



# Uranium sorption on bentonite modified by octadecyltrimethylammonium bromide

Marek Majdan<sup>a,\*</sup>, Stanisław Pikus<sup>a</sup>, Agnieszka Gajowiak<sup>a</sup>, Dariusz Sternik<sup>a</sup>, Emil Zięba<sup>b</sup>

<sup>a</sup> Maria Curie Skłodowska University, Faculty of Chemistry, 20-031 Lublin, Poland

<sup>b</sup> Catholic University of Lublin, SEM Laboratory, 20-718 Lublin, Poland

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## ABSTRACT

The sorption of U(VI) on octadecyltrimethyl-bentonite was investigated at the pH values of the aqueous phase ranging from 3 to 10 and the concentrations of U(VI): 0.1–1 mmol/dm<sup>3</sup>. The concentrations of alkylammonium cation in bentonite were increased from 21% to 150% of CEC (cation exchange capacity). It was determined that the sorption of U(VI) on modified bentonite, i.e. the distribution constant –  $K_d$  decreases with the percent of mineral modification until it attains a minimum at 76% of CEC and then increases again. The effective sorption of U(VI) was found to be in the pH range: 6–10 for the modified bentonite and was explained as the consequence of U(VI) anionic hydroxy complexes sorption.

Both FT-IR and XRD spectra of the modified bentonite were analyzed and provided arguments for the existence of surfactant cations in the form of monolayer and bilayer in the interlamellar space of bentonite. In turn the luminescence spectra of bentonite suspensions, i.e. their character at different values of pH, proved the existence of hydroxide-like planar polymeric U(VI) species in the bentonite phase at pH 9.

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## 1. Introduction

The occurrence of radioactive uranium in soil, rocks, groundwater [1,2] due to its radioactivity and toxicity, is a serious problem from the environmental viewpoint. Research concerning uranium chemical toxicity began in the mid-twentieth century and since then it has been known, that like many other heavy metals, such as lead, chromium, nickel and mercury, uranium presence in the environment can be hazardous to health. While many studies have focused only on the possibility of kidney damage, several papers have emphasized other, more troublesome effects of uranium toxicity. In particular, cellular and animal studies have shown that uranium is a kidney toxin, neurotoxin, immunotoxin, mutagen, carcinogen and teratogen [3–6].

In turn, the main radiological hazard from uranium is alpha radiation. When inhaled or ingested, alpha radiation is the most damaging form of ionising radiation [7].

The sorption of metal ions on natural sorbents such as: rectorite [8], montmorillonite [9], attapulgite [10], bentonite [11] starts to play a very important role in the environmental remediation. Several investigations have been completed concerning the elimination of U(VI) from the aqueous environment using different sorbents [12–18]. Among these studies smectites have been con-

sidered and have been found as effective in U(VI) sorption [19] due to their high cation exchange capacity and high specific surface area. This property of smectites, especially montmorillonite, was exploited in the construction of reactive barriers or preparation of backfilling materials [20–22] preventing from the U(VI) emission to the groundwater and soil from the radioactive waste storage tanks. It is worth of mentioning the removal of uranium from contaminated ground water using zero valent iron [23], which is currently under evaluation at several U.S. Department of Energy (DOE) facilities. In this method uranium removal occurs via adsorption onto iron corrosion products and by reduction to less soluble valence states by reactions with elemental iron.

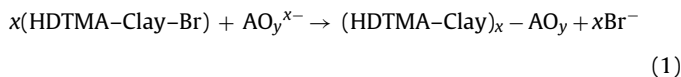
Relatively minor attention is paid to the U(VI) sorption on smectites modified by large organic cations, so-called organoclays [24]. The incorporation of a large organic cation into the clay structure changes its hydrophilic properties to hydrophobic. For this reason, the organoclay is a hybrid material, i.e. it is capable of sorbing organic contaminants, such as aliphatic or aromatic hydrocarbons [25] and anions, such as  $I^-$ ,  $TcO_4^-$  present in the nuclear waste [26,27], together with cations, i.e.  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Ni^{2+}$ ,  $UO_2^{2+}$  [28,29]. Apart from that due to the hydrophobicity of clay surfaces, filtration or air sparging/flotation processes of organoclay (loaded with U(VI)) suspensions can occur more readily when compared with those related to the unmodified clay.

The mechanism of the anion sorption on organoclays can be explained through the electrostatic interaction between the respective anions and the positively charged bilayer of surfactant cations, formed as a result of Van der Waals interaction between

\* Corresponding author. Tel.: +48 81 5375729; fax: +48 81 5333348.

E-mail addresses: [marek@hermes.umcs.lublin.pl](mailto:marek@hermes.umcs.lublin.pl), [m052004@yahoo.com](mailto:m052004@yahoo.com) (M. Majdan).

alkyl chains present in their structure. The best example for that phenomenon was reported by Li and Bowman [30] in their work concerning the sorption of nitrates, chromates and arsenates on the kaolinite modified by HDTMA (hexadecyltrimethylammonium bromide). The authors established an ion-exchange character of anions sorption, i.e. replacement of  $\text{Br}^-$  ions bound by means of the bilayer of  $\text{HDTMA}^+$  cations by anions according to the reaction:



where A is N, Cr or As.

The positively charged surfaces of organokaolinite are the result of the surfactant bilayer formation, which was supported by a 2:1 ratio of HDTMA adsorbed to the counterion and by positive electrophoretic mobility measurement [31,32].

Predicting the future storage and transport of uranium in the contaminated environments needs the description of the processes determining the distribution of uranium between the aqueous and solid phases. Therefore we have recently described the U(VI) sorption changes upon the modification of bentonite by hexadecyltrimethylammonium bromide (HDTMA) [24].

In this work we decided to carry on the research by modifying the bentonite with octadecyltrimethylammonium bromide (ODTMA). Firstly, we tried to confirm our model for sorption of U(VI) based on the molar fractions of hydroxycomplexes in the aqueous phase. Secondly, we tried to introduce a new element to the research describing quantitatively the change of U(VI) sorption percentage with its initial concentration in the aqueous phase. This research problem is often found in the literature when discussing metal sorption isotherms. However, such an approach to the problem is purely theoretical and contributes little to the practice. What is the most interesting and intriguing is that we have selected ODTMA surfactant since we have expected to find a significant difference between ODTMA- and HDTMA-bentonite, as the lengths of the alkyl chains are 27.8 and 25 Å for ODTMA and HDTMA cations respectively [33,34], hence the delamination of the bentonite structure should be a little stronger in the ODTMA case and also sorption of U(VI) should be different in comparison with the HDTMA case.

