

Surface modification of a zeolite and the influence of pH and ionic strength on the desorption of an amine

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Abstract. The adsorption of stearyltrimethylbenzylammonium chloride (SDBAC) on the clinoptilolite–heulandite rich tuff in dependence on the applied temperature was studied. The maximal amount of sorbed SDBAC was 123 mmol/kg in the case of thermally treated zeolite tuff (100 °C) and a warm surfactant solution (80 °C). The amount and properties of water adsorbed on the organo-zeolite (OZ) as well as the bonding between the organic species and the zeolite were investigated by DTA, TG, DTG and IR analyses. During gradual heating in an oxidizing atmosphere, the adsorbed organic material was oxidized, giving rise to significant exothermic peaks. The adsorption of water vapor decreased with increasing SDBAC loading up to 75 mmol/kg of zeolite, which can be ascribed to an intensification of the hydrophobic characteristics of the surface. With loadings above the 75 mmol/kg, the adsorption of water vapor increased. Desorption of SDBAC from the organo-zeolite under environmentally relevant conditions: distilled water, pH 3 and 10 buffers, as well as aqueous NaCl and CaCl₂ solutions, was investigated. OZs with loadings up to their external cation exchange capacity value (75 mmol/kg) were stable under all of the applied conditions.

Keywords: organo-zeolite, quaternary amine, surface modification, ion exchange.

INTRODUCTION

Natural zeolites are hydrated aluminosilicate minerals characterized by cage-like structures, with high internal and external surface areas, and high cation exchange capacities.¹ In contrast to clays, zeolites can occur as millimeter or greater sized particles and are free of shrink-swell behavior. As a result, zeolites exhibit superior hydraulic characteristics and are suitable for use in filtration systems.^{2,3} These minerals have been particularly useful in removing cationic species such as ammonium and some toxic metals from water.^{4–6} They have also been used to re-

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move radioactive cationic species (^{137}Cs , ^{90}Sr) from nuclear plant wastewaters and contaminated groundwaters.^{7,8}

The permanent negative charges on the surface of clays and zeolites enable them to be modified by cationic surfactants, which results in the enhancement of adsorption of organic contaminants.⁹ The mechanism of sorption depends strongly on the type of mineral. In a study of HTAB sorption by a vermiculitic subsoil, it was found that the hexadecyltrimethylammonium bromide (HTAB) sorption was up to 3.5 times the cation exchange capacity (CEC) of the soil.¹⁰ In previous studies, it was shown that the sorption of cationic surfactant onto zeolite involves both cation exchange and hydrophobic bonding.^{11,12} Long chain quaternary ammonium cations are too large to enter the zeolite channels or access the internal cation exchange positions. Li and Bowman showed that HTAB is sorbed only on the external surface of zeolite, kaolinite and illite and that the obtained HTAB bilayers differed only in their packing densities, due to the different surface charge densities of the examined minerals.¹³ Sullivan *et al.*¹⁴ studied the sorption of HTAB onto the surface of a zeolite and observed that at low loading levels, the surfactant is retained by ion exchange and forms a monolayer. If the surfactant concentration in solution exceeds the external cation exchanged capacity (ECEC), the hydrophobic tails of the surfactant molecules associate to form a bilayer. The resultant surfactant-modified zeolite is capable of the simultaneous sorption of anions, cations, and non-polar molecules from water.¹³ Tomasevic-Canovic *et al.*¹⁵ examined the adsorption of mycotoxins by a zeolite modified with SDBAC, in amounts less than the ECEC value, by a wet (activation in suspension) and a dry process (tribochemical process). The method of preparation of the OZs had little influence on the adsorption of mycotoxins.

The development of permeable barrier technologies for the clean-up of contaminated groundwater has expanded in the past few years.^{16–18} Application of OZs as a barrier material offers several advantages, including: abundant mineral deposits, their low cost and the possibility of the preparation of selective organo-zeolites for target contaminants.

