram of the CPE and CPME (a: with AH raw clay and C_{14}-AH organoclays; b:with DI raw clay and C_{14}-DI organoclays). Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; Ag/AgCl reference electrode saturated with KCl 0.1 mol/L; scanning rate ν=50 mV/s.



(**a**) (**b**)

Figure 3. Cyclic voltammogram of the CPE and CPME (a: with AH raw clay and C_{16}-AH organoclays; b: with DI raw clay and C_{16}-DI organoclays). Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=50 mV/s.

The difference in potential between the anodic and cathodic peaks (ΔEp) is 330 mV for the carbon paste electrode (CPE). For the CPME with raw clays, CPME (AH) and CPME (DI), the potential difference between the anodic and cathodic peaks is 520 mV. When the CPME is based on organoclays~~,~~ the potential difference (ΔEp) is ranged from 140 to 170 mV, therefore lower than those of the CPE and the CPME with raw clays, which indicates an easy electron transfer process on the surface of the CPME with organoclays [9,22]. These results indicate a modification of the surface properties of clays after intercalation of the cationic surfactants into the clays interlayers, as seen in the increase of the d_{001} basal spacing of the organoclays [15].

For the CPE the potentials of oxidation and reduction are 0.29 V and −0.04 V, respectively, and for the CPME based on raw clays, the potentials of oxidation are 0.35 V and 0.40 V and those of reduction are −0.10 V and −0.12 V, for CPME (AH) and CPME (DI), respectively. In the case of CPME with organoclays, the potential of oxidation are ranged from 0.21V to 0.24 V and the potential of reduction are ranged from 0.07V to 0.08V. Experimental data drawn from the cyclic voltammograms of the CPE and CPME (with raw clays and organoclays) are summarized in Table 2. The current of the two peaks increased from 32 and −42 µA for CPE to values ranging from 44 to 55 µA and −71 to −89 µA for the CPME with organoclays (Table 2).

Table 2. Experimental data drawn from the cyclic voltammograms of the CPE and CPME (with raw clays and organoclays). Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; Ag/AgCl reference electrode saturated with KCl 0.1 mol/L; scanning rate 50 mV/s.

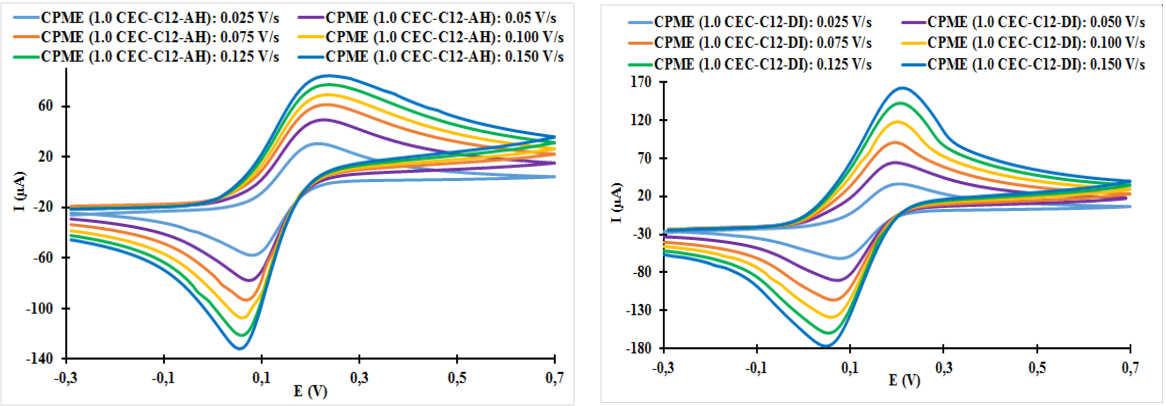
Electrodes	Epa (V)	Epc (V)	ΔE (mV)	I_{pa} (µA)	I_{pc} (µA)	$\lvert I_{pa}/I_{pc}\rvert$
CPE (0)	0.29	−0.04	330	32.43	−42.0	0.772
CPME (DI)	0.35	−0.10	520	32.86	−44.34	0.741
CPME (AH)	0.40	−0.12	520	36.78	−33.28	1.105
CPME (1.0 CEC-C_{12}-AH)	0.23	0.08	150	44.37	−71.63	0.620
CPME (2.0 CEC-C_{12}-AH)	0.23	0.07	160	51.49	−78.54	0.656
CPME (1.0 CEC-C_{12}-DI)	0.24	0.07	170	53.04	−85.49	0.620
CPME (2.0 CEC-C_{12}-DI)	0.24	0.08	160	51.49	−78.53	0.656
CPME (1.0 CEC-C_{14}-AH)	0.22	0.08	140	45.78	−76.61	0.598
CPME (2.0 CEC-C_{14}-AH)	0.21	0.07	140	49.92	−72.42	0.689
CPME (1.0 CEC-C_{14}-DI)	0.22	0.08	140	53.04	−85.49	0.620
CPME (2.0 CEC-C_{14}-DI)	0.21	0.07	140	49.45	−77.98	0.634
CPME (1.0 CEC-C_{16}-AH)	0.22	0.08	140	54.85	−84.81	0.647
CPME (2.0 CEC-C_{16}-AH)	0.21	0.07	140	51.74	−87.09	0.594
CPME (1.0 CEC-C_{16}-DI)	0.22	0.08	140	53.88	−89.03	0.605
CPME (2.0 CEC-C_{16}-DI)	0.21	0.07	140	55.41	−87.02	0.637

