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FTIR and zeta potential measurements of sepiolite treated with some organosilanes

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Abstract

Sepiolite has been treated with some organosilanes including dimethyloctadecylchlorosilane (DMODCS), dimethyldichlorosilane (DMDCS), and 3-aminopropyltriethoxysilane (3-APT). FTIR measurements have been used to discuss the interactions between sepiolite surface and organosilane molecules. The disappearance of OH stretching peaks of sepiolite has shown the strong interactions between the surface and organosilane molecules. H-bonds have also been indicated by the frequency shifts of OH stretching vibrations. The changes in the electrokinetic properties of the treated sepiolite samples have been investigated by following the zeta potential of the particles as a function of pH. The treatment of sepiolite with 3-APT causes a shift of isoelectronic point (IEP) from 7.8 to 9.7, to a more basic value compared to sepiolite itself. DMODCS and DMDCS-treated sepiolite samples have, however, been found to have isoelectronic points in more acidic region than that of sepiolite, which are 5.2 and 5.6, respectively.
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1. Introduction

Sepiolite is a natural hydrated magnesium silicate clay mineral with $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4 \cdot 8H_2O$ as unit cell formula and structurally formed by an alternation of blocks and tunnels that grow up in the fiber direction (*c*-axis) [1]. Each structural block is composed of two tetrahedral silica sheets and a central octahedral sheet containing magnesium. Due to the discontinuity of the external silica sheet a significant number of silanol (Si–OH) groups are present at the surface of this mineral. The clay mineral sepiolite is currently widely used as a raw material due to its powerful sorbent properties: its ability to adsorb organic species of a different nature, neutral molecules and organic cations [2].

Recently the modification of solid surfaces in order to improve their surface properties has increasingly gained great importance. Aue et al. [3] studied the modification of silica gel in order to improve its chromatographic properties. The hydrothermal treatment and covering the surface by a nonextractable polymer layer were achieved. The adsorption of polymers, including nonionic polymers, leads to changes in the surface electrical properties of suspensions. The adsorption of copolymers of poly(acrylamide) grafted to poly(vinyl alcohol) on a silica surface from aqueous solutions has been investigated [4]. Bouhamed et al. investigated the adsorption of brush copolymers, 2-acrylamido-2-methylpropane-sulfonic acid sodium salt and methoxypolyethyleneglycol methacrylate, on to alumina particles suspended in water. Changes in the electrokinetic properties of the alumina particles after addition of the copolymers were investigated by following the zeta potential of the particles as a function of pH. In the presence of the copolymer, a continuous shift of the isoelectric point (IEP) to

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more acidic values was observed [5]. Prado and Airoldi [6] developed a route for the immobilization of 2,4-dichlorophenoxyacetic acids on silica by modifying the surface with 3-(trimethoxysilyl) propylamine previously.

Silanes have an important role in the fast-growing field of advanced materials. Silanes act as adhesion promoters, coupling agents as well as surface primers. Much work has been performed to gain insight into the mechanisms, which are responsible for the enhanced properties induced by these compounds [7]. Immobilization of organosilane reagents on inorganic oxide surfaces is finding widespread application in a broad field of today's science and technology. Some examples are chromatography, immobilization of enzymes, the modification of electrodes, coatings and catalysis [8]. Organosilanes are effective agents for the modification of surfaces of catalyst supports, especially by rendering the surface less hydrophilic by removing or modifying the surface hydroxyl groups. Stefan et al. [9] demonstrated the modification mechanism of silica, silica–alumina, and aluminum silicate with chlorotrimethylsilane. Braggs et al. [10] studied the electrochemical properties of kaolinite before and after modification with chlorodimethyloctadecylsilane. Sudhölter et al. [8] treated the silica gel surface with 3-aminopropylethoxysilane and then characterized the surface by using solid state NMR techniques.