The efficiency of an OZ as an adsorbent for selected contaminants from water depends strongly on the surfactant coverage of the mineral surface. It is very important to investigate the parameters which influence the adsorption of the surfactant and to examine the properties of organo-zeolites with different surfactant loadings. Differential thermal analysis (DTA) of the organo-mineral complexes together with thermogravimetry (TG) and infrared spectroscopy (IR) offer information concerning the thermal reactions, properties and stability of the complexes, the amount and properties of the water adsorbed in the organo-minerals and on the bonding between the organic species and the clay. Hence, the objective of this study was to investigate the desorption of SDBAC from the zeolite surface under different ionic strengths and pH of aqueous solutions over longer periods of time.

EXPERIMENTAL

Materials

Raw zeolite tuff from the Beočin deposit in Serbia was used as the starting material for the surface modification experiments. The chemical composition (Table I) was determined by atomic absorption spectroscopy (AAS) using a Perkin Elmer-730 instrument. X-Ray diffraction (XRD) analysis was performed using a Philips PW-730 instrument. Qualitative mineralogical analysis of the zeolitic sample was performed in transmitted light using a polarization microscope "JENAPOL-U" Zeiss-Jena (xylene immersion method). Objectives of magnification from 10 to 50 \times were used for mineral identification. After crushing and grinding, the sample was sieved to obtain particles between 0.4–0.8 mm in size.

The surfactant SDBAC was purchased from Hoechst, Germany, with the specification of technical purity (an active ingredient content of 75–80 %). The manufacturer's data sheet indicated that the surfactant, besides the active ingredient, also contained propan-2-ol and water, which was taken into consideration when calculating the concentration of surfactant in a solution.

Cations exchanged in the adsorption processes

The cation exchange capacity (CEC) of the zeolites of different particle sizes was determined using a standard procedure with ammonium chloride solution. The external cation exchange capacity (ECEC) of the raw samples was determined by the method of Ming and Dixon.¹⁹ The cations exchanged in the adsorption process were determined by the following standard methods: the Na⁺ and K⁺ ions were detected using a flame photometer and the sum of the Mg²⁺ and Ca²⁺ ions was determined by titration with EDTA.

Adsorption experiments

The influence of the temperature on the adsorption of SDBAC onto the zeolite sample was examined. The same quantity (100 g) of the starting zeolite and zeolite thermally treated at 100 °C for 2 h were added to 100 ml (solid content of 50 %) of SDBAC solutions of different concentrations (50, 75, 100 and 150 mmol SDBAC/dm³), the temperatures of which were either 25 or 80 °C. After addition of the cold or hot zeolite, the temperature of the suspension was measured, t_0 . The prepared suspensions were denoted as: I – cold zeolite–cold solution (CZ–CS); II – cold zeolite–warm solution (CZ–WS); III – warm zeolite–cold solution (WZ–CS) and IV – warm zeolite–warm solution (WZ–WS). The suspensions were mechanically mixed for 30 min and the final temperature measured, t_{30} . Then the suspensions were filtered and the filtrates collected. The solid samples were washed out with two portions of distilled water, dried at 70 °C and analysed for non-adsorbed SDBAC and exchanged inorganic cations. The non-adsorbed surfactant in the supernatants was analyzed by a two-phase titration technique using dimidium bromide and disulphine blue as indicators (Akzo Chemie, WV/2.001-2). This technique is based on the formation of a complex between an anionic surfactant (sodium dodecyl sulphate) and a cationic surfactant, which is soluble in chloroform and changes color from blue through colorless to pink in the presence of indicators.^{20,21} The adsorption experiments were performed at room temperature.

To measure the ability of the obtained OZ to adsorb water vapor, the dried samples were kept in a relative atmospheric humidity of 100 % (saturated solution of NaCl) for 24 h. The mass changes resulting from water vapor adsorption were measured.

Thermal and IR analysis

Before thermal analysis, the samples were kept in a relative atmospheric humidity of 75 % for 24 h. The TG/DTA analyses were carried out in the temperature range of 20–600 °C, at a heating rate of 10 °C/min. A Netzsch STA-409 EP apparatus was used. IR spectra were obtained on the Hewlett Packard IR spectrometer, in the range of 4000–400 cm⁻¹, using KBr pellets.