3.2. Diagnosis of the Fast, Quasi Fast or Slow Character of the System $\boldsymbol{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}}$ *on the CPE or CPME*

The diagnosis of the fast, quasi-fast, or slow characters of the system was carried out by varying the scanning rate from 0.025 to 0.150 V/s in the range of potential from -0.3 to 0.7 V.

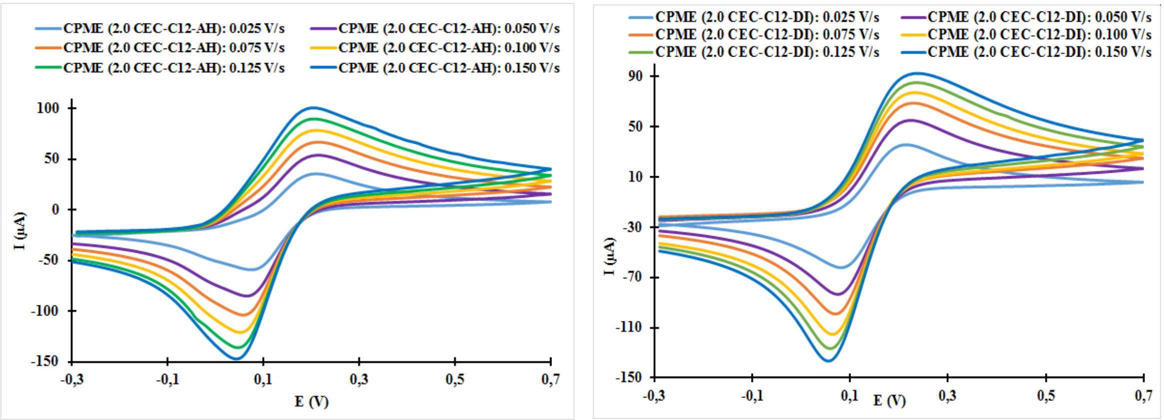
3.2.1. Effect of Scanning Rate on the Cyclic Voltammetry Response of Organoclays Modified Carbon Paste Electrode (CPME)

Figures 4–9 represent the cyclic voltammograms of carbon paste modified electrode (CPME), based on organoclays, at different scanning rates ranging from 0.025 to 0.150 V/s and a range of potential from −0.3 to 0.7 V. Successive sweeping, for scanning rate going from 0.025 to 0.150 V/s, always produces similar voltammograms, which indicates that the system is stable under the experimental conditions (Figures 4–9). It is also observed that both the anodic and cathodic currents intensities increase with increasing the scanning rate and this result is similar to those reported previously [7,14,20,21].



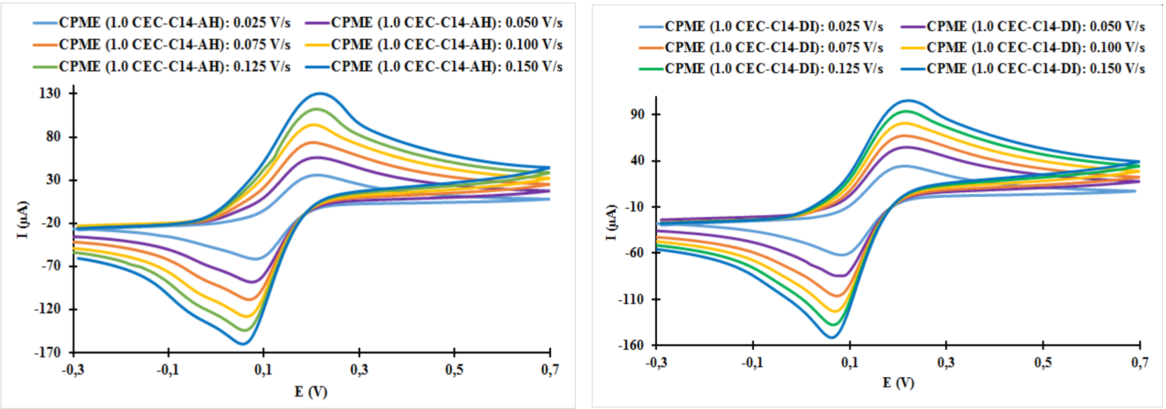
(**a**) (**b**)