There is an upsurge of interest in recent years to utilize clay minerals in environmental studies. Sepiolite is a good adsorbent for organic species because it exhibits a variety of attractive properties such as high specific surface area, porosity, and surface activity. Sepiolite is therefore used in a large spectrum of areas where sorptive, catalytic, and rheological properties are exploited. Thus, sepiolite is commonly used in oil refining; wastewater treatment; the removal of odor, drug and pesticide carriers, paper, detergent, etc. [11]. Investigations on sepiolite have so far focused more on its sorptive properties. A number of investigators have studied the interaction of water and various organic reagents with sepiolite. The adsorption of organics on clay surface, the sorption properties of bipyridine [12,13], amino pyridine [14,15] and biquinoline [16] were reported by Akyüz et al. The same authors also worked on the sorption behavior of pyrimidine onto natural sepiolite and montmorillonite from Anatolia using FTIR spectrometry [17]. Kara et al. [18] studied the adsorption of cobalt from aqueous solutions onto sepiolite. The adsorption of diquat, paraquat and methyl green on sepiolite [19], and the ammonium adsorption with sepiolite [20], the adsorption and interactions of methyl green with montmorillonite and sepiolite [21], the interaction of amines on sepiolite and polygorskite by infrared measurements [22], the removal of aromatic amines from aqueous solutions by activated sepiolite [23], the access of cationic dye into the structural micropores of

sepiolite [2], the comparison of the adsorption characteristics of azo-reactive dyes on mesoporous minerals [24] have also been investigated. Alkan et al. [25–27] studied the use of sepiolite as an adsorbent for removal of anionic dyes such as reactive blue 221, acid blue 62, acid red 57 and acid yellow 49 from aqueous solutions. They showed that the sorption capacity of the sepiolite is comparable to other adsorbents and sepiolite has a considerable potential as an adsorbent for dyestuffs in commercial systems.

In the ceramics industry and design of nanocomposite materials, especially in clay–water colloidal systems, the electrokinetic properties of the colloidal particles identify the optimal conditions of a well-dispersed system [11]. For a long time, measurements of the electrokinetic potential have been used in colloid chemistry, mainly for the calculation of electrostatic interaction forces in colloidal systems. Moreover, electrokinetic measurements are increasingly successful in characterizing solid surfaces. Studies on the effects of pH, surface-active agents, etc. on the electrokinetic potential give valuable information about the nature of solid surfaces [28].

As can be understood from the considerations above, the surface interactions that occur at the interface when sepiolite is incorporated into aqueous dispersions before and after modification by organosilanes have not been studied. Therefore the developments of zeta potentials in aqueous systems and, consequently, the electrical double layer properties of the sepiolite surface as a function of pH have been examined before and after surface modification with organosilanes in the present study. Complementary infrared spectroscopic studies are included to provide evidence as to the mode of attachment of the organosilanes.

2. Experimental

2.1. Materials

Sepiolite sample used was obtained from Aktaş Lületaşı-Eskişehir regions of Anatolia (Turkey). The sample was treated before using in the experiments as follows: Natural samples were first cleaned mechanically from the visible impurities, and then were ground and sieved to obtain a 150-μm-size fraction. The suspension containing 10 g/l sepiolite was mechanically stirred for 24 h in distilled water, and after waiting a couple of minutes the supernatant suspension was filtered. Then, the solid sample was dried at 105 °C, and sieved again to obtain a150-μm size [25–27]. The chemical analysis of sepiolite has shown a composition given in Table 1. The cation exchange capacity (CEC) of the sepiolite sample was determined by the ammonium acetate method, density by the pycnometer method and, the

Table 1
Chemical composition of sepiolite used in the study

Component	Weight %
SiO_2	53.47
MgO	23.55
CaO	0.71
Al_2O_3	0.19
Fe_2O_3	0.16
NiO	0.43
LoI	21.49

LoI: loss ignition of sepiolite.

Table 2
Some physicochemical properties of sepiolite used in the study

Parameters	Value
Surface area ($m^2 g^{-1}$)	342
Density ($g cm^{-3}$)	2.5
Cation exchange capacity (meq $100 g^{-1}$)	25
pH of solution	8.55

specific surface areas measured by BET N_2 adsorption (Micromeritics Flow Sorb II-2300 equipment). The results obtained as physicochemical properties of sepiolite have been summarized in Table 2.

