Sorption phenomena of modification of clinoptilolite tuffs by surfactant cations

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ABSTRACT

The sorption of cationic surfactant hexadecyltrimethylammonium (HDTMA) onto the solid/liquid interfaces of different clinoptilolite rich tuffs (CT) is examined. Examined were CT from Serbia with 75% clinoptilolite, CT from Turkey with 70% clinoptilolite, and CT from Croatia with 60% clinoptilolite. The sorption of HDTMA cations increased in the following order: CT from Serbia > CT from Turkey > CT from Croatia. The maximum amounts of sorbed HDTMA cations, normalized with regard to external cation exchange capacities of tuffs, were 1.79, 1.70, and 1.14 for Serbian, Turkish, and Croatian CT. FTIR analysis of samples with the maximum amount of sorbed HDTMA cations showed that HDTMA chains on Serbian CT adopt mainly a stretched all-*trans* conformation, while at the surfaces of CT from Turkey and Croatia the amount of *gauche* conformations increased. The zeta potentials of CT samples with the maximum amount of sorbed HDTMA cations and the sorption of benzoate anions on these samples increased in the following order: CT from Turkey > CT from Serbia > CT from Croatia. It can be assumed that on the surface of CT from Turkey iron (hydr)oxide clusters or nanoparticles with positive surface sites are present, due to which the isoelectric point is sifted toward lower and the zeta potential toward higher values. Therefore, the sorption of benzoate anions on modified CT from Turkey is also higher.

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1. Introduction

Zeolites are crystalline, hydrated aluminosilicates of the group I and group II elements, in particular sodium, potassium, magnesium, calcium, strontium, and barium. Structurally the zeolites are "framework" aluminosilicates that are based on an infinitely extended three-dimensional network of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra linked to each other by sharing all of the oxygens. In the formation of synthetic or natural zeolites, part of the Si^{4+} atoms by Al^{3+} atoms creates a negative charge at the Al–O tetrahedra that is balanced by an inorganic metal cation (Na^+, K^+, Ca^{2+}, Mg^{2+}) [1].

By replacement of inorganic cations with organic cations (usually of quaternary ammonium structure), it is possible to convert a naturally hydrophilic property of zeolite into a hydrophobic and organophilic property.

It was shown for clinoptilolite tuffs (CT) that when the concentration of cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) is changed, the configuration of surfactant changes from monolayer to bilayer. The compensating inorganic cations in the crystal structure of clinoptilolite are not available for exchange with HDTMA cations. The diameter of carbohydrate chain of HDTMA cation is 0.4 nm, the length is 2.3 nm, and the diameter of the polar head $-N^+(CH_3)_3$ is 0.694 nm, which makes it too large to penetrate the largest channels of clinoptilolite, which have dimensions 0.42×0.72 nm. Reactions in the system of CT and HDTMA cations therefore involve only external cation exchange capacity (ECEC, fraction of total CEC), leaving the internal cation exchange capacity unchanged and still accessible for small ions [2].

According to the literature, the HDTMA cation sorption maxima ranged from 58 to 266 mmol/kg CT. The maximum sorption of HDTMA cations and the ECEC appear to be controlled by CT crystal size, aggregate size, and aggregate porosity, rather than by the total CEC [2]. Other factors that can influence the HDTMA sorption maxima should be also taken into account: the geological origin of the zeolites, their cation and framework composition, and their impurities (such as forms of silica, feldspars, clay minerals, metal oxide/hydroxide nanoparticles, clusters, microcrystals, or agglomerates on the external zeolite surface).

Since the sorption of hydrophobic organic species onto a solid is a strong function of the solid's organic carbon content, the CT modified with HDTMA cations can be used as sorbents to remove hydrophobic organic contaminants from water [3]. If sorption of

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HDTMA cations results in the change of a negative surface charge to positive, the sorption of organic and inorganic anions is also possible [4–7].

Understanding the mechanism of surfactant sorption and the subsequent conformation of surfactants on the mineral surface is crucial to understanding the interaction of the sorbed surfactants with organic and inorganic compounds in solution and predicting the stability of the sorbed surfactants [8,9].

The aim of the present work is to examine the sorption phenomena of clinoptilolite tuff modification by HDTMA cations. The isotherms of sorption of HDTMA cations on CT, the zeta potentials of modified CT and the amounts of exchanged cations from CT were examined. FTIR analysis of CT samples with the maximum amount of sorbed HDTMA cations and the sorption of benzoate anions ($C_6H_5COO^-$) onto modified CT were analyzed too.

2. Experimental

2.1. Materials

The quaternary ammonium salt hexadecyltrimethylammonium bromide (HDTMA-Br, Merck), with molar mass 364.46 g/mol and minimum 99% active substance, was used. The critical micelle concentration (CMC) of HDTMA-Br at 30 °C was 0.94 mmol/dm^3, as estimated by conductivity measurements of aqueous HDTMA-Br solutions at different concentrations.

The sorption of HDTMA cations was applied to three clinoptilolite-rich tuffs: CT from Turkey (Bigadic), CT from Croatia (Donje Jesenje), and CT from Serbia (Igros). The samples of CT had particles smaller than 0.125 mm. The mineralogical composition of CT was determined by X-ray powder diffraction (Philips X.pert instrument). The chemical composition of CT was determined by classical chemical analysis. The cation exchange capacity (CEC) of CT was determined by measurement of equilibrium concentrations of exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) in the supernatant by atomic absorption spectrometry (AA-6800, Shimadzu) after saturation of the samples with NH_4^+ ions [10].