## 2. Materials and methods

### 2.1. Materials

Octadecyltrimethylammonium-bentonite (ODTMA-bentonite) was prepared from sodium bentonite (marked as bNa) according to the procedure given in our recent paper, related to HDTMA-bentonite [24]. The raw sodium bentonite was delivered by Sigma Aldrich, and was converted to bNa bentonite by equilibration with NaCl (Sigma Aldrich 99.99% purity) solution. The 1 g samples of bNa were equilibrated using a mechanical shaker with 100 cm<sup>3</sup> of 1:1 aqueous solutions/ethanol solutions of octadecyltrimethylammonium bromide (ODTMA-Br, Sigma Aldrich, 98% purity) for 4 h. at 60 °C. The initial concentrations of ODTMA-Br in the aqueous phase were: 0.0014, 0.0028, 0.0042, 0.0056, 0.007, 0.0084, 0.0098, 0.0112, 0.0126 and 0.0140 mol/dm<sup>3</sup>. After filtration and washing twice with hot water, the solid residues were dried in air, powdered in the agate mortar and passed through a 0.1 mm sieve. The concentration of C in the 2 mg samples was determined using the Perkin Elmer 2400 C H N analyzer. The molar concentration of ODTMA<sup>+</sup> cation in the samples  $c_{\text{ODTMA}}(\% \text{CEC})$ , referred to the number of ODTMA<sup>+</sup> moles per 1 g of the inorganic part of the samples, was calculated

according to the formula:

$$c_{\text{ODTMA}}(\% \text{CEC}) = \frac{100(1/\text{CEC})(n_c/21)}{[1 - (n_c/21)M_{\text{ODTMA}^+}]} \quad (2)$$

where  $n_c$  denotes the number of C moles in 1 g of the sample,  $\text{CEC} = 7.9 \text{ mmol/g}$  is the cation exchange capacity of the bentonite determined by cobalthexamine complex method [35], whereas  $M_{\text{ODTMA}^+}$  is the molecular mass of ODTMA<sup>+</sup> cation (312.6 g). The obtained ODTMA-bentonite samples were marked as: b21, b37, b57, b76, b91, b100, b106, b112, b134, b150 in accordance with the fractions of the CEC value.

### 2.2. Uranium (VI) sorption

Uranium (VI) sorption on ODTMA-bentonite (b21...b150; 0.1 g samples) was conducted according to the procedure given by Majdan et al. [24]. As an aqueous phase (100 cm<sup>3</sup>) the solutions of uranyl acetate (Lachema n.p. Brno, p.a.) were used. The detailed concentration of U(VI)  $c_{\text{in}}$  in the initial solutions, ranging from 0.1 to 1 mmol/dm<sup>3</sup> was determined by the Arsenazo III method [36]. A mechanical shaker was used for the equilibration of phases maintaining 150 oscillations/min. The temperature of 23 °C and 6 h of shaking time were maintained during all sorption experiments. In the final phase solutions were filtered, centrifuged and the U(VI) concentration in the equilibrium phase  $c_{\text{eq}}$  was determined. The values of U(VI) concentrations in the bentonite phase and its distribution constants  $K_d$  were found from the simple equations:

$$c_b = \frac{(c_{\text{in}} - c_{\text{eq}})V}{m} \quad (3)$$

$$K_d = \frac{c_b}{c_{\text{eq}}} \quad (4)$$

where  $V$ ,  $m$  are the volume of the aqueous phase (in dm<sup>3</sup>) and the mass of the sample (in g). The pH of the aqueous phases was controlled using a combined glass electrode connected to the pH-meter (CX-731 type, Elmetron Co.).

The standard error of  $K_d$  determination, based on triple measurements, was within 15%.

### 2.3. XRD analysis

X-ray diffraction powder measurements were performed using a conventional DRON-3 diffractometer (Russia). The conditions of these measurements were as follows: radiation, Cu K $\alpha$ ; wavelength discrimination, Ni filter, pulse height analyzer; detector, scintillation; divergence slit, 0.3°; receiving slit, 0.15°; range of  $2\theta$ , 10–90°; step size, 0.02°; count time per step, 20 s; calibration standards, SRM640/NIST.

### 2.4. FT-IR spectrograms

The FT-IR spectra of ODTMA-bentonite samples were recorded in the transmission mode at room temperature by means of the 1725X Perkin Elmer instrument using the KBr pellet technique (1:20) with the resolution 2 cm<sup>-1</sup>. The KBr was dried at 200 °C for 24 h, then 560 mg KBr was homogenized with the bentonite sample in a ball grinder (produced by Narva Brand-Erbisdorf, Germany). The tablets (radius 1 cm, thickness 0.1 cm) were prepared using the hydraulic press.

### 2.5. Thermal decomposition spectra

Thermogravimetric analysis was performed using a derivatograph Q-1500D (MOM, Hungary) with simultaneous recording of TG, DTG and DTA curves in relation to temperature and time under

quasi-isothermal conditions (heating rate: 10 °C/min, temperature range: 20–900 °C, sample mass: 100 mg).