2.2. Electrokinetical measurements

Zeta potentials of sepiolite samples were measured at 20 ± 1 °C using a Zeta Meter 3.0 equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particle and converts the electrophoretic mobility into zeta potential in terms of Smoluchowski equation. A 0.12 g amount of the solid sample was conditioned in 50 ml of 0.001 M NaCl solutions at various final pHs for 24 h in a shaking bath. Before installing for measurements, the suspension was kept for 5 min to let the larger particles settle. Each data point is an average of approximately 20 measurements. The pH of the suspension was adjusted using dilute HCl and NaOH [29]. All solutions were prepared using bidistilled water. The pH of the suspension was measured using a pH meter (Orion 920A).

2.3. Treatment of sepiolite samples

Dimethyloctadecylchlorosilane (DMODCS), dimethyldichlorosilane (DMDCS), and 3-aminopropyltriethoxysilane (3-APT) were the compounds used for treating sepiolite. Chemical formula of the compounds have been given in Fig. 1.

2.3.1. Treatment with dimethyloctadecylchlorosilane (DMODCS)

The modification reactions were performed with about 2 g of sepiolite samples and 9.36 mmol of dime-
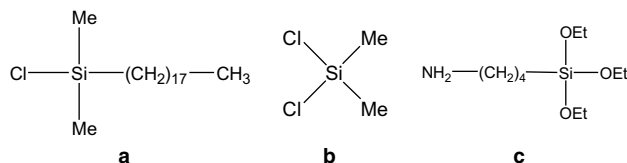

Fig. 1. The chemical formula of modifying agents: (a) DMODCS, (b) DMDCS, (c) 3-APT.

thyloctadecylchlorosilane (DMODCS) in the presence of 0.42 mmol dry pyridine in 30 ml toluene. The mixtures were refluxed for 6 h. After cooling, the packings were dispersed in chloroform, filtered, and washed with chloroform, methanol and 70% methanol aqueous solution. Washing was repeated in the same solutions in reverse order and then dried at 120 °C for 24 h in vacuo [31].

2.3.2. Treatment with dimethyldichlorosilane (DMDCS)

About 1.66 g of sepiolite was refluxed for 6 h in a soxhlet by 30 vol.% of dimethyldichlorosilane (DMDCS) in toluene [30]. The mixture was cooled, filtered, washed with chloroform and methanol and dried at 120 °C for 24 h. Then FTIR spectra of sepiolite treated with DMDCS were obtained in KBr pellets.

2.3.3. Treatment with 3-aminopropyltriethoxysilane 3-APT)

A suspension of 1 g sepiolite in 100 ml m-xylene (dried over anhydrous $CaCl_2$) was refluxed for 48 h with 6.65 ml freshly distilled 3-aminopropyltriethoxysilane. The solid was isolated by suction filtration and extracted with benzene and methanol in soxhlet apparatus for 24 h. In some cases, part of our batch was washed additionally with water. Finally, the compound was dried at 80 °C under vacuum ($p \sim 0.3$ Torr), [8].

3. Results and discussion

3.1. FTIR study

FTIR spectra of the sepiolite samples treated with DMODCS, DMDCS and 3-APT were obtained. Infrared spectra of the samples were measured by using Perkin Elmer BX 2 FTIR spectrophotometer in KBr pellets.

In order to study the interaction between the sepiolite surface and the modifier, the FTIR spectra of the following samples have been measured:

(a) modifier used (aimed to estimate the peaks arising from modifier and changes on it after modification),
(b) sepiolite sample (to observe any changes on sepiolite during the modification process and comparing the modified sample),

(c) modified sepiolite sample (enabled us to observe the peaks arising from the modifier on the surface and any kind of changes on the sepiolite samples),

(d) modified sepiolite with sepiolite-background (scanning the same amount of sepiolite sample as a background are omitted the peaks arising from sepiolite by subtracting and visualize the modifier on the surface,

(e) mechanical mixture of sepiolite and modifier (gave the interaction on the surface by comparing a simple mixture and modified structure).

Sepiolite contains four different types of water molecules: (i) hygroscopic, (ii) zeolitic, (iii) bound and (iv) hydroxyl water [32]. In sepiolite, the most probable binding sites on the sepiolite surface are surface hydroxyls and Lewis acidic centers [17].