Desorption of the SDBAC from the organo-zeolite

The stability of the OZs in different buffers (3 and 10), distilled water (pH~5.5) and at different ionic strengths (1 M NaCl and 1 M CaCl₂) were investigated. A boric acid – potassium chloride

buffer and a potassium hydrogenphthalate buffer were used for the pH 3 and pH 10 media, respectively. OZs with different SDBAC loading (2.5 g) were added to 50 cm³ of prepared solutions and mechanically mixed on a rotary shaker for 2 h and then left to stand for 24 h. Subsequently, the supernatants were centrifuged and tested for SDBAC desorbed (solutions of different pH). The desorption cycle was repeated 30 times (days). After this period, the samples were washed out with distilled water and analyzed by IR spectrophotometry (solutions with different ionic strengths). These experiments were performed at room temperature.

RESULTS AND DISCUSSION

The chemical composition of the employed zeolite is given in Table I. The X-ray diffraction pattern of the zeolite tuff is shown in Fig. 1.

TABLE I. The chemical composition of the zeolitic tuff from the Beočin deposit

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI*
Wt. %	66.87	13.46	0.98	3.85	0.69	0.37	2.23	11.45

*Loss of ignition.

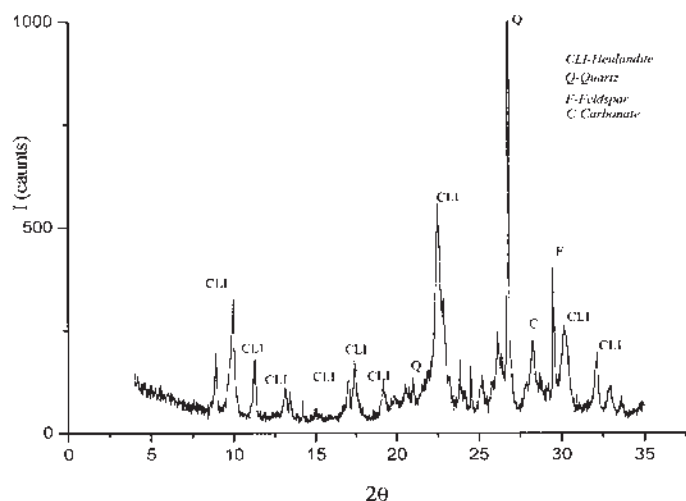


Fig. 1. X-Ray diffraction pattern of the zeolitic tuff from the Beočin deposit.

The clinoptilolite content of the zeolite was ~80% (based on semi-quantitative mineralogical analysis). From Fig. 1, it can be seen that the main impurities in the zeolite were quartz, feldspar and carbonate. The total cation exchange capacity (CEC) for the tuff sample was 1470 mmol/kg, whereas the external cation exchange capacity (ECEC) was 75 mmol/kg. The dominant cation in the exchangeable positions was Ca²⁺, followed by K⁺, Mg²⁺ and Na⁺.

Temperature influence

One of the factors that influence the reactivity of the zeolite surface is the physically adsorbed water present on the mineral surface, which can be removed by thermal treatment of the sample.²² The influence of temperature on the adsorption of the cationic surfactant was studied by adding the starting and a thermally

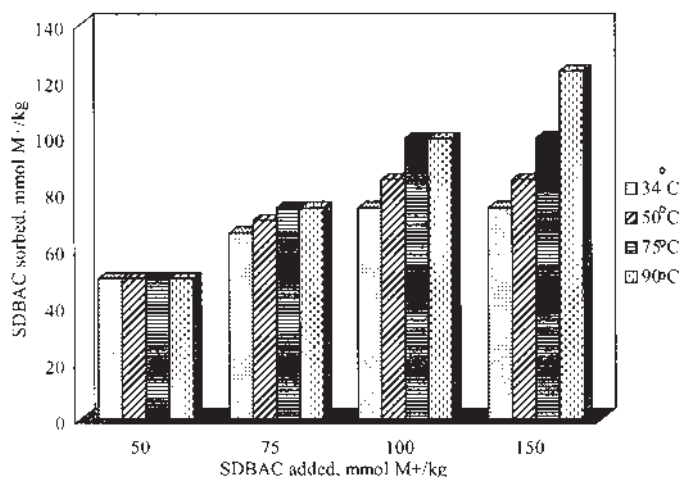


Fig. 2. The influence of temperature on the adsorption of SDBAC onto zeolite.

treated (100 °C) sample to surfactant solutions, the temperature of which were either 25 or 80 °C. Four groups of adsorption mixtures were prepared as described in the experimental section. The amounts of SDBAC sorbed on the zeolite sample *versus* the amount of added surfactant are shown in Fig. 2.

The hydration of zeolite tuff is an exothermic reaction which caused the temperature of the CZ-CS suspension to increase to 34 °C. Immediately after mixing, the temperatures of the other suspensions were 50, 75 and 90 °C for WZ-CS, CZ-WS and WZ-WS, respectively. As it can be seen in Fig. 2, the influence of temperature is related to the amount of added surfactant. The temperature had no influence on the adsorption of surfactant when the SDBAC was present in the amount of 50 mmol M⁺/kg of zeolite (Fig. 2). With increasing of amount of SDBAC in suspension, the influence of temperature follows the order: CZ-CS < WZ-CS < CZ-WS < WZ-WS (*i.e.*, with increasing initial concentration of the suspension, 34, 50, 75 and 90 °C, respectively). When the quantities of added SDBAC were 75 and 100 mmol M⁺/kg of zeolite, it was sufficient to warm the surfactant solution (80 °C) to obtain complete adsorption. As can be seen from the above results, the temperature has a significant positive influence for obtaining OZs with higher SDBAC loadings. Surface coverage of the organo-mineral is an important factor determining its adsorption efficiency for different contaminants. Thus, non-polar organic compounds are most efficiently sorbed on OZs when the surfactant is present at, or below, a full monolayer coverage.²³ On the contrary, bilayer formation results in a reversal of the charge on the external surface of the zeolite, providing sites where anions can be exchanged or retained, while neutral species can partition into the hydrophobic core.²⁴

The results of the amounts of cations released from the zeolite during the modification process are shown in Table II.

The amounts of the cations released into the liquid phase during treatment with 50 mmol SDBAC/kg of zeolite were the same irrespective of the applied treatment. In the case of WS-WZ (thermally treated zeolite added to warm solution), with concen-

trations of 75, 100 and 150 mmol of added SDBAC/kg zeolite, the amounts of cations released were almost same. These results were expected according to the ECEC value of the sample (75 mmol M^+ /kg). Adsorption of SDBAC in an amount greater than the ECEC value is attributed to the formation of a second layer on the mineral surface. Nevertheless, the ion exchange reaction is favored by increasing temperature of the suspension. Sullivan¹⁴ investigated the adsorption of HTA-Br onto a zeolite surface and measured the Br^- ions in solution to distinguish between monolayer sorption *versus* bilayer and admicelle sorption. They found little Br^- sorption at treatment levels up to 100 % of the ECEC. At levels above the ECEC, the Br^- sorption increased sharply and was nearly linear with HTA sorption.

TABLE II. The content of the exchanged cations in the filtrate after surfactant modification

SDBAC added, mmol/kg of zeolite	Content of inorganic cations in the filtrate, mmol M^+ /kg zeolite			
	CZ-CS	WZ-CS	CZ-WS	WZ-WS
50	46	46	46	46
75	46	65	75	75
100	46	63	77	74
150	45	50	67	72

In a controlled humidity system, the results of water adsorption onto organo-zeolite sample (group IV – temperature of the suspension was 90 °C) with different surfactant loadings are presented in Fig. 3.

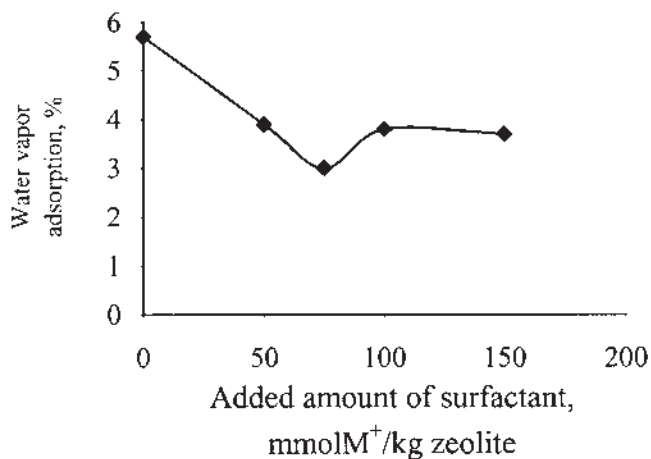


Fig. 3. Adsorption of water vapor on different SDBAC loaded organo-zeolites.

The adsorption of water vapor decreased linearly with increasing surfactant loading up to 5 mmol/kg, when a minimum on the adsorption curves can be observed (Fig. 3). Sample Z 0 adsorbed 5.7 mass %, whereas the sample OZ 75 retained 3.0 mass % of water vapor. It was expected that this sample would be the most hydrophobic because of the monolayer coverage of its surface. With loadings above 75 mmol/kg, the water adsorption increased, which could be ascribed to an

peak at 278 °C for the surfactant) is the most intensive and increased with increasing surfactant loading. The shoulder at 277 °C, which corresponds to the oxidation of SDBAC, is an indication of physisorbed SDBAC.

IR spectra of the unmodified sample and OZ samples with different SDBAC loadings are presented in Fig. 5.

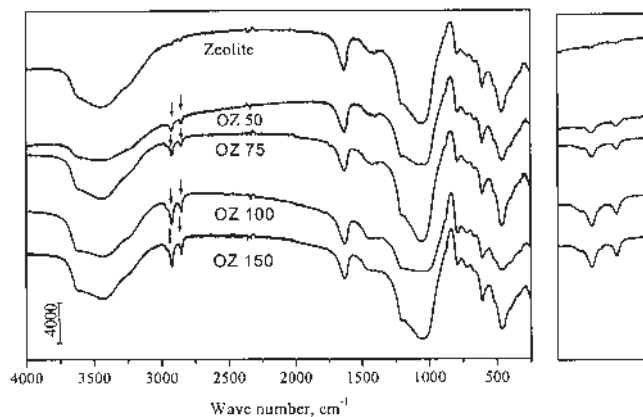


Fig. 5. IR spectra of the organo-zeolite samples.

The organo-zeolites, in contrast to the unmodified zeolite, have two intense bands around 2850 and 3000 cm^{-1} , which are assigned to asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibration of C-CH₂ of the alkyl chain, respectively.^{26,27} The intensities of these peaks increased with increasing surfactant loading. The

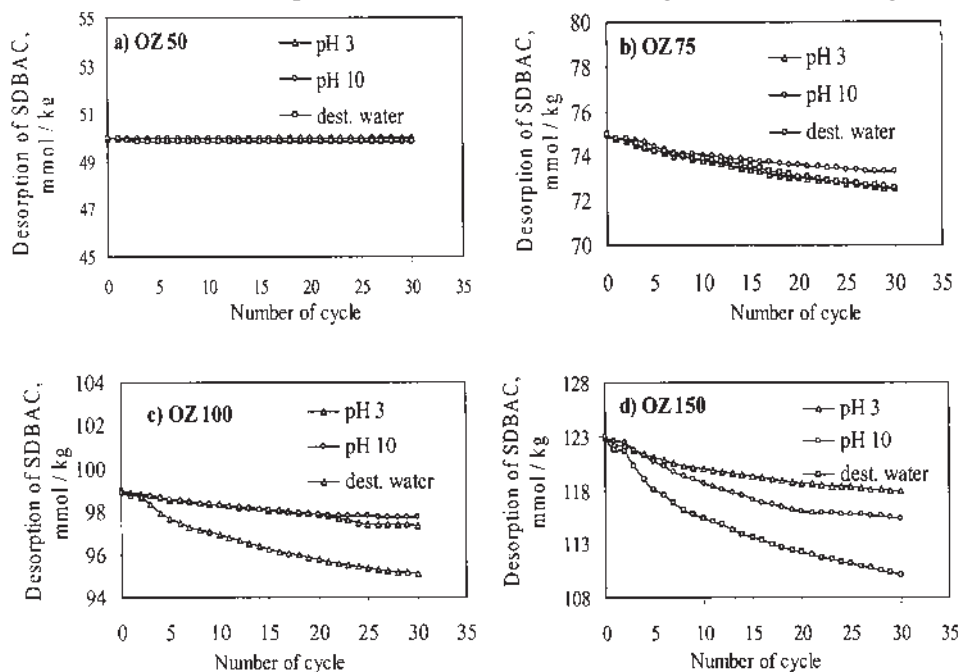


Fig. 6. Desorption of SDBAC in the treatment with buffer solutions (pH 3 and 7) and distilled water.

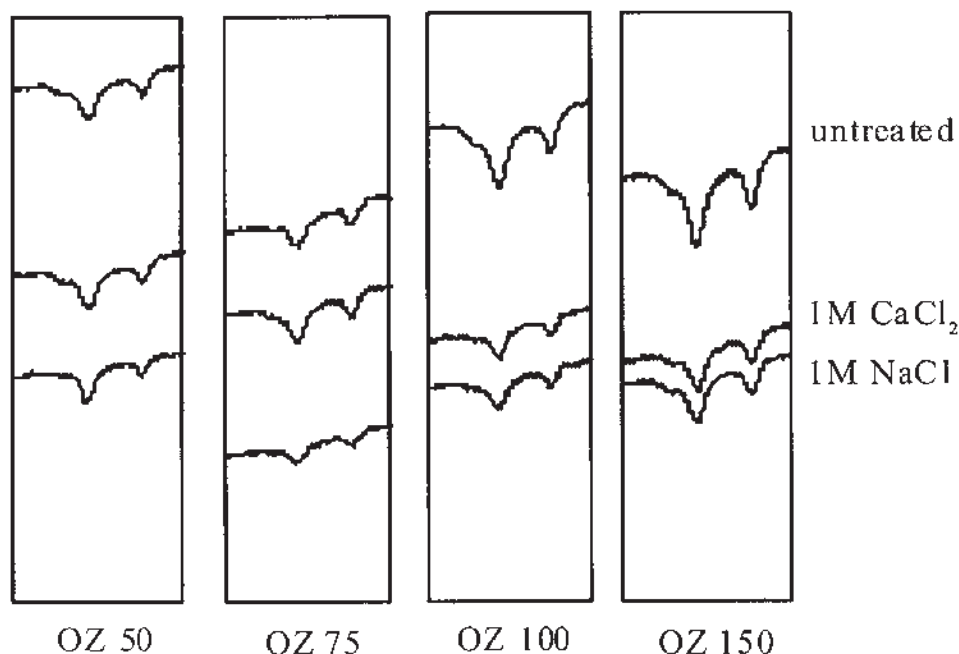


Fig. 7. IR spectra of organo-zeolites treated with 1M NaCl and CaCl_2 for 30 days.

structure sensitive bands ($400\text{--}1400\text{ cm}^{-1}$) are not affected by the surfactant treatment. The strong band appearing at around 1650 cm^{-1} due to the bending mode of water is weaker for the organo-zeolites than for the unmodified zeolite. The weakening of this band can be ascribed to an intensification of the hydrophobic characteristics of the organo-zeolite samples, which is in agreement with the results for the adsorption of water vapor.

The chemical stability of the OZs was investigated by treatment with buffer solutions of pH 3 and 7, distilled water and aqueous 1 M solutions of NaCl and CaCl_2 . The results for the amount of SDBAC released during treatment with the buffer solutions and distilled water are presented in Fig. 6.

As can be seen from Fig. 6a, the stability of the sample OZ 50 was not influenced by pH. The other OZ samples were the least stable in distilled water, probably due to the low ionic strength, which caused a weakening of the tail-tail interactions. At the end of experiment, more than 95 % of the initial adsorbed SDBAC remained on the sample after treatment with solutions of different pH. The largest amount of SDBAC was desorbed from the sample OZ 150, about 10 % after 30 days of treatments. Li and coworkers obtained similar results for the desorption of HTAB from OZs in laboratory batch and column studies.²⁸ Desorption of hexadecyltrimethylammonium chloride (HDTMAC) after 11 cycles of treatment with H_2O_2 and H_2O (low ionic conditions) was 15–17%. Tomasevic-Canovic *et al.* investigated the stability of OZs with surfactant loadings up to 50 mmol/kg, obtained

by wet and dry processes, after electrolyte treatments at pH 1, 7 and 10.¹⁵ The results confirmed that OZs are completely stable in the investigated pH region.

The standard titration method for the determination of SDBAC is not applicable in solutions of high ionic strength, such as 1M NaCl and 1M CaCl₂. After treatment of the OZs with these solutions for 30 days, the samples were analyzed by IR spectroscopy (Fig. 7).

As can be seen from Fig. 7, there were no significant changes in the peak position and intensities after treatment with solutions of high ionic strength for samples OZ 50 and OZ 75. With further increasing of surfactant loading (OZ 100 and OZ 150), the peak intensities were lower compared to those of the untreated sample. Although the amount of SDBAC desorbed can not be quantitatively determined, it can be seen that a large part of the SDBAC remained bound to the zeolite surface. Li and coworkers²⁸ showed that nearly 30 % of bound HDTMAC was desorbed after treatment with 1 M CsCl. However, such high concentrations of ions are rarely encountered, even in highly contaminated systems. These results clearly showed that the OZs having a monolayer coverage of the surface (up to 75 mmol/kg) are stable under different extreme conditions.

CONCLUSIONS

SDBAC sorbed onto the zeolite forms bilayer, with the first layer retained by cation exchange between inorganic cations, while the second layer is retained by hydrophobic bonding between the surfactant molecules. Maximal adsorption of 123 mmol M⁺/kg was achieved by warming surfactant solution and thermally treating the zeolite. The thermal behavior, as well as IR spectra, was greatly influenced by the amount of surfactant adsorbed. Thermal analysis and the results for the adsorption of water vapor indicated the formation of multilayers on the zeolite surface. The experimental results demonstrated that the OZs with surfactant loadings up to 75 mmol/kg exhibit long-term chemical stability over the pH region from 3 to 10 and under high ionic strength conditions. The largest amount of surfactant was desorbed from the sample OZ 150, about 10 %, after treatment with distilled water.

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ИЗВОД

ПОВРШИНСКА МОДИФИКАЦИЈА ЗЕОЛИТА И УТИЦАЈ рН И ЈОНСКЕ
ЈАЧИНЕ НА ДЕСОРПЦИЈУ АМИНАЈОВАН ЛЕМИЋ^а, СЕНИША МИЛОШЕВИЋ^а, МАРИЈА ВУКАШИНОВИЋ^б,
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Испитиван је утицај температуре на адсорпцију стеарилдиметилбензил-амонијум-хлорида (SDBAH) на природном зеолитском туфу. Максимална адсорбована количина SDBAH износила је 123 mmol/kg зеолита у случају термичког третирања зеолита (100 °C) и загревања раствора SDBAH (80 °C). Начин везивања између површинског модификатора и зеолита испитан је методама DTA, TG, DTG и IR анализа. Током постепеног загревања у атмосфери ваздуха, адсорбована органска фаза се оксидује што се манифестује егзотермним пиковима на DTA кривама. Адсорпција водене паре опада са порастом садржаја органске фазе до вредности 75 mmol/kg, што се може приписати повећању хидрофобности узорака органско-зеолита. Са даљим повећањем садржаја органске фазе, адсорпција водене паре је интензивнија. У раду је испитана десорпција SDBAH са органско-зеолита при различитим рН вредностима и јонским јачинама водених раствора. Резултати су показали да су органско-зеолити са садржајем SDBAH до вредности 75 mmol/kg зеолита стабилни у свим примењеним условима.

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