## 2.6. Luminescence spectra

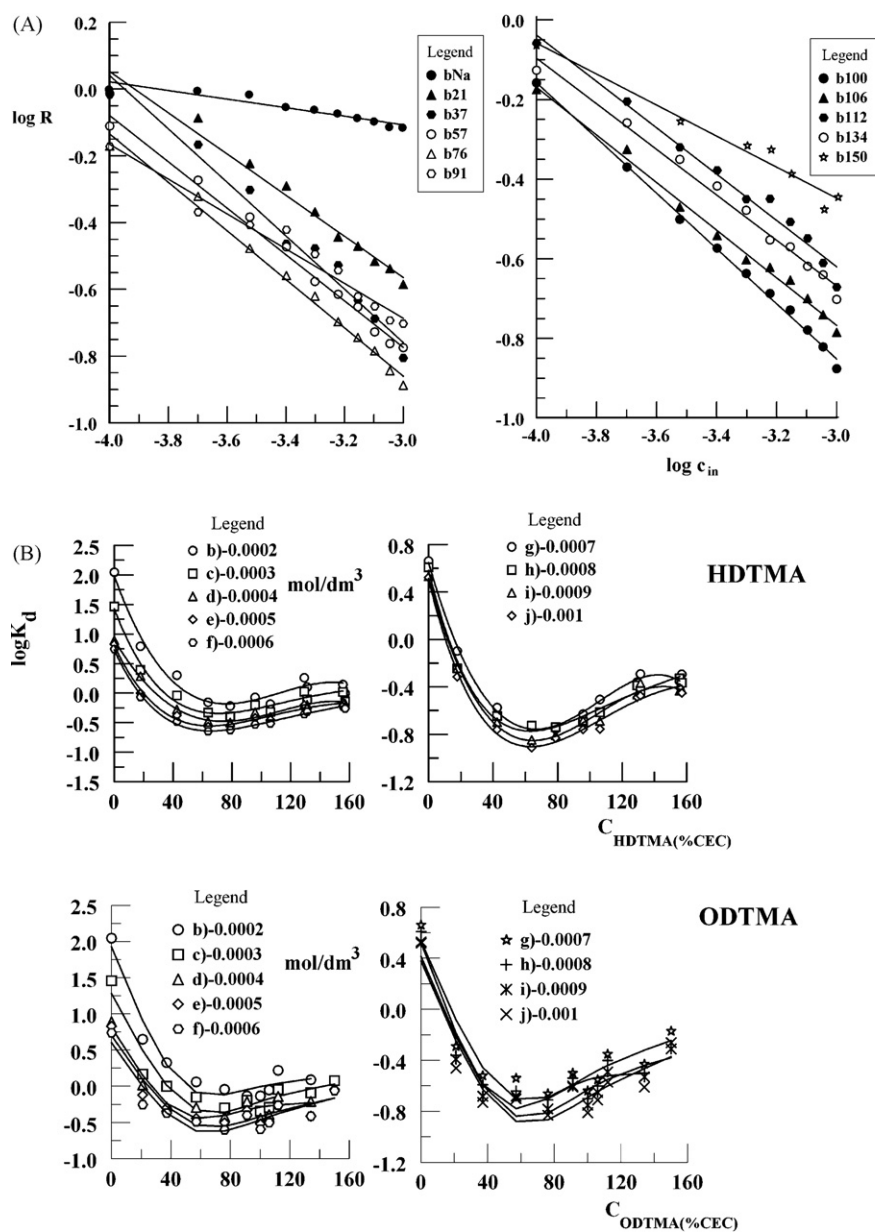
The luminescence spectra of the aqueous/bentonite suspensions were recorded using the FP-6300 Jasco spectrofluorometer, which was equipped with the Xe lamp as a light source, monochromator with holographic grating (1500 grooves/mm modified Rowland mount), siliconphotodiode, photomultiplier tube.

The suspensions were prepared by equilibration of 50 cm<sup>3</sup> of 0.1 mmol/dm<sup>3</sup> of uranyl acetate solution with 0.05 g of b100 for 2 h at room temperature using a magnetic stirrer (Cole Parmer Co., model 4802-02). The equilibrium pH of the solution was adjusted to 5 and 9 by NaOH in separate sample suspensions, whereas the

concentration of U(VI) in the solid phase was found from the difference between the initial and equilibrium concentrations of U(VI) in the aqueous phase.

## 2.7. Scanning electron microscopy measurements

The chemical composition of the bentonite samples in 50 randomly selected sites of the surface was determined by the standardless scanning electron microscopy method (SEM) using a microscope LEO SEM 1430 VP with the EDX detector. The concentrations of C, O, Na, Mg, Al, Si, K, Ca, Fe, U were determined in 50 randomly selected points on the bentonite surface. The electron beam penetrated the samples for about 1 μm. The concentrations of particular elements were found based on the energy-dispersive spectra, EDX.



**Fig. 1.** The influence of U(VI) initial concentration and bentonite modification on the U(VI) sorption. (A) The change of U(VI) removal  $\log R$  depending on the initial concentration in the aqueous phase  $\log c_{in}$  ( $c_{in}$  in mol/dm<sup>3</sup>; temperature 23 °C, shaking time 6 h, aqueous phase volume 100 cm<sup>3</sup>, adsorbent mass 0.1 g, equilibrium pH 4.8–5). (B) The change of distribution constants  $K_d$  of U(VI) between the aqueous and bentonite phases depending on the surfactant concentration in the bentonite phase (the numbers denote the initial concentration  $c_{in}$  of U(VI) in mol/dm<sup>3</sup>; concentration of surfactant  $C_{ODTMA} (\%CEC)$  related to cation exchange capacity of mineral; the HDTMA case was taken from Ref. [24]).

**Table 1**  
Parameters of the dependence:  $\log R$  vs.  $\log c_{in}$ .

Bentonite	Coefficients of the model equation: $\log R = b + a \log c_{in}$	$r^2$	$c_b$ , mmol/g for $c_{in} = 0.1$ – $1$ mmol/dm <sup>3</sup>	$R$ , %
bNa	$a = -0.13$ ; $b = -0.49$	0.952	0.1 ( $c_{in} = 0.1$ ) 0.77 ( $c_{in} = 1$ )	100 77
b21	$a = -0.62$ ; $b = -2.41$	0.99	0.1	100
b37	$a = -0.80$ ; $b = -3.16$	0.987	0.26 0.096 0.156	26 96 16
b57	$a = -0.69$ ; $b = -2.86$	0.995	0.077 0.168	77 17
b76	$a = -0.73$ ; $b = -3.03$	0.996	0.067 0.13	67 13
b91	$a = -0.52$ ; $b = -2.25$	0.981	0.067 0.198	67 20
b100	$a = -0.69$ ; $b = -2.63$	0.998	0.0695 0.133	70 13
b106	$a = -0.60$ ; $b = -2.56$	0.996	0.067 0.164	67 16
b112	$a = -0.58$ ; $b = -2.36$	0.99	0.087 0.21	87 21
a134	$a = -0.57$ ; $b = -2.38$	0.994	0.075 0.199	75 20
b150	$a = -0.39$ ; $b = -3.73$	0.98	0.085 0.354	85 35

### 3. Results and discussion

#### 3.1. The change of U(VI) removal depending on initial concentration

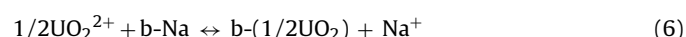
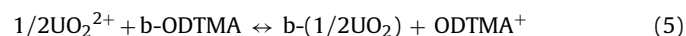
Fig. 1 (part A) includes the changes of U(VI) removal  $\log R$ , defined as  $\log c_b/c_{in}$  (where  $c_b$  is the U(VI) concentration in the ODTMA-bentonite phase), depending on the initial concentration of U(VI)  $\log c_{in}$  in the aqueous phase. There is an evident decrease of U(VI) removal with its initial concentration as a result of gradual reduction of the active sorption sites number in the sorbent structure. The slope of line representing the dependence  $\log R$  vs.  $\log c_{in}$ , characteristic of sodium bentonite, is lower than that for the remaining forms of modified bentonite. There is only a small change of removal  $R$  from 100% to 77% for bNa with  $c_{in}$  rise from 0.1 to 1 mmol/dm<sup>3</sup> at approximately constant initial pH values of the aqueous phase ( $pH_{in} = 5$  and 4.8 respectively), contrary to sudden drop of  $R$  values from 100% to 26% for b21 (Table 1). This fact is a consequence of the obstruction in  $UO_2^{2+}$  ions exchange with the spaciouly extended surfactant cations ODTMA<sup>+</sup>, entrapped in the interlamellar space of bentonite contrary to the ease of exchange of  $UO_2^{2+}$  with  $Na^+$  ions loosely bound by negatively charged clay framework. Moreover, the drastic change of the above mentioned slope when bNa is compared with b21 is the evidence for the blocking of the entrance to the mineral pores and therefore of screening of active sorption sites of bentonite by spaciouly extended surfactant cations.