Figure 4. Cyclic voltammogram of CPME modified (a: with 1.0 CEC-C$_{12}$-AH and b: with 1.0 CEC-C$_{12}$-DI). Electrolyte KCl support 0.1 mol/L containing ([Fe(CN)$_6$]$^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



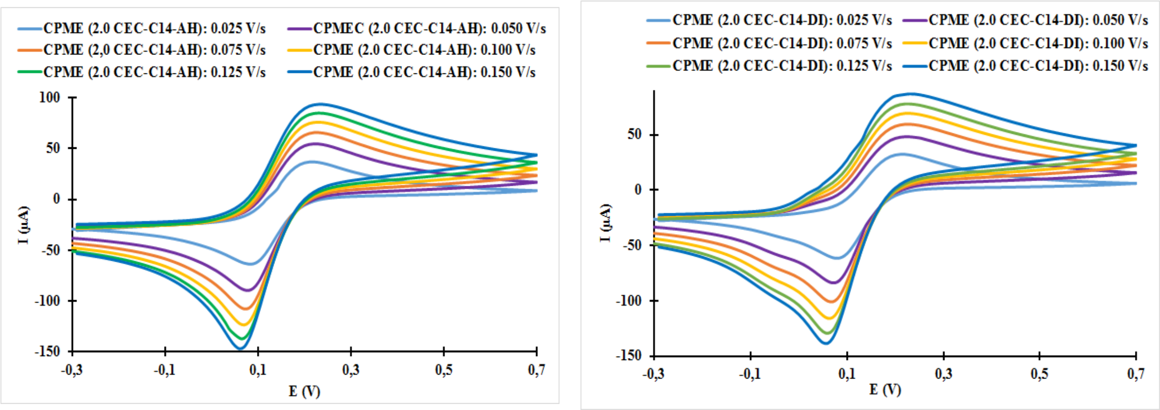
(**a**) (**b**)

Figure 5. Cyclic voltammogram of CPME modified (a: with 2.0 CEC-C$_{12}$-AH and b: with 2.0 CEC-C$_{12}$-DI). Electrolyte KCl support 0.1 mol/L containing ([Fe(CN)$_6$]$^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



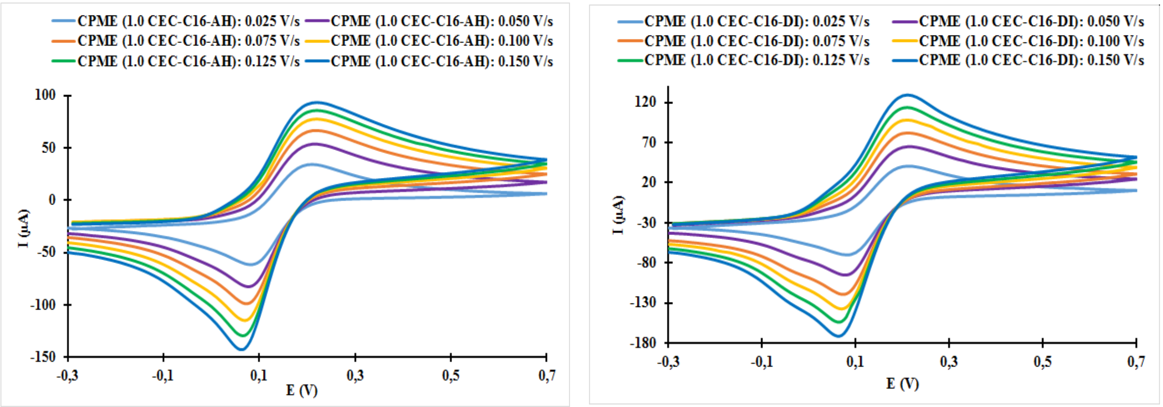
(**a**) (**b**)

Figure 6. Cyclic voltammogram of CPME modified (a: with 1.0 CEC-C$_{14}$-AH and b: with 1.0 CEC-C$_{14}$-DI). Electrolyte KCl support 0.1 mol/L containing ([Fe(CN)$_6$]$^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



