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Article in *Фізика і хімія твердого тіла* · March 2018

DOI: 10.15330/pcss.19.1.66-73

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The Kinetics of Adsorption Binding of Ba²⁺ Ions by Trimethylsilylated Silica

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It was established that incomplete substitution of free silanols of fumed silica surface on (CH₃)₃Si-groups leads to an increase in the ability of modified SiO₂ to adsorb Ba²⁺ cations from an electrolyte solution. Silica with 48.3% of trimethylsilyl (TMS) groups adsorbs 1.8 mmol·g⁻¹ of Ba²⁺ cations from 0.01 M BaCl₂ solution, that in 3 times more than the adsorption of these cations by unmodified silica.

It was found that the adsorption of cations by basic and modified silica is well described by the pseudo-second order Lagergren equation. The high adsorption activity of silica with chemisorbed TMS-groups is due to the formation of local regions with relatively large values of negative and positive electrostatic potentials in the vicinity of grafted TMS-groups.

Keywords: silica, silanols, chemisorption, trimethylsilyl groups, adsorption binding of ions.

Стаття поступила до редакції 02.02.2018; прийнята до друку 05.03.2018.

Introduction

Aerodispersed amorphous silica, obtained by combustion of silicon-containing substances (SiCl₄, CH₂SiCl₃) in air-hydrogen flame at 1100-1350°C, are used as adsorbents in medicine, biology, chromatography, carriers of active substances in catalysis, polymer fillers, thickening of liquids environments, etc. [1-5]. Fumed silica acquire new useful properties as a result of the chemical modification of their surface, in particular, due to incomplete substitution of their silanols (hydroxyls) on TMS (CH₃)₃Si-groups. The investigation of the effect of grafted (CH₃)₃Si-groups on the physicochemical properties of aerodispersed silica revealed that the change of the chemical state of the oxide material surface in such way increases its adsorption properties. Modified silica with 37.2 % of grafted TMS-groups binds a large amount of water – up to 5 g of H₂O per 1 g of SiO₂ [6]. The silica surface becomes especially active, i.e. adsorbs nonpolar molecules of methane and hydrogen when a hydration degree $h = 0.05$ (0.005 g of H₂O per 1 g of SiO₂). It was also found that the organosilica acquires lyophilic properties as a result of the substitution of 30-50 % of silanols on the TMS-groups [7]. In the aqueous medium, the interparticle interaction decreases and the interaction of the particles' surface with the molecules of the

aqueous medium increases. Modified silica suspensions have higher equilibrium viscosity compared to that of basic silica, moreover SiO₂ particles do not lose the ability to thicken the dispersed medium even when their fractal structure is destroyed by ultrasonic field.

At present, the search for materials that are capable to adsorb the heavy metal ions is being used to solve environmental problems. Since the new properties of trimethylsilylated silica are due to a change in the distribution of the electrostatic potential on its surface, it can be expected that chemical modification of the surface also increases SiO₂ activity as regards adsorption binding of metal ions in aqueous media.

The purpose of this work is to investigate the effect of incomplete trimethylsilylation of the silica surface on its ability to adsorb Ba²⁺ ions from the aqueous medium, as well as to study the kinetics of the binding of these ions of the basic and modified SiO₂.

I. Objects and methods

An aerodispersed product A-300, obtained by combustion of SiCl₄ vapor in a hydrogen-air flame at 1100-1350°C in industrial conditions, was as the basic silica for chemisorption of (CH₃)₃Si-groups on its surface [9, 10]. The specific surface of silica was 302 m²·g⁻¹, the

concentration of free silanol groups on its surface – 0.8 mmol·g⁻¹.

The trimethylethoxysilane (CH₃)₃SiOC₂H₅ (TMES) (Sigma-Aldrich, USA) was used as