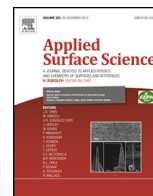




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Structural characterization of hexadecyltrimethylammonium-smectite composites and their potentiometric electrode applications

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ABSTRACT

Organosmectites were prepared by the intercalation of hexadecyltrimethylammonium cations at various ratios into interlayer of Unye smectite. Structural, thermal, morphological and textural properties of the synthesized organosmectites were characterized. Afterwards, a novel potentiometric PVC-membrane thiocyanate selective electrode was prepared based on the obtained hexadecyltrimethylammonium modified smectites as electroactive material. The basal spacing values of organosmectites were observed in the range of 15.61 and 35.50 Å. Powder X-ray diffraction data show that the surfactant cations penetrated into the smectite layers with different molecular arrangements. Modification of smectite with hexadecyltrimethylammonium led to appreciable decreases in the intensities of the FTIR bands at 3402 and 1635 cm⁻¹ and the new characteristic vibrational bands at 2927, 2850, 1472 and 722 cm⁻¹ originating from the surfactant molecules appeared. The thermal analysis data showed that the decomposition of surfactant species occurred in the temperature range of 170–720 °C and the amount of dehydrated water gradually decreased with the increase in surfactant amount. The intercalation of surfactant species within the gallery spacing led gradually to smaller surface areas. In addition, the electrophoretic mobility values indicate that excess surfactant loadings also generate positive charges on the organosmectite surfaces. The most convenient membrane composition resulting in the best potentiometric performance was investigated. The optimum membrane composition was determined to have 20.0% (w/w) 2.5CEC.HDTMA-smectite, 26.0% (w/w) PVC, 54.0% (w/w) DBP. The fabricated electrode exhibited a linear response over the thiocyanate concentration range of 1.0 × 10⁻⁴–1.0 × 10⁻¹ M ($R^2 = 0.9996$) with a slope of -48.6 mV/decade. The detection limit, response time and pH working range were determined as 4.3 × 10⁻⁵ M, ~10 s and 4–8, respectively. The proposed electrode exhibited selective potentiometric response to thiocyanate comparable to most of the common anions.

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1. Introduction

Clay minerals have been widely used as adsorbent, ion exchanger, additive, rheological control agent and catalyst in many fields of industry because of their strong adsorption ability, high surface area, porosity, high cation exchange capacity, hydration and perfect swelling (only for smectites) properties [1–10]. However, the surface chemistry and structural properties of natural clay minerals limit their further potential applications in various

industrial areas. Therefore, in the past decades, numerous studies have been done related to modification of clays by using various methods [11–16]. The organophilization process which leads to the formation of a class of new material known as organoclays is commonly used for modifying the interlayer structure and surface properties of clay minerals [17–21]. Organoclays are prepared by adsorption of organic reagents such as cationic, anionic, non-ionic and amphoteric surfactants with various types and sizes [22–26]. The adsorption of organic cations primarily takes places by the replacement of inorganic cations in the clay with the organic cations, but in the presence of excess organic cations secondary adsorption of organic cations may occur by hydrophobic interactions inside the interlayer or on the smectite external surface [27].

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Clay particles, with anionic charges at the plate surfaces and pH-dependent charges at the edges, have a negative net charge [28,29]. The penetration of cationic surfactants not only changes the surface properties from hydrophilic to hydrophobic but also may change the charge of the raw clay layer from negative to positive if the excess of organic cations available [30–33].

Due to the improved structural and surface properties, organoclays have been widely utilized in environmental purifications, antibacterial paints, rheological control agents, biomaterials, precursors for synthesis of polymer–clay nanocomposites, catalysis, membranes, electric materials, foundry, drilling muds and nanocomposites fields as selective adsorbent, ion-exchanger, reinforcing filler and catalyst [34–57]. In addition, preparations of clay modified electrodes have been recently gaining importance in electrochemical sensor and biosensor developments [58–64]. Potentiometric detections performed by using ion-selective electrodes (ISEs) are frequently used popular analysis techniques owing to their many advantages, such as convenient selectivity, lower detection limit, wide working range, high accuracy and precision, fast response, simple measurement process, simple design, low price, no irreversible effect on the tested material, no prior separation, from the matrix and feasible use in colored and turbid samples [65,66]. Some studies and reviews related to clay modified electrodes in voltammetric applications have been performed [67–70]. There appear a few potentiometric studies related to surfactant modified zeolites [71,72]. Organo-modified smectites may be considered as a potential electroactive material in potentiometric electrode application due to the anion exchanger properties. However, there seemed to be no potentiometric electrode study based on organo-modified smectites.

In the present study, initially, the structural properties of raw Unye smectite and hexadecyltrimethylammonium bromide (HDTMABr) modified smectites prepared with the treatments of surfactant at various ratios were characterized by using powder X-ray diffraction (PXRD), attenuated total reflection Fourier transform infrared (ATR-FTIR), thermogravimetry-derivative thermogravimetry (TG-DTG) and differential thermal (DTA) analyses, scanning electron microscopy (SEM), electrophoretic mobility measurement and surface area measurement techniques. Afterwards, potentiometric characteristics of the synthesized HDTMA-modified smectites were investigated by using them as electroactive material in the constructions of novel PVC membrane anion-selective electrodes.