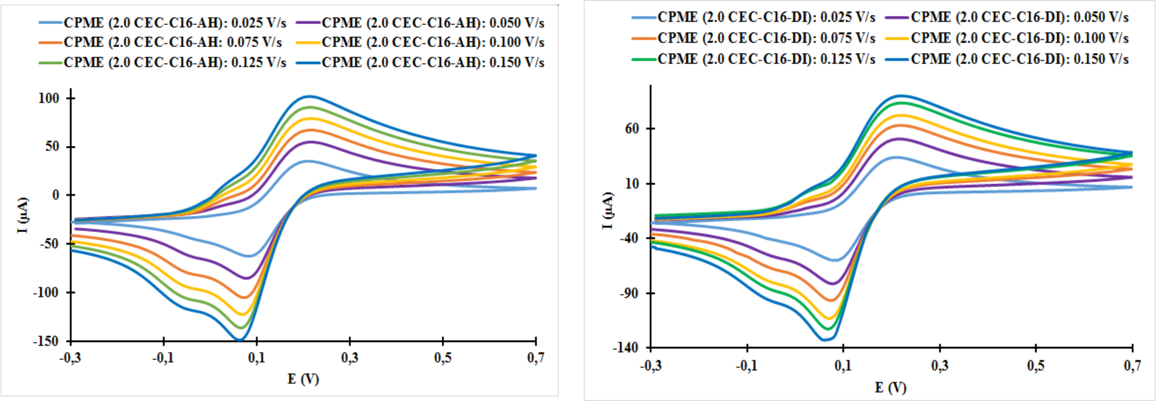
(**a**) (**b**)

Figure 7. Cyclic voltammogram of the CPE and CPME modified (a: with 2.0 CEC-C$_{14}$-AH and b: with 2.0 CEC-C$_{14}$-DI). Electrolyte support KCl 0.1 mol/L containing ([Fe(CN)$_6$]$^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



(**a**) (**b**)

Figure 8. Cyclic voltammogram of CPME modified (a: with 1.0 CEC-C$_{16}$-AH and b: with 1.0 CEC-C$_{16}$-DI). Electrolyte support KCl 0.1 mol/L containing ([Fe(CN)$_6$]$^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



(**a**) (**b**)

Figure 9. Cyclic voltammogram of the CPE and CPME (a: with 2.0 CEC-C$_{16}$-AH and b: 2.0 CEC-C$_{16}$-DI). Electrolyte support KCl 0.1 mol/L containing ([Fe(CN)$_6$]$^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.

Table 3 recapitulates the experimental data drawn from the cyclic voltammograms of electrodes based on carbon paste modified with organoclays, for variable scanning rates ranging from 0.025 to 0.150 V/s. Table 3 shows that the value of ΔEp = Epa-Epc increases with the scanning rate (ν) and the values of the potentials Epa and Epc are related to the variation of ν, which indicates that the system is slow.

Table 3. Experimental data drawn from the cyclic voltammograms of the CPE modified with 1.0 CEC-C_{12}-AH and 2.0 CEC-C_{12}-DI. Electrolyte support KCl 0.1 mol/L containing $[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; Ag/AgCl reference electrode saturated with KCl 0,1 mol/L; scanning rate ν=25-150 mV/s.