2.2. Methods

2.2.1. Sorption of HDTMA onto CT samples

Surfactant solutions were prepared with deionized water. Concentrations of HDTMA-Br were 0.045, 0.095, 0.48, 0.70, 0.90, 1.55, 2.6, 3.70, 5.20, 6.60, 8.0, and 9.90 mmol/dm^3, i.e., more and less than the CMC. Mixtures of 2.0 g of the CT sample and 0.1 dm^3 of surfactant solutions were stirred at 30 °C (above the Kraft point, which is 25 °C) for 48 h on a mechanical shaker (Innova 4080) at 150 rpm. The suspension was centrifuged for 20 min and the supernatant was analyzed. The concentration of residual surfactant was determined as content of total organic carbon (Shimadzu TOC-5050A analyzer) in the obtained supernatant. Concentration of sorbed HDTMA cation in mmol/g was calculated from the mass balance equation (1) as

$$Q_e = (c_0 - c_e)\frac{V}{m}, \tag{1}$$

where c_0 and c_e are the initial and equilibrium liquid-phase concentrations of surfactant solution (mmol/dm^3), respectively; V is the volume of surfactant solution (dm^3), and m is the mass of clinoptilolite tuff sample used (g).

Supernatant solutions were analyzed by atomic absorption spectrometry for desorbed amounts of Na^+, K^+, Ca^{2+}, and Mg^{2+}. The surfactant-modified samples were filtered through a Büchner funnel and filter paper (blue band). The samples were washed with distilled water until reaction with 1% $AgNO_3$ solution was negative. The modified samples were dried at room temperature.

2.2.2. FTIR spectroscopy

FTIR spectra were taken on a Bruker Equinox 55 interferometer using the KBr pressed disk technique. For each KBr pellet, 1 mg of tuff and 100 mg of KBr were weighted, ground in an agate mortar, and pressed. Spectra were recorded over the spectral range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.2.3. Electrokinetic (zeta) potential measurements

The zeta potential of surfactant-modified samples was measured by a Zetasizer 3000 instrument. The electrophoretic mobility of the particles was automatically calculated and converted to the zeta potential using the Smoluchowski equation. Each CT sample (0.010 g) was suspended in distilled water (0.050 dm^3) by mixing for 15 min. The samples were allowed to stand for 5 min. An aliquot taken from the supernatant was used for measurements of zeta potential. The average value of 10 measurements was taken as a representative potential.

2.2.4. Sorption of benzoate anions onto CT samples modified with HDTMA

An aqueous solution of benzoate anions was prepared by dissolving Na benzoate (Fluka) in deionized water. The sorption of benzoate anions onto CT samples modified with different concentrations of HDTMA was examined. Mixtures of 0.2 g of unmodified or HDTMA-modified CT samples and 0.01 dm^3 of 1.0 mmol/dm^3 benzoate solution were continuously stirred at 25 °C for 24 h on a mechanical shaker (Innova 4080) at 150 rpm. Then each mixture was centrifuged and the concentration of residual benzoate anions was determined by HPLC method, using an HP 1090 HPLC instrument with a DAD detector.

3. Results and discussion

3.1. Mineralogical and chemical analysis of CT samples

According to X-ray powder diffraction analysis (Fig. 1), the sample of CT from Serbia contained approximately 75% clinoptilolite. Several minor constituents, including calcite, analcime, plagioclase feldspars, biotite, and quartz (approximately 5% of each), were also determined in the sample. The CT from Turkey consisted of approximately 70% clinoptilolite, subordinate opal-CT and quartz (10–15% of each), and traces of K-feldspars and biotite (5% of each). The CT from Croatia consisted of approximately 60% clinoptilolite. Important constituents, present in concentrations of 10–15% each, were plagioclase feldspars and quartz, while K-feldspars and celadonite were present as traces (<5% of each). Results of the quantitative chemical composition of the studied CT are given in Table 1.

3.2. Cation exchange capacities (CEC) of CT samples

Results of the CEC determination (Table 2) show that the main exchangeable cations in samples of CT from Turkey and CT from Serbia were Ca^{2+} ions, whereas Na^+ ions were the main exchangeable cations in the sample of CT from Croatia. The sample of CT from Serbia had the largest CEC of 1.71 meq/g, while CEC of CT from Croatia was 1.60 meq/g and CEC of CT from Turkey 1.35 meq/g. The higher CEC of CT from Croatia than of CT from Turkey could be explained by the mobile extraframework $Na^+(H_2O)_n$ ions as the main exchangeable cation in the Croatian CT and the presence of minerals of secondary importance, such as plagioclase feldspars (tectosilicate group) and celadonite, $KFe^{3+}(Mg,Fe^{2+})Si_4O_{10}(OH)_2$ (mica group), which could increase the CEC numerical values. Also, due to the high content of Fe_2O_3 in CT from Turkey (Table 1), the existence of iron (hydr)oxide clusters or nanoparticles on the external surface cannot be excluded, due