Table 1 shows also the concentrations  $c_b$  of U(VI) in the bentonite phase for the lowest and highest initial concentrations  $c_{in}$ , i.e. for 0.1–1 mmol/dm<sup>3</sup>. In fact, there is an evident decrease of the maximum in  $c_b$  values when bNa is compared with b76 from 0.77 to 0.13 mmol/g. The sorption capability of bentonite in relation to U(VI) decreases, but it is still sufficient for elimination of U(VI) from groundwaters, where its concentration in different sites was found to be in the range from a few to several hundred of  $\mu\text{g}/\text{dm}^3$  [5,37].

#### 3.2. Surfactant loading influence on U(VI) sorption

Fig. 1 (part B) presents the change of the distribution constant  $\log K_d$  of U(VI), defined as  $\log c_b/c_{eq}$  (where  $c_{eq}$  is the equilibrium concentration of U(VI) in the aqueous phase), between the aqueous and bentonite phases with the percentage of bentonite modifica-

tion, i.e. %CEC. For comparative purposes, analogical change for HDTMA-bentonite is included. One can observe the drop of  $\log K_d$  values to  $-0.8$  both for HDTMA- and ODTMA-bentonite and its further increase to  $-0.4$  value. The drop in  $\log K_d$  values is the result of the decrease of mobile  $Na^+$  ions concentration in the bentonite with the percentage modification increase. For ODTMA-bentonite, when compared with HDTMA-bentonite, the micelles formation, Van der Waals interaction among the alkyl chains of ODTMA cations and between them and the clay framework is a little stronger [34], but not very much; otherwise the visible difference in  $\log K_d$  of U(VI) for HDTMA- and ODTMA-bentonite would be observed. For both cases an evident obstacle in the replacement of HDTMA<sup>+</sup> and ODTMA<sup>+</sup> by  $UO_2^{2+}$  cations is observed. The increase of  $\log K_d$  values, visible at 64% and 76% of CEC for HDTMA- and ODTMA-bentonite respectively, is as we mentioned earlier [24]: the result of increase of interlamellar distance  $d_{001}$  bentonite, easier penetration of its interlamellar region by  $UO_2^{2+}$ ,  $UO_2(OH)^+$  or  $(UO_2)_3(OH)_5^+$  ions and in consequence shift of their equilibrium exchange reactions with  $Na^+$  surfactant cations to the right, according to the scheme:



where the symbol  $b$  refers to the negatively charged bentonite framework.

The idealized sorption process of U(VI) on bentonite is given in Fig. 2. For the surfactant loadings larger than 76% of CEC the “detachment” of ODTMA<sup>+</sup> ions, forming the bilayer, from the bentonite framework is easier when compared with the case of surfactant loadings lower than 76% of CEC. Therefore the earlier mentioned increase of  $\log K_d$  values of U(VI) is observed.

We have analyzed the XRD patterns, FT-IR and thermal decomposition spectra of bentonite samples to better understand the state of the surfactant in the bentonite structure.

Fig. 3 presents the summary of XRD analysis of the bentonite samples. The interlamellar distance  $d_{001}$  was calculated based on the XRD patterns. One can notice the increase of the  $d_{001}$  values from 10.85 Å (for bNa) to 19.2 Å (for b150). According to Xi in ODTMA-montmorillonite with the surfactant loading from 20% to 60% of CEC, the surfactant cations form a lateral-monolayer in the interlamellar space of mineral and at point 60% of CEC show the transition status varying from the lateral-monolayer to the lateral bilayer arrangements [38,39], similarly to HDTMA case [40]. The

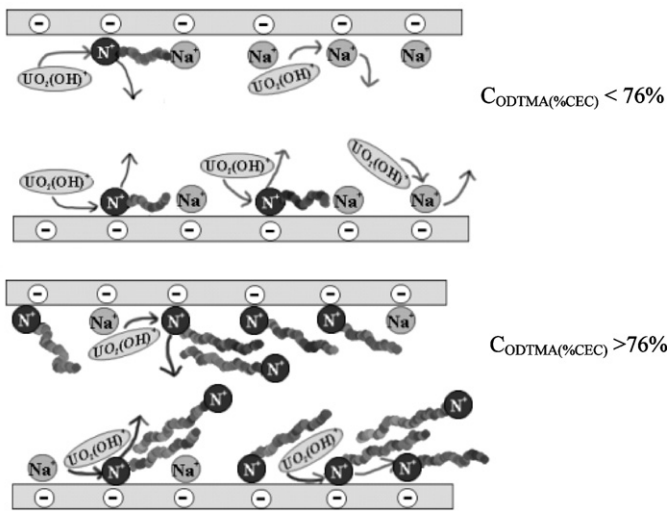


Fig. 2. The idealized view of U(VI) sorption on the modified bentonite.

interlayer surfactant in 80% CEC montmorillonite assumes arrangements of lateral bilayers. In connection with this one can conclude that the observed increase of  $\log K_d$  values of U(VI) at 76% of CEC in our experiment is the consequence of ODTMA cations bilayer formation.

The FT-IR spectra of bentonite (Fig. 4) show a remarkable downward shift of the bands attributed to the stretching vibrations C–H in CH<sub>2</sub> groups of the surfactant alkyl chains [32,39,41–43] with the increase of surfactant loading. The band attributed to asymmetric stretching vibration shifts from 2857 to 2851 cm<sup>-1</sup>, whereas that related to the symmetric stretching vibration changes its position from 2930 to 2924 cm<sup>-1</sup>. This is probably the consequence of the concentration increase of the surfactant cations appearing in their ordered *trans* form of their hydrocarbon chain and decrease of the concentration of *gauche* (disordered) conformers [44–47]. One can presume that for the concentration of the surfactant below 60% of CEC the arrangement of the surfactant is a lateral-monolayer form with *gauche* conformation, where the amine ions are situated

parallel to the interlayer and individually separated. For a larger concentration of surfactant, i.e. higher than 76% of CEC, the lateral-monolayer arrangement converts into the lateral bilayer.