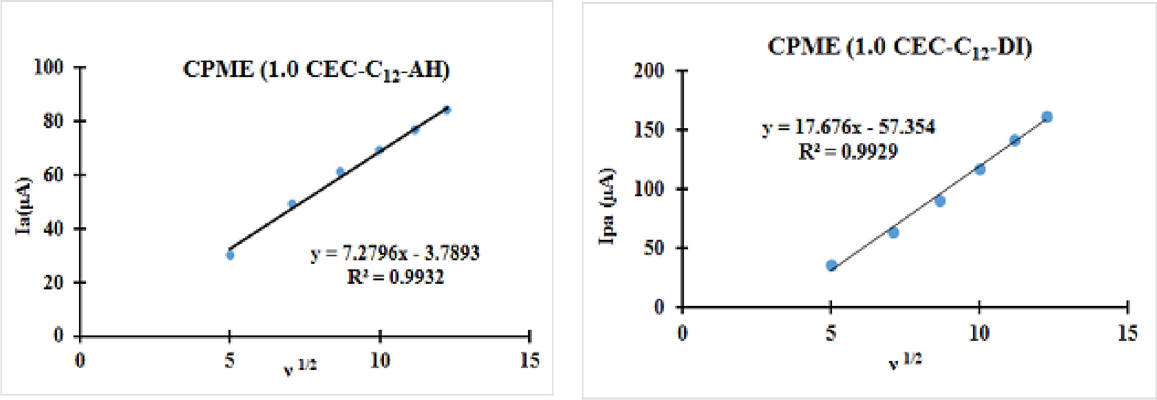
Electrodes	ν (V/s)	Epa (V)	Epc (V)	ΔE (mV)	$\|I_{pa}/I_{pc}\|$
CPME (1.0 CEC-C_{12}-AH)	0.025	0.22	0.08	140	0.82
CPME (1.0 CEC-C_{12}-AH)	0.050	0.23	0.08	150	0.74
CPME (1.0 CEC-C_{12}-AH)	0.075	0.23	0.07	160	0.67
CPME (1.0 CEC-C_{12}-AH)	0.100	0.24	0.06	180	0.64
CPME (1.0 CEC-C_{12}-AH)	0.125	0.24	0.06	180	0.65
CPME (1.0 CEC-C_{12}-AH)	0.150	0.24	0.06	180	0.65
CPME (1.0 CEC-C_{12}-DI)	0.025	0.20	0.08	120	0.92
CPME (1.0 CEC-C_{12}- DI)	0.050	0.20	0.07	130	0.89
CPME (1.0 CEC-C_{12}- DI)	0.075	0.20	0.06	140	0.85
CPME (1.0 CEC-C_{12}- DI)	0.100	0.20	0.06	140	0.78
CPME (1.0 CEC-C_{12}- DI)	0.125	0.21	0.05	150	0.71
CPME (1.0 CEC-C_{12}- DI)	0.150	0.21	0.05	150	0.59
CPME (2.0 CEC-C_{12}- AH)	0.025	0.21	0.07	140	0.60
CPME (2.0 CEC-C_{12}- AH)	0.050	0.21	0.07	140	0.64
CPME (2.0 CEC-C_{12}- AH)	0.075	0.21	0.06	150	0.64
CPME (2.0 CEC-C_{12}- AH)	0.100	0.21	0.05	160	0.65
CPME (2.0 CEC-C_{12}- AH)	0.125	0.20	0.05	160	0.66
CPME (2.0 CEC-C_{12}- AH)	0.150	0.21	0.04	170	0.69
CPME (2.0 CEC-C_{12}-DI)	0.025	0.21	0.08	130	0.90
CPME (2.0 CEC-C_{12}-DI)	0.050	0.23	0.07	160	0.81
CPME (2.0 CEC-C_{12}-DI)	0.075	0.22	0.07	150	0.73
CPME (2.0 CEC-C_{12}-DI)	0.100	0.23	0.06	170	0.71
CPME (2.0 CEC-C_{12}-DI)	0.125	0.24	0.06	180	0.68
CPME (2.0 CEC-C_{12}-DI)	0.150	0.24	0.06	180	0.64
CPME (1.0 CEC-C_{14}-AH)	0.025	0.21	0.08	130	0.58
CPME (1.0 CEC-C_{14}-AH)	0.050	0.21	0.07	140	0.64
CPME (1.0 CEC-C_{14}-AH)	0.075	0.20	0.07	130	0.68
CPME (1.0 CEC-C_{14}-AH)	0.100	0.20	0.06	140	0.73
CPME (1.0 CEC-C_{14}-AH)	0.125	0.22	0.06	160	0.77
CPME (1.0 CEC-C_{14}-AH)	0.150	0.22	0.06	160	0.82
CPME (1.0 CEC-C_{14}-DI)	0.025	0.21	0.08	130	0.56
CPME (1.0 CEC-C_{14}- DI)	0.050	0.22	0.07	150	0.65
CPME (1.0 CEC-C_{14}- DI)	0.075	0.21	0.07	140	0.63
CPME (1.0 CEC-C_{14}- DI)	0.100	0.21	0.07	140	0.66
CPME (1.0 CEC-C_{14}- DI)	0.125	0.22	0.07	130	0.68
CPME (1.0 CEC-C_{14}- DI)	0.150	0.22	0.06	160	0.70
CPME (2.0 CEC-C_{14}-AH)	0.025	0.21	0.08	130	0.58
CPME (2.0 CEC-C_{14}-AH)	0.050	0.22	0.08	140	0.61
CPME (2.0 CEC-C_{14}-AH)	0.075	0.23	0.07	160	0.62
CPME (2.0 CEC-C_{14}-AH)	0.100	0.23	0.07	160	0.62
CPME (2.0 CEC-C_{14}-AH)	0.125	0.23	0.07	160	0.62