FTIR spectra of the original and treated sepiolite samples are shown in Figs. 2–5, respectively. The Mg_3OH band at 3762–3578 cm^{-1} characterized by weak bonding strength is ascribed to the presence of OH groups in the octahedral sheet and the OH stretching vibration in the external surface of sepiolite. On the other hand, the 3430 and 1662 cm^{-1} bands are respectively assigned to the OH stretching, representing the zeolitic water in the channels and bound water coordinated to magnesium in the octahedral sheet. The band at 1447 cm^{-1} developed due to the hydroxyl bending vibration again reflects the presence of bound water. The Si–O coordination bands at 1208 and 1015 cm^{-1}
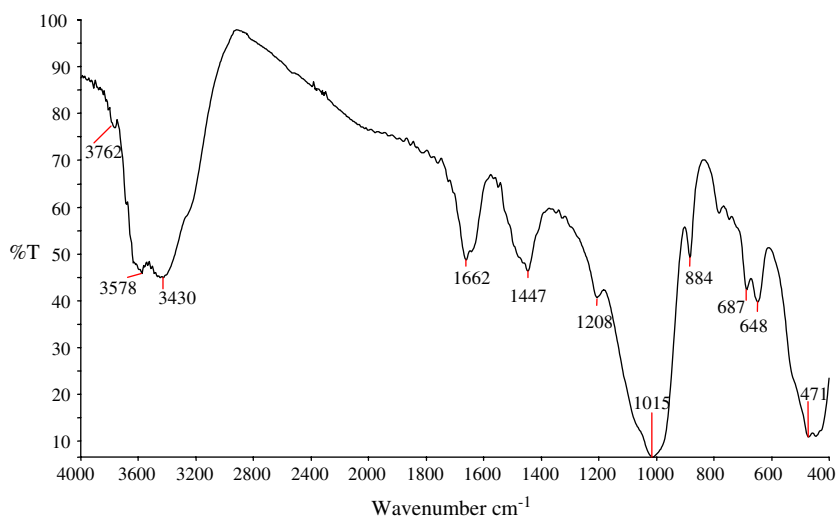

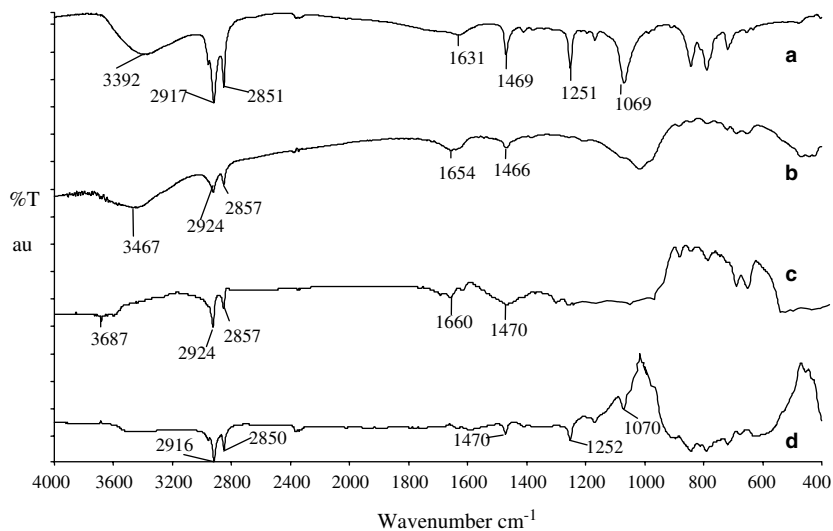Fig. 2. FTIR spectra of sepiolite used for modification.