The thermal decomposition spectra (derivative mass losses-DTG) of the bentonite (Fig. 5, part A) show the stepwise decrease of the dehydration temperature from 100 to 69 °C from bNa to b150 samples as a result of the rupture of hydrogen bonds between the water molecules under the influence of sparsely extended surfactant cations and consequently an easier release of water from the bentonite structure. At the same time the intensity of the peak related to dehydration decreases as a consequence of the decrease of water concentration in the bentonite samples. The peak at 304 °C is attributed to oxidation and decomposition of the surfactant [38,48]. The shift of its position to lower temperatures with the bentonite modification is the evidence for two kinds of surfactant cations, i.e. that bound via electrostatic forces by the negatively charged bentonite network and the other one interacting via Van der Waals forces with their partners in the lateral bilayers. The downward temperature shift of the peak at 689 °C, attributed to bentonite dehydroxylation, is the evidence for loosening of the bentonite structure when the surfactant cations penetrate the interlamellar space. The changes in the clay structure during the modification process are, however, not strong enough to damage the Si–O or Al–O bonds. We have not noticed any change of the molar ratio Si/Al with the surfactant concentration rise during inspection of the SEM EDX analysis results (Fig. 5, part B).

### 3.3. The pH influence on the U(VI) sorption

Fig. 6 represents the change of the concentration of U(VI) in the bentonite depending on the pH. The following equation, explained in our recent work [24], was used for the estimation of the role of different U(VI) hydroxycomplexes in its sorption:

$$\log c_b = \log [K0\alpha_{UO_2^{2+}} + K11\alpha_{UO_2(OH)^+} + K12\alpha_{UO_2(OH)_2} + K13\alpha_{UO_2(OH)_3^-} + K14\alpha_{UO_2(OH)_4^{2-}} + K35\alpha_{(UO_2)_3(OH)_5^+} + K37\alpha_{(UO_2)_3(OH)_7^-}] \quad (7)$$

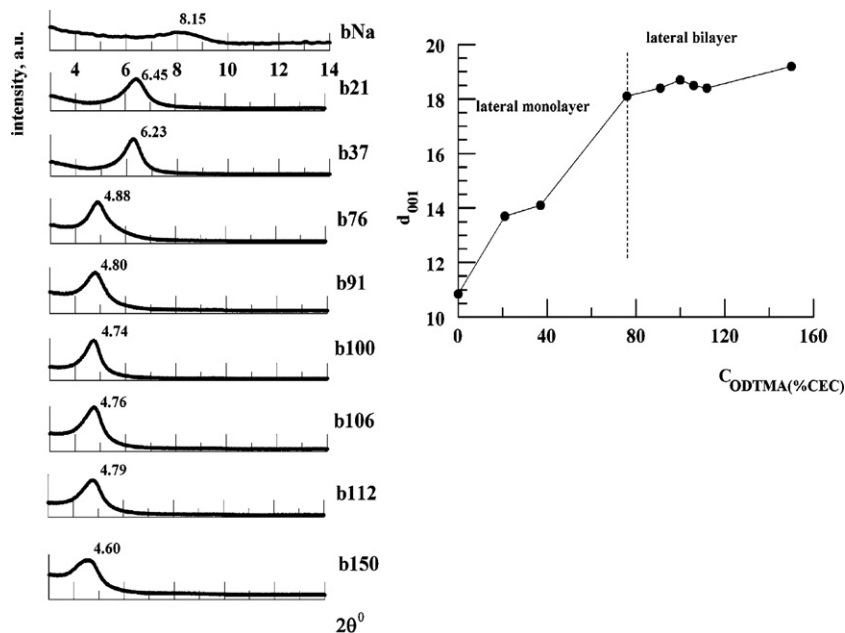


Fig. 3. The summary of XRD analysis of bentonite samples. Left: XRD patterns. Right: the change of interlamellar distance  $d_{001}$  with surfactant concentration.

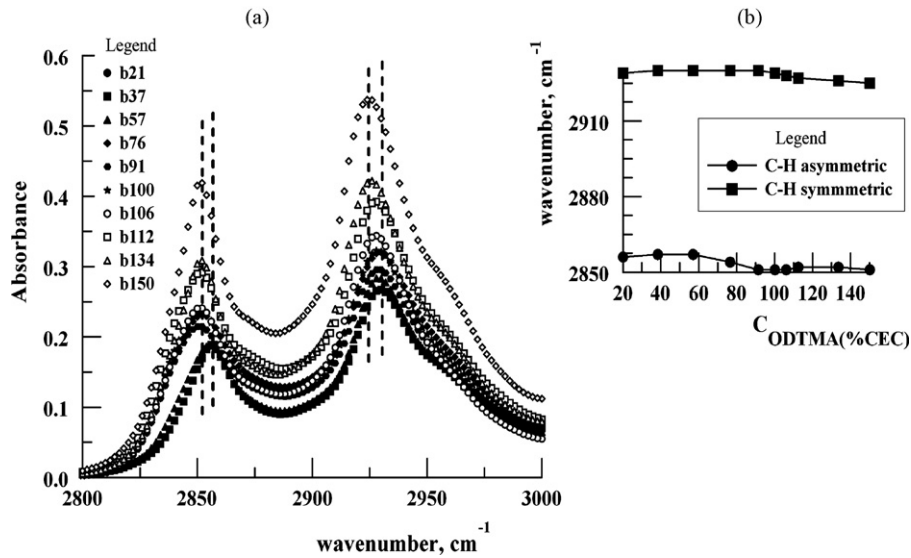


Fig. 4. The summary of FT-IR analysis of bentonite samples.