2. Experimental

2.1. Materials

The clay used as the starting material in the preparation of organosmectite samples was Unye bentonite which is an important mineral resource in Turkey. Unye bentonite was crushed into small particles and mechanically ground. The non-clay impurity fractions were removed by decantation with deionized water. It was purified by conventional sedimentation method and dried at 90 °C. Then, the sample was ground through 200 mesh sieve and sealed in a glass tube for use. 15 g of the dried raw smectite (RS) was converted to Na-smectite (Na-S) by treating three times with 1000 mL of 0.1 M NaCl solution at room temperature, each one is overnight [11,12]. The obtained Na-smectite was washed with deionized water thoroughly and AgNO₃ test was applied to the filtrate. The solid product (Na-S) which was dried at 105 °C was ground to 200 mesh. The CEC value of Na-S was determined as 79 mequiv./100 g clay by methylene blue adsorption techniques [73]. This method is complicated by the dimerization of methylene blue when the concentration exceeds about 7×10^{-6} mol L⁻¹ [74–76]. The present experiments

were conducted at lower concentration than this limit value in only the presence of monomers.

Membrane solvent; tetrahydrofuran (THF) and membrane components; high molecular weight poly(vinylchloride) (PVC), o-nitrophenyloctyl ether (NPOE), dibutyl phthalate (DBP), dioctyl phthalate (DOP), bis(2-ethylhexyl) sebacate (DOS) and potassium tetrakis(4-chlorophenyl)borate (KTCIPB) were all purchased from Sigma–Aldrich (Bucks, Switzerland).

All chemicals and sodium salts of the anions used in selectivity studies were in analytical grade and purchased from Sigma–Aldrich.

2.2. The preparation of the HDTMA-smectite materials

2 g Na-S for each HDTMA-smectite sample was firstly dispersed in 100 mL deionized-water by magnetic stirrer for 24 h at room temperature. Simultaneously, certain amounts of HDTMABr in the concentration range of 0.5–3.0 CEC for each of six samples were dissolved in 200 mL deionized-water and then stirred for 1 h at 70 °C. The HDTMA solutions were slowly added drop wise into the suspensions of the Na-S and the mixtures were stirred slightly to prevent foaming at 80 °C for about 15 h. The organosmectite solids were separated by centrifugation at 10,000 rpm and washed thoroughly with deionized water several times and then dried at 60 °C overnight. The resultant organosmectites were labeled as 0.5CEC.HDTMA-S, 1.0CEC.HDTMA-S, 1.5CEC.HDTMA-S, 2.0CEC.HDTMA-S, 2.5CEC.HDTMA-S and 3.0CEC.HDTMA-S according to HDTMA/CEC mass ratio.

The PXRD patterns were taken at ambient temperatures on a PANalytical Empyrean diffractometer using Ni filtered CuK_α radiation ($\lambda = 1.54050$ Å; 45 kV and 40 mA; step size: 0.026(2 θ); scan step time: 296.565 s; sample preparation: top fill). The ATR-FTIR spectra of the samples were recorded on Thermo Nicolet 6700 spectrophotometer in the region 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. The powder sample was placed on the diamond crystal and pressed with a micrometer-controlled compression clamp. The TG and DTA curves were scanned using a PYRIS Diamond TG/DTG apparatus in a dynamic air atmosphere (heating rate: 10 °C min⁻¹, platinum crucibles, mass ~10 mg and temperature range: 30–1100 °C). Calcinated α -alumina was taken as the reference. SEM observations were carried out utilizing the Zeiss EVO LS 10 instrument. Nano-ZSP (Malvern, UK) zeta potential analyzer was utilized to measure the electrophoretic mobility of the RS, Na-S and organosmectites at room temperature and various pH values (2–12). At least five measurements were recorded for each sample and then average values taken. Nitrogen adsorption/desorption isotherms were measured at 77 K (–196 °C) with a Quantachrome Autosorb-IQ-2 analyzer (Florida, USA). The samples were degassed in vacuum at 120 °C for 6 h prior to the measurements at 77 K. Specific surface areas (S^{BET}) were calculated applying the Brunauer–Emmett–Teller (BET) method to the adsorption data in the relative pressure (P/P_0) range 0.05–0.35. The micropore surface area (tS^{MP}) and micropore volume (tV^{MP}) were calculated by *t*-plot analysis. Mesopore surface areas ($B_{BJH}S^{MP}$) and volumes ($B_{BJH}V^{MP}$) were determined using the BJH method.

2.3. Potentiometric measurements and measurement cell

The potentiometric measurements were conducted by using a laboratory-made computer-controlled high-input impedance potentiometric measurement system. The system has a home-made software program to monitor dynamic response of the electrode. Throughout the measurements, saturated calomel electrode (Gamry) was used as reference electrode. Ag/AgCl was also used as internal reference electrode (Gamry).

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