Fig. 3. FTIR spectra of (a) DMODCS, (b) modified sepiolite, (c) modified sepiolite with sepiolite background, (d) sepiolite and DMODCS mechanical mixture. A vertical offset for all spectra are introduced for clarity.
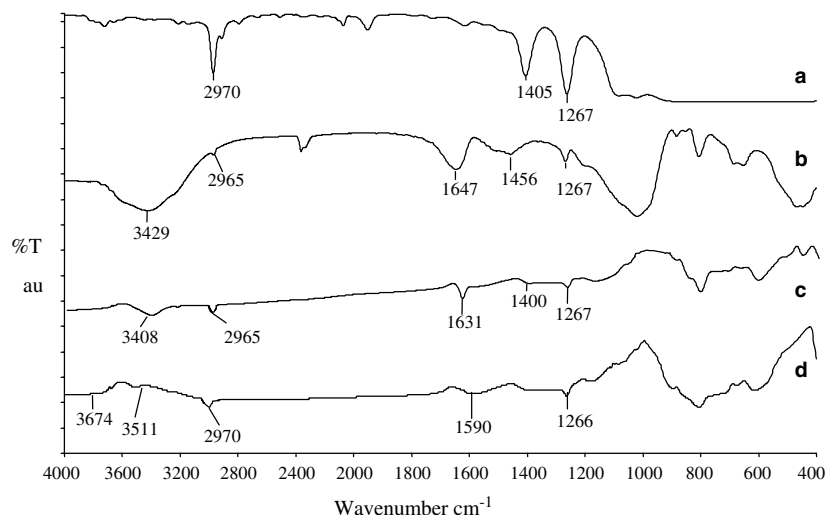
Fig. 4. FTIR spectra of (a) DMDCS, (b) modified sepiolite, (c) modified sepiolite with sepiolite background, (d) sepiolite and DMDCS mechanical mixture. A vertical offset for all spectra are introduced for clarity.
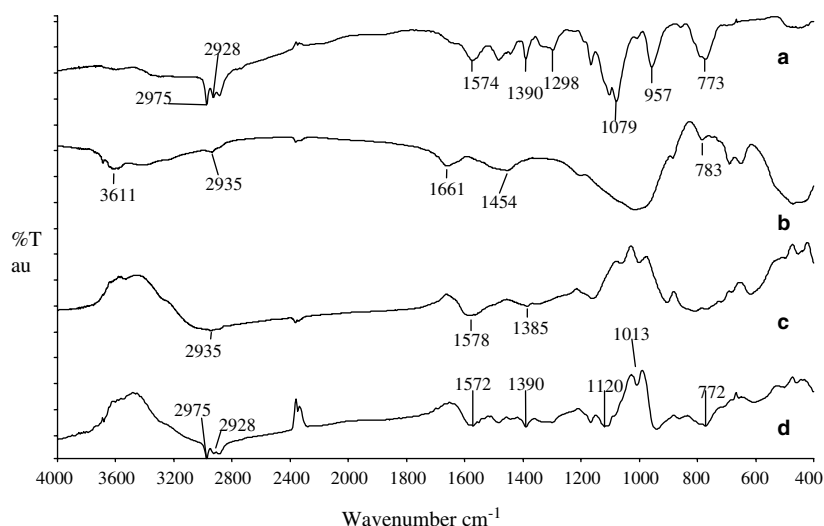

Fig. 5. FTIR spectra of (a) 3-APT, (b) modified sepiolite, (c) modified sepiolite with sepiolite background, (d) sepiolite and 3-APT mechanical mixture with sepiolite background. A vertical offset for all spectra are introduced for clarity.

represent the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet [33].

In Figs. 3–5, the deviations that have been observed in the vibration frequencies of IR spectrum of organosilane-added sepiolite are considered as the indicators of the interaction between the modifying molecules and sepiolite particles. The adsorption of a polar or a nonpolar molecule perturbs the stretching vibrations of Si–OH groups of external surface and causes to shift to lower wavenumber [34]. On the other hand the perturbation observed on the zeolitic and bound water vibrations of sepiolite indicates that some of organosilane molecules enter the interior channels and replace zeolitic water molecules. The frequency shifts may indicate the formation of new H-bonds between bound/zeolitic water and organosilane molecules whereas weakening in intensity of the v(OH) vibration of the zeolitic water is the indication that modifier molecules replace part of the zeolitic water [17].

The adsorption of DMODCS, DMDCS and 3-APT on sepiolite has a significant effect on the H_2O and hydroxyl group vibrations as seen in Figs. 3–5. As can be seen in these figures, zeolitic and bound water vibrations are found to decrease in intensity after adsorption of modifier molecules. The shoulder observed at 3762 cm^{-1} ascribed to the OH stretching vibration of the Mg–OH group in the FTIR spectrum of untreated sepiolite (Fig. 2), and disappears in the FTIR spectrum
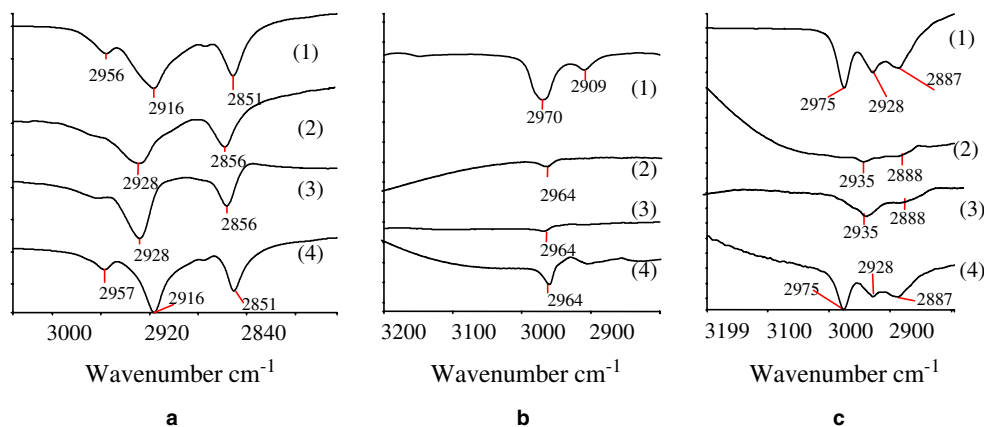
Fig. 6. FTIR C–H region spectra of samples (a) DMODCS, (b) DMDCS, (c) 3-APT.

of the treated sepiolite samples (curves b and c in Figs. 3–5). Similarly, the band at 3430 cm^{-1} characterized by the effect of OH stretching vibration [13], on bound water, is shifted after interaction with 3-APT molecules; this indicates the formation of hydrogen bonds through the N of the amino group with the bound water [33].

The organosilane modification on the sepiolite has shown a similar feature on the FTIR spectra like Si–O bonds, the biggest difference should be at the C–H vibrational region. Thus, we considered the C–H region individually. Fig. 6 illustrates the C–H vibration region of the samples.

DMODCS shows the C–H stretching at 2956, 2916 and 2851 cm^{-1} in Fig. 6a1. After modification on sepiolite (Fig. 6a1) the peak at 2956 disappears while those at 2916 and 1851 shift to the 2928 and 2856, respectively. These shifts may be attributed to the formation of H-bonds background defined spectra (Fig. 6a3) show these peaks at the same frequency with strong intensities due to the subtraction of peaks arising from sepiolite. The mechanical mixture (Fig. 6a4) has shown the same peaks with the modifier without losing 2956 cm^{-1} peak.

In the DMDCS case, the most significant point is that the mechanical mixture gave similar FTIR spectra with the modified sample. This unexpected result may attribute to the reactivity of the DMDCS. The peaks in Fig. 6b1 at 2970 and 2909 cm^{-1} disappeared and a new peak at 2964 appeared in each case.

On the modification of 3-APT losing triethoxy group constructs the observation of modified species on the sepiolite difficult at the C–H region. However, the comparison modified sepiolite with 3-APT and the mechanical mixture; it is easy to see the disappearance of the 2975 cm^{-1} peak (Fig. 6b1) which is due to the ethoxysilane in the modified sepiolite. On the modified sepiolite by the disappearance of the 2975 cm^{-1} peak, the C–H stretching at 2829 and 2886 shifted to 2935 and 2888 cm^{-1}, respectively. Mechanical mixture keeps the peaks arising from ethoxy groups showing that there is no interaction by simple mixing.

As can be understood from the indication of spectroscopic results, the organosilane molecules adsorbed on sepiolite are coordinated to the Lewis acidic sites and/or surface hydroxyls by H-bonding interaction through nitrogen lone pairs. Moreover, some of the adsorbed 3-APT molecules may enter the interior channels of the sepiolite structure by replacing zeolitic water and involving H-bonding interaction with the zeolitic/bound water molecules [17].

3.2. Electrokinetic properties

For a long time, measurements of the electrokinetic potential have been used in colloidal systems. Moreover, electrokinetic measurements are increasingly successful in characterizing solid surfaces. Electrokinetic phenomena can be observed by the contact of a solid surface with a polar liquid medium, because of the existence of an electric double layer at the solid–liquid interface.

The electric double layer consists of two regions: a fixed layer and a diffused layer. Between these two parts lies a "surface of shear" or "slipping plane". Externally used electrical or mechanical forces cause a relative movement between the fixed part and the diffused part. The potential at this surface is called the electrokinetic or zeta (ζ) potential. Different compositions of the liquid phase (for example, changes of pH or electrolyte concentration) cause changes in this double layer. This can be made evident by electrokinetic results.

Sepiolite may be considered as a mixture of oxides of SiO_2 and MgO; therefore sepiolite as a whole exhibits amphoteric characteristics. The surface of sepiolite can acquire a negative or positive charge resulting from substitutions within the lattice of the solid of Si^{4+} and Mg^{2+} breaking of Si–O–Si (siloxane group) at the surface during grinding as shown in Fig. 7. Zeta potential, ζ, occurs at the slipping plane of a solid immersed in a water solution and can be directly related to the magnitude and sign of the surface charge [35]. The zeta potential is therefore used for measuring the potential of solid at
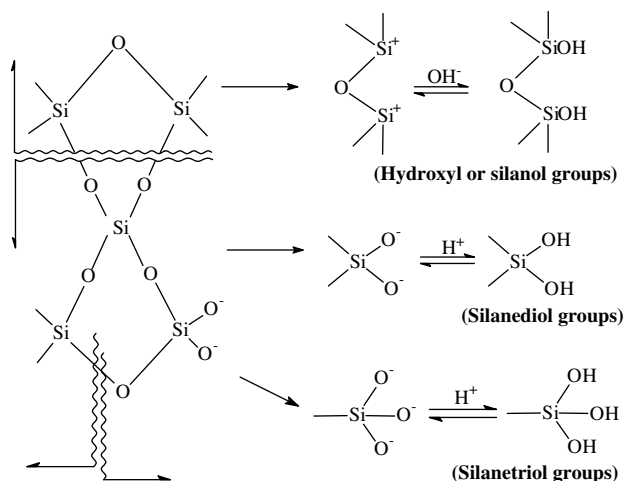
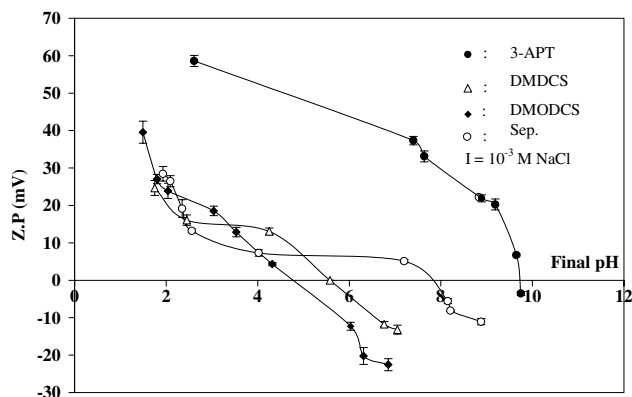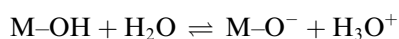Fig. 7. Broken bonds and surface charge development in silicates.

Fig. 8. The effect of pH on the zeta potential of modified sepiolite samples.
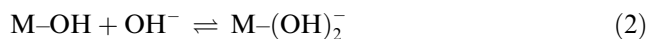
the shear plane to characterize its electrokinetic behavior, because the surface potential is not directly measurable. The zeta potential of sepiolite given in Fig. 8 as a function of suspension pH indicates that its surface is positive at low pH and is negative at higher pH. H^+ and OH^- are most likely the potential-determining ions (pdi) for hydrous oxides. The pdi are specifically bound cations or anions that result in net surface charge. The potential determining role of H^+ and OH^- is most readily accounted for by realizing that the pH-dependent charge of an oxide results from acid–base reactions at the surface [36]:

$$M-OH_2^+ \rightleftharpoons M-OH \rightleftharpoons M-O^- \qquad (1)$$
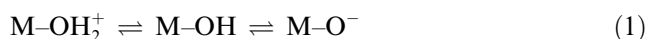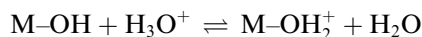
where M stands for a metal or metalloid central ion, i.e. Si or Mg. It is convenient to visualize the surface sites as converted on hydration to surface hydroxo groups of M–OH groups that can dissociate protons:

$$M-OH + H_2O \rightleftharpoons M-O^- + H_3O^+$$

or

$$M-OH + OH^- \rightleftharpoons M-(OH)_2^- \qquad (2)$$

or accept protons:

$$M-OH + H_3O^+ \rightleftharpoons M-OH_2^+ + H_2O$$

or

$$M-OH \rightleftharpoons M^+ + OH^- \qquad (3)$$

The increase of pH results in increase of $M-O^-$ or $M-(OH)_2^-$ in terms of reaction (2), i.e. the negative charge of the particles is the result of dehydroxylation or deprotonation of the surface. In the acidic pH range sepiolite particles display a positive zeta potential due to the protonation of the surface groups to form $M-OH_2^+$ groups according to reaction (3). The pH_{IEP} also indicates that at this point, the electrophoretic mobility is zero, that is, the ζ-potential is zero.

These equations imply that the hydrous oxides are like diprotic acids with two dissociable protons. At the pH_{IEP}, which is defined as pH at which the charge density of the surface is zero [36]:

$$[M-OH_2^+] = [M-O^-] \qquad (4)$$

As seen from the zeta potential of sepiolite treated with 3-APT versus pH in Fig. 8, 3-APT is the most effective modifier on the surface charge. Zeta potential of the modified perlite shifts to much positive values. Although sepiolite has a pH_{IEP} at 7.8, 3-APT-modified sepiolite has a pH_{IEP} at about 9.7. By operating at pH values on either side of the pH_{IEP}, the surface charges are reversed, that is, at pH values lower than 9.7 the surface becomes positively charged, while it is negatively charged after pH 9.7. The fact that the sepiolite treated with 3-APT has a pH_{IEP} at 9.7 shows that the surface has gained a basic characteristic, because the molecule attached to the surface has dissociable basic molecule groups. When the surface of a solid is attached with a group bearing a dissociable basic molecule, pH_{IEP} of the solid is expected to shift to basic region. We suppose that 3-APT molecules were attached to the hydroxyl groups of the sepiolite surface. In that case it may be expected to find basic surface properties in electrokinetic investigations because of the existence of the $-NH_2$ group. These findings confirm that a strong interaction has occurred between 3-APT and sepiolite surface, in which a covalent bonding is formed.

In the case of a nonpolar surface without dissociable molecule groups, the surface lose partially its amphoteric behavior, so that pH_{IEP} should be obtained at pH below 7. The dependence of zeta potential on the suspension pH for the DMODCS and DMDCS-treated sepiolite samples shown in Fig. 8 confirms that they cause to reduce pH_{IEP} about 5–6. Because these compounds have nonpolar molecular structure, they can slightly lower the pH_{IEP}.

4. Conclusions

FTIR studies show that sepiolite surface can be modified by treating with organosilanes, such as dimethyldichlorosilane (DMDCS), 3-aminopropyltri-ethoxysilane (3-APT), and dimethyloctadecylchloro-silane (DMODCS). According to zeta potential measurements, 3-APT gives a basic character to the surface and causes the pH_{IEP} to shift from 7.8 (pH_{IEP} of nonmodified sepiolite) to 9.7 (pH_{IEP} of 3-APT-modified sepiolite), while DMDCS and DMODCS behave as nonpolar modifying agents reducing the pH_{IEP} to lower pH, i.e. from 7.1 to 5.6 for the DMDCS-modified sepiolite, 5.2 for the DMODCS-modified sepiolite.

Acknowledgements

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