CPME (2.0 CEC-C_{14}-AH)	0.150	0.23	0.06	170	0.64
CPME (2.0 CEC-C_{14}-DI)	0.025	0.21	0.08	130	0.52
CPME (2.0 CEC-C_{14}-DI)	0.050	0.22	0.07	150	0.57
CPME (2.0 CEC-C_{14}-DI)	0.075	0.23	0.06	170	0.59
CPME (2.0 CEC-C_{14}-DI)	0.100	0.23	0.06	170	0.60
CPME (2.0 CEC-C_{14}-DI)	0.125	0.23	0.06	170	0.60
CPME (2.0 CEC-C_{14}-DI)	0.150	0.23	0.06	170	0.70
CPME (1.0 CEC-C_{16}-AH)	0.025	0.21	0.08	130	0.56
CPME (1.0 CEC-C_{16}-AH)	0.050	0.22	0.08	140	0.65
CPME (1.0 CEC-C_{16}-AH)	0.075	0.22	0.07	150	0.68
CPME (1.0 CEC-C_{16}-AH)	0.100	0.22	0.07	150	0.68
CPME (1.0 CEC-C_{16}-AH)	0.125	0.22	0.07	150	0.67
CPME (1.0 CEC-C_{16}-AH)	0.150	0.22	0.06	160	0.66
CPME (1.0 CEC-C_{16}-DI)	0.025	0.21	0.08	130	0.58
CPME (1.0 CEC-C_{16}-DI)	0.050	0.21	0.08	130	0.68
CPME (1.0 CEC-C_{16}-DI)	0.075	0.21	0.07	140	0.69
CPME (1.0 CEC-C_{16}-DI)	0.100	0.21	0.07	140	0.71
CPME (1.0 CEC-C_{16}-DI)	0.125	0.21	0.06	150	0.74
CPME (1.0 CEC-C_{16}-DI)	0.150	0.21	0.06	150	0.76
CPME (2.0 CEC-C_{16}-AH)	0.025	0.21	0.08	130	057
CPME (2.0 CEC-C_{16}-AH)	0.050	0.22	0.08	120	0.65
CPME (2.0 CEC-C_{16}-AH)	0.075	0.22	0.07	150	0.64
CPME (2.0 CEC-C_{16}-AH)	0.100	0.22	0.07	150	0.65
CPME (2.0 CEC-C_{16}-AH)	0.125	0.21	0.07	140	0.67
CPME (2.0 CEC-C_{16}-AH)	0.150	0.21	0.06	150	0.69
CPME (2.0 CEC-C_{16}-DI)	0.025	0.21	0.08	130	0.57
CPME (2.0 CEC-C_{16}-DI)	0.050	0.22	0.08	140	0.63
CPME (2.0 CEC-C_{16}-DI)	0.075	0.22	0.07	150	0.66
CPME (2.0 CEC-C_{16}-DI)	0.100	0.22	0.07	150	0.64
CPME (2.0 CEC-C_{16}-DI)	0.125	0.22	0.07	150	0.68
CPME (2.0 CEC-C_{16}-DI)	0.150	0.22	0.06	160	0.68

The $|I_{pa}/I_{pc}|$ ratios are different from 1 (Tables 2 and 3), confirming well that the system is slow. The difference between Ipa and Ipc values could also be explained by the modification of the surface properties due to various phenomena which occur on the surface of the organoclays modified carbon paste electrodes [9,22].

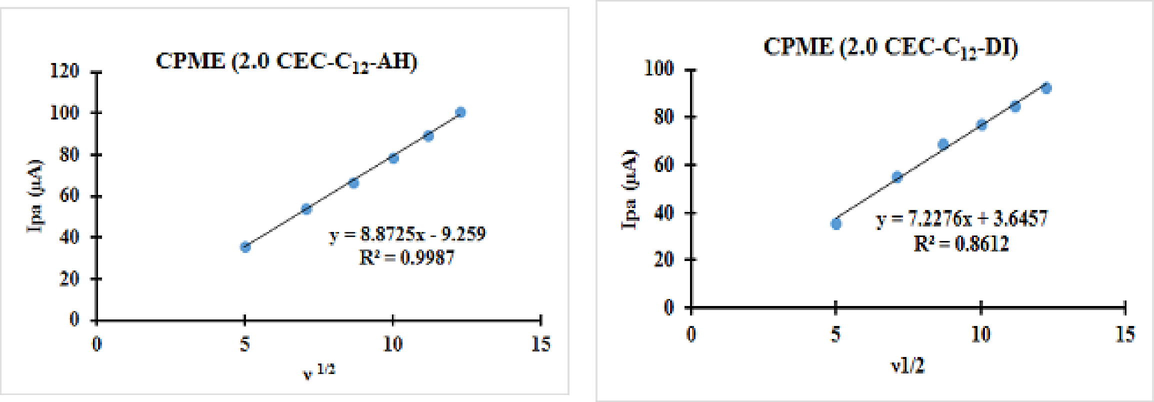
3.2.2. Relationships between the Scanning Rate and the Anodic Peak Intensity

Figures 10–15 represent the curve of Ipa = $f(\nu^{1/2})$ for the organoclays modified carbon paste electrodes.



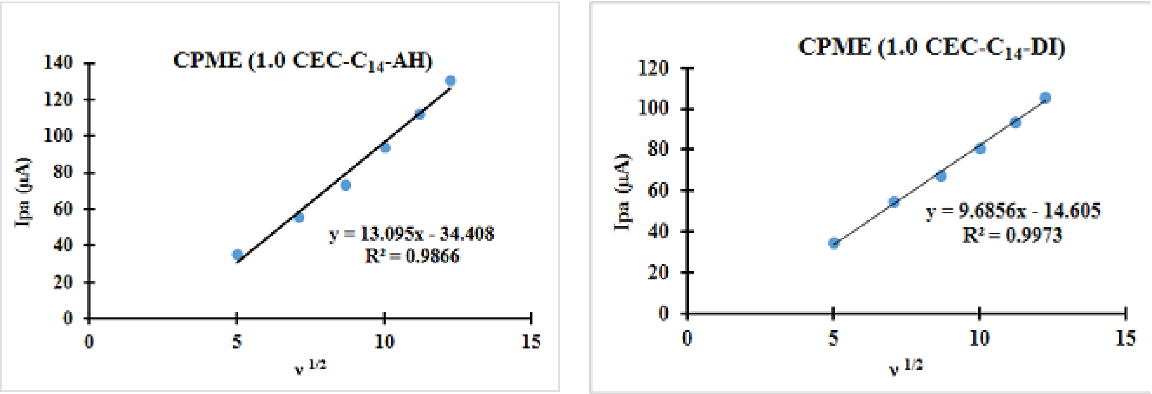
(**a**) (**b**)

Figure 10. Curve of $I_{pa} = f(v^{1/2})$ of CPEM modified with a: 1.0 CEC-C_{12}-AH; b: 1.0 CEC-C_{12}-DI. Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0,1 mol/L; scanning rate ν=25-150 mV/s.



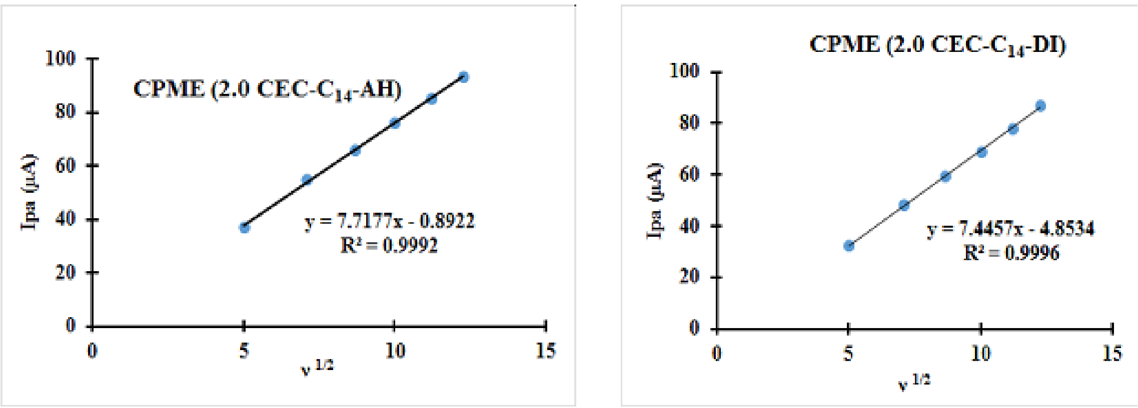
(**a**) (**b**)

Figure 11. Curve of $I_{pa} = f(v^{1/2})$) of CPEM modified with a: 2.0 CEC-C_{12}-AH; b: 2.0 CEC-C_{12}-DI. Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0,1 mol/L; scanning rate ν=25-150 mV/s.



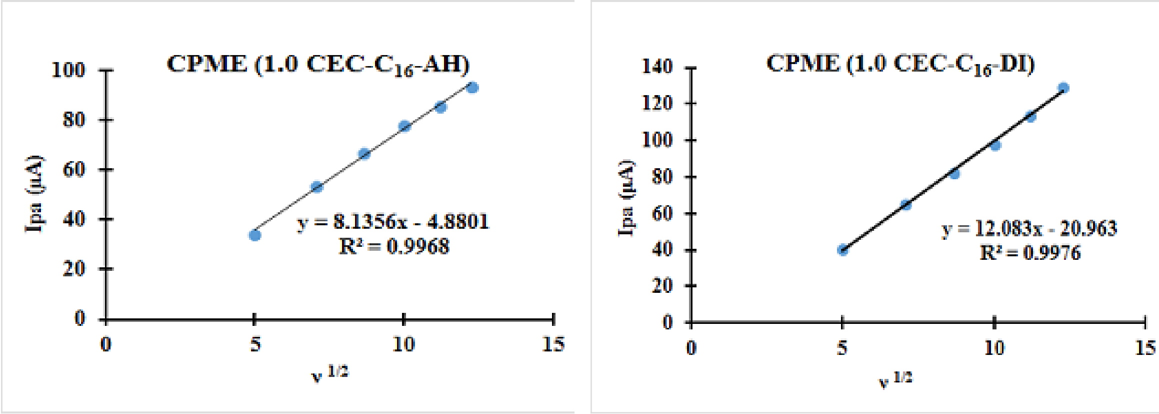
(**a**) (**b**)

Figure 12. Curve of $I_{pa} = f(v^{1/2})$ of CPEM modified with: a: 1.0 CEC-C_{14}-AH; b: 1.0 CEC-C_{14}-DI. Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



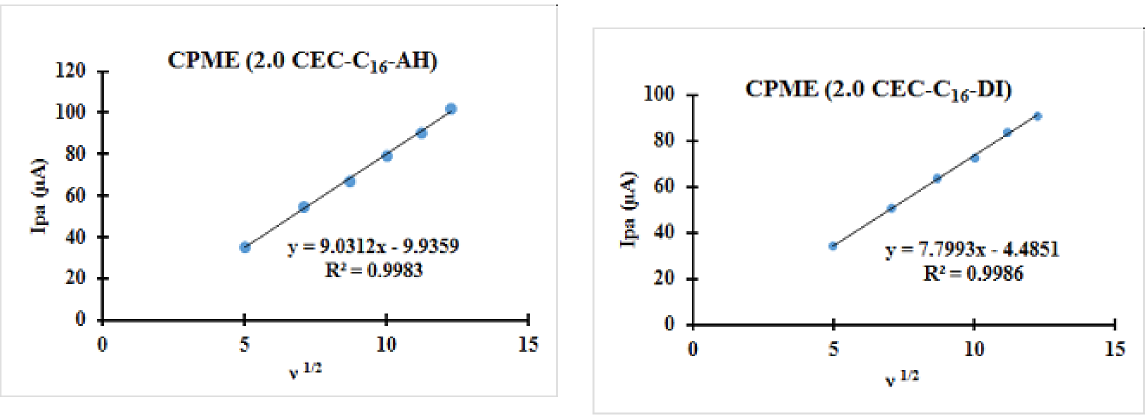
(a) (b)

Figure 13. Curve of $I_{pa} = f(\nu^{1/2})$ of CPEM modified with a: 2.0 CEC-C$_{14}$-AH; b: 2.0 CEC-C$_{14}$-DI. Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



(a) (b)

Figure 14. Curve of $I_{pa} = f(\nu^{1/2})$ of CPEM modified with: a: 1.0 CEC-C$_{16}$-AH; b: 1.0 CEC-C$_{16}$-DI). Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.



(a) (b)

Figure 15. Curve of $I_{pa} = f(\nu^{1/2})$ of CPEM modified with: a: 2.0 CEC-C$_{16}$-AH; b: 2.0 CEC-C16-DI. Electrolyte KCl support 0.1 mol/L containing ($[Fe(CN)_6]^{3-}$) 8.0 10^{-3} mol/L; electrode of Ag/AgCl reference saturated with KCl 0.1 mol/L; scanning rate ν=25-150 mV/s.

The curves Ipa = f($\nu^{1/2}$) of the CPME based on organoclays show a linear variation (R^2>0.99, except in the case of *2.0 CEC-C₁₂-DI and 1.0 CEC-C₁₄-AH*) of the anodic peak current intensity as a function of $\nu^{1/2}$, indicating that the electrochemical reaction is controlled by a process of diffusion (Figures 10–15).

Falaras and Petridis [10] reported the increase of Ipa with both the scan rates and the square root of scan rates for the cyclic voltametry response of the electrochemical probe $[Fe(CN)_6]^{3-}$ at the organoclay modified carbon paste interface; the organoclayclay was obtained by soaking the clay in 10^{-2} mol.L^{-1} cetyltrimethylammonium bromide (C_{16}) aqueous solution. Ranđelović et al. [23] have studied the electrocatalitic behaviour of serpentinite modified carbon paste electrode and reported that Ipa increased with increasing potential scan rate and varied linearly with the square root of the scan rates ($\nu^{1/2}$). From the literature, it is known that linear increase of the anodic peak current intensity (Ipa) with the square root of the potential scan rates sustains that the electron transfer is controlled by the diffusion of the electroactive species onto the electrode surface [14,21,23–25]. Since the results obtained in the present work indicate a linear relationships between the anodic peak current intensity and the square root of the scan rates, it is then suggested that the electrochemical reaction of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ onto the CPME is under diffusion control.

4. Conclusion

The present work has showed that cyclic voltammetry can be used to characterize surfactants modified smectite clays by studying the response of the electrochemical probe, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, on the carbon paste electrode modified with organoclays, which were prepared via solid-state intercalation of cationic surfactants. The results showed that the intensities of the anodic and cathodic peaks didn't increase when the working electrode was based on carbon paste modified with the raw clays (AH or DI), whereas the intensities of the peaks increased significantly when the working electrode consisted of carbon paste modified with organoclays. This increase in the intensity of the current indicated an improvement of the surface conductivity of the carbon paste electrode when they are modified with organoclays and this is certainly due to the intercalation of the cationic surfactants. The experimental data obtained in the present work gave evidence of the strong interaction of the organoclays with the electrochemical probe, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, in the same way as the ones prepared via liquid-state intercalation.

Author Contributions: Conceptualization, I.G. and B.G.; methodology, I.G. and B.G.; software, I.G., and B.G. ; validation, I.G. and B.G.; formal analysis, I.G., and B.G.; investigation, I.G. and B.G.; resources, I.G. and B.G.; data curation, I.G.; writing—original draft preparation, I.G.; writing—review and editing, I.G. and B.G.; visualization, B.G.; supervision, B.G.; project administration, B.G.; funding acquisition, B.G. All authors have read and agreed to the published version of the manuscript.

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