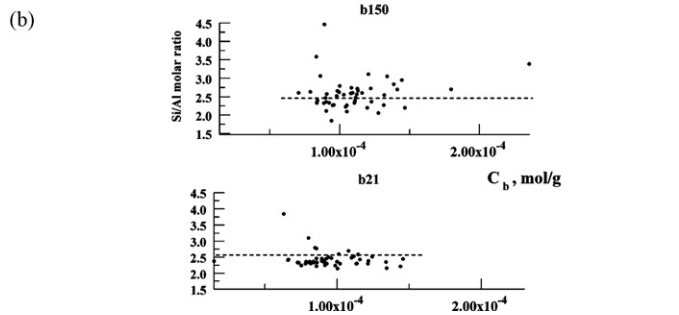
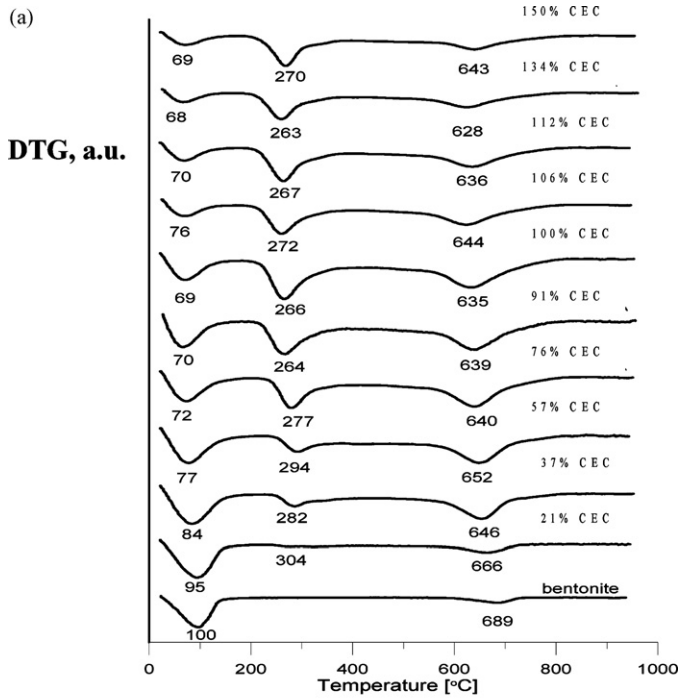


Fig. 5. The DTG spectra of bentonite samples (A) and the change of Si/Al molar ratio depending on the surfactant concentration in bentonite phase (B).

where the symbol  $\alpha$  refers to the molar fraction of the particular hydroxy complex of U(VI), calculated based on the stability constants of the U(VI) complexes using the Medusa software [49] and the PSI Plot program (Polysoftware International Inc.), whereas the symbol  $K$  represents the sorptive parameter of the particular complex in the aqueous phase, i.e. its influence on the U(VI) concentration  $c_b$  in the bentonite phase.

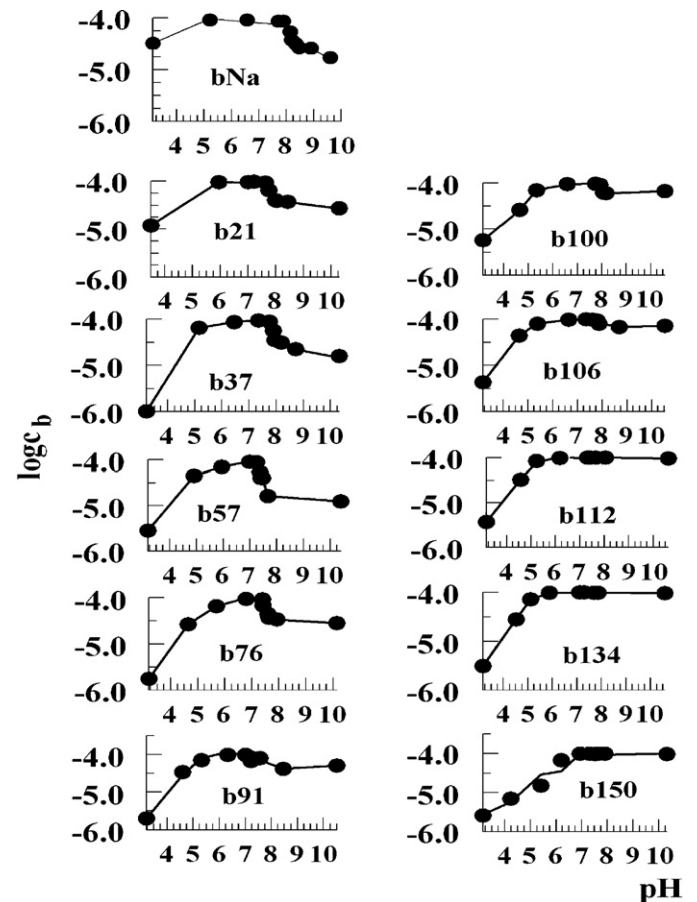


Fig. 6. The change of U(VI) sorption on bentonite depending on the pH (initial concentration of U(VI) 0.1 mmol/dm<sup>3</sup>, temperature 23 °C, shaking time 6 h, aqueous phase volume 100 cm<sup>3</sup>, adsorbent mass 0.1 g, the bNa case taken from Ref. [24]).

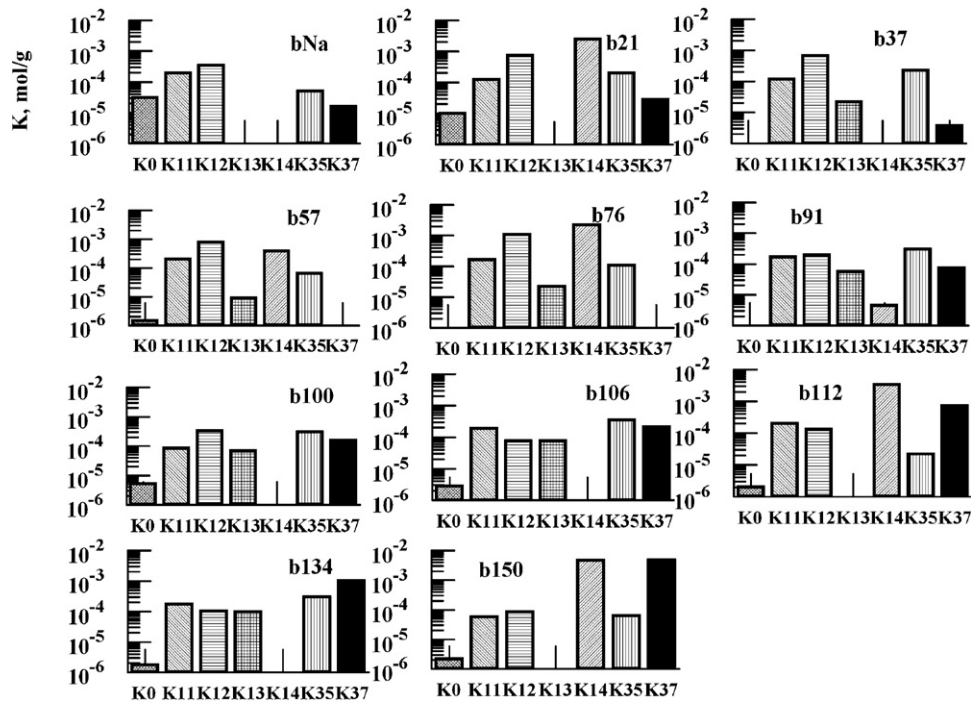


Fig. 7. The diagrams showing the sorptive parameters  $K$  of U(VI) species:  $\text{UO}_2^{2+}$ ,  $\text{UO}_2\text{OH}^+$ ,  $\text{UO}_2(\text{OH})_2$ ,  $\text{UO}_2(\text{OH})_3^-$ ,  $\text{UO}_2(\text{OH})_4^{2-}$ ,  $(\text{UO}_2)_3(\text{OH})_5^+$ ,  $(\text{UO}_2)_3(\text{OH})_7^-$  (K0, K11, K12, K13, K14, K35, K37 respectively) for different bentonite forms: bNa...b150.

The concentration  $[\text{UO}_2^{2+}]$  of the free uncomplexed  $\text{UO}_2^{2+}$  ions, necessary for the evaluation of molar fractions  $\alpha$  of particular complexes for different  $[\text{OH}^-]$  concentrations was found from:

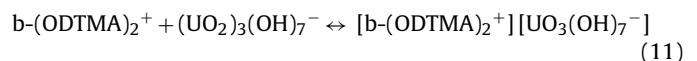
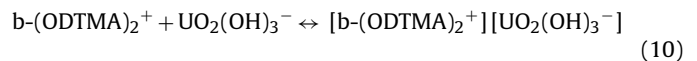
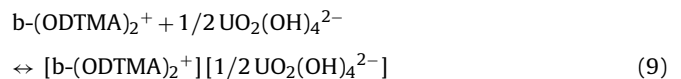
$$c_{\text{eq}} = [\text{UO}_2^{2+}] + \beta_{11}[\text{UO}_2^{2+}][\text{OH}^-] + \beta_{12}[\text{UO}_2^{2+}][\text{OH}^-]^2 + \beta_{13}[\text{UO}_2^{2+}][\text{OH}^-]^3 + \beta_{14}[\text{UO}_2^{2+}][\text{OH}^-]^4 + 2\beta_{11}[\text{UO}_2^{2+}]^2[\text{OH}^-] + 2\beta_{22}[\text{UO}_2^{2+}]^2[\text{OH}^-]^2 + 3\beta_{34}[\text{UO}_2^{2+}]^3[\text{OH}^-]^4 + 3\beta_{35}[\text{UO}_2^{2+}]^3[\text{OH}^-]^5 + 3\beta_{37}[\text{UO}_2^{2+}]^3[\text{OH}^-]^7 + 4\beta_{47}[\text{UO}_2^{2+}]^4[\text{OH}^-]^7 \quad (8)$$

The U(VI) acetate complexes were intentionally neglected. Using the Medusa software minor participation of  $\text{UO}_2(\text{CH}_3\text{COO})^+$  in the overall U(VI) concentration in the pH range: 2–6 and its lack for  $\text{pH} > 6$  for total  $[\text{UO}_2^{2+}] = 0.0001 \text{ mol/dm}^3$  was observed.

For all investigated ODTMA loadings of bentonite, b21–b150% of CEC, a good fit between the calculated and experimental values of  $\log c_b$  was found; the values of determination coefficients  $r^2$  were always higher than 0.98.

From Fig. 7 one can observe that irrespective of surfactant loading, i.e. from 21% to 150% of CEC, all investigated U(VI) complexes have a positive influence on  $\log c_b$  values. It means that apart from electrostatic forces between the negatively or positively charged bentonite surface and the cationic or anionic U(VI) hydroxy-complexes, the specific interaction between the amphoteric montmorillonite sites:  $>\text{AlOH}$ ,  $>\text{SiOH}$  and the uranyl hydroxy-complexes or probable formation of hydrogen bonds between the U(VI) complexed species and the bentonite surface may decide upon the U(VI) sorption. For example, the parameter  $K_{14}$ , characteristic of the anionic complex  $\text{UO}_2(\text{OH})_4^{2-}$ , appears in the diagrams for samples: b21, b57 with surfactant concentration far from the 100% of CEC. Therefore one can presume that it is bound via nonelectrostatic forces. A similar phenomenon can be observed for the  $\text{UO}_2(\text{OH})_3^-$  and  $(\text{UO}_2)_3(\text{OH})_7^-$  complexes. Their sorptive parameters:  $K_{13}$ ,  $K_{37}$  for the samples b21, b37, b57 appear before the charge reversal of bentonite surface. Of course, the increase

of the  $K_{37}$  parameter values for the samples: b91–b150 is a strong argument for the interaction of the  $(\text{UO}_2)_3(\text{OH})_7^-$  complex with the positively charged bilayer of the surfactant cations  $\text{b}-(\text{ODTMA})_2^+$  present in the interlamellar space of bentonite, responsible for the plateau in the course of the dependence  $\log c_b$  vs. pH for the samples: b112–b150. Certainly, it is not clear whether the ionic pair  $[\text{b}-(\text{ODTMA})_2^+][(\text{UO}_2)_3(\text{OH})_7^-]$  is formed, or the oligomeric complex  $(\text{UO}_2)_3(\text{OH})_7^-$  dissociates and the species:  $[\text{b}-(\text{ODTMA})_2^+][1/2 \text{UO}_2(\text{OH})_4^{2-}]$ ,  $[\text{b}-(\text{ODTMA})_2^+][\text{UO}_2(\text{OH})_3^-]$  are intercalated in the bentonite structure. This suggestion appears when we observe high  $K_{13}$  and  $K_{14}$  values in the case of the samples: b106, b112, b134, b150. Summing up, the most likely scenario of U(VI) anions sorption by ODTMA-bentonite is as follows:



In turn, the ion  $\text{UO}_2^{2+}$  has negligible influence on the U(VI) sorption on the modified bentonite. The value of  $K_0$  parameter is small for all observed mineral samples. One can conclude that it is a consequence of relatively stronger hydration of  $\text{UO}_2^{2+}$  ion in comparison with other U(VI) complex ions and its tendency to stay in the aqueous phase during the sorption process.

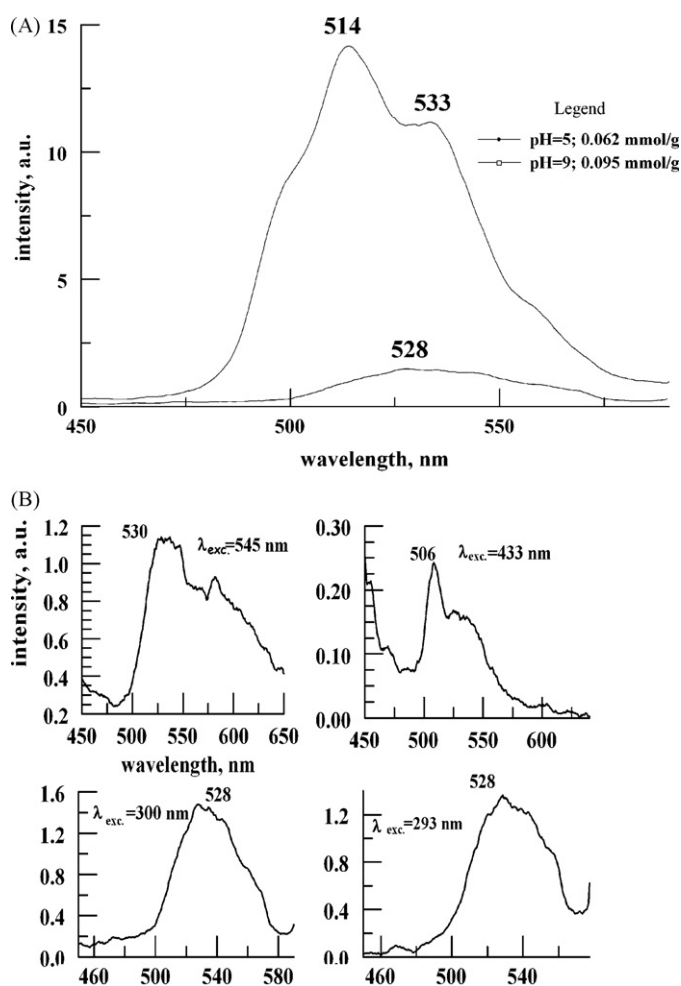
It is interesting that the neutral complex  $\text{UO}_2(\text{OH})_2$ , with its sorption parameter  $K_{12}$  in the range  $10^{-4}$  to  $10^{-3} \text{ mol/g}$ , independently of ODTMA loading, precipitates probably as a hydroxide-like polymeric species in the bentonite phase. The ionic products values:  $\text{pI} = -\log[\text{UO}_2^{2+}][\text{OH}^-]^2$  given in Table 2 are close to 22.46, the value of  $\text{UO}_2(\text{OH})_2$  solubility product [50].

**Table 2**

The ionic products  $pI = -\log[UO_2^{2+}][OH]^2$  referring to the aqueous phases equilibrated with the modified bentonite samples ( $c_{in} = 0.1 \text{ mmol/dm}^3$ , aqueous phase  $100 \text{ cm}^3$ , bentonite sample  $0.1 \text{ g}$ ).

Bentonite	pH	pI
b21	10.3	22.38
b37	10.4	22.36
b57	10.1	22.40
b76	10.5	22.30
b91	10.6	22.64
b100	10.5	22.84
b106	10.5	22.87
b134	10.6	23.77
b150	10.3	23.64

Fig. 8 (part A) shows the comparison of the U(VI) luminescence spectra in the bentonite suspensions for different equilibrium pH. It is easy to notice that the band in the spectrum for pH 9 is poorly structured when compared with the one for pH=5, which has two maxima at 514 and 533 nm. It means that the nearest surroundings of  $UO_2^{2+}$  ion in the complexes sorbed at pH 5 and 9 are completely different. A similar phenomenon was observed by Chrisholm–Brause for the U(VI) sorption on montmorillonite for the pH range: 3.5–5.8 [51] and was explained as a consequence of hydroxide-like planar polymeric species formation at higher pH, different from uranium hydroxide, i.e. from schoepite.



**Fig. 8.** The luminescence spectra of bentonite suspensions. (A) The case of b100 bentonite suspensions loaded with U(VI) at pH 5 and 9 (numbers denote the concentration of U(VI) in bentonite phase). (B) The case of b100 bentonite suspensions (loaded with U(VI)) for different excitation wavelengths.

However, the problem is more complicated since, in our opinion, at least two different hydroxy complexes of U(VI) in the sorbent phase are formed at pH=9. This conclusion is drawn from the observation that evidently different spectra for the U(VI) suspensions were observed, when different excitation wavelengths were applied (Fig. 8, part B). One can see the difference in the shape of the bands as well as in the location of peaks, i.e. they are placed at 528, 506, 530 nm for the excitation wavelengths: 293, 300, 433, 545 nm respectively.

#### 4. Conclusions

1. ODTMA-bentonite is characterized by large sorption affinity for U(VI) in a wide pH range, i.e. from pH 6 to 10, when compared with sodium bentonite, where the effective sorption is limited merely to 5–7 pH range. This is a result of the anionic complexes sorption; among them the sorption of  $(UO_2)_3(OH)_7^-$  is the most probable. Apart from anionic complexes, i.e.  $(UO_2)(OH)_3^-$ ,  $(UO_2)(OH)_4^{2-}$ ,  $(UO_2)_3(OH)_7^-$  species, the following U(VI) hydroxy species, present in the aqueous phase, have the influence on U(VI) concentration in the bentonite phase:  $UO_2^{2+}$ ,  $UO_2(OH)^+$ ,  $(UO_2)_3(OH)_5^+$ . They interact with modified bentonite through exchange with sodium or surfactant cations. The complex  $UO_2(OH)_2$  forms probably precipitate in the bentonite phase, but the stoichiometry and structure of the polymeric hydroxide-like species needs further investigation.

Further studies concerning the applicability of ODTMA-bentonite in the sorption of other anionic complexes of U(VI), especially those occurring in the groundwater:  $UO_2(CO_3)_2^{2-}$ ,  $UO_2(CO_3)_3^{4-}$ ,  $UO_2(HPO_4)_2^{2-}$  are necessary.

2. The decrease of U(VI) sorption with the bentonite percentage modification and its increase at the critical CEC point, very similar for ODTMA and HDTMA, is very interesting from the theoretical viewpoint. It is the evidence for a stepwise change in the configuration of surfactant cations arrangement in the interlamellar space of bentonite. Further studies concerning the influence of surfactant cations structure, i.e. the length of alkyl chains on U(VI) sorption change, are necessary. The unexpected similarity between the HDTMA- and ODTMA-bentonite in respect to U(VI) sorption may result from the fact that the stronger dehydration and delamination of the bentonite structure under the influence of surfactant cation with the longer alkyl chain are probably suppressed by the stronger Van der Waals interaction between the longer alkyl chains as well as the alkyl chains and the bentonite framework.
3. The evaluation of U(VI) sorption data using the straight line dependence:  $\log(R)$  vs.  $\log(c_{in})$ , instead of well known different kinds of sorption isotherms based on complex model equations, is very important from the practical viewpoint, since the possibility of easy prediction of U(VI) sorption is based on its initial concentration in the aqueous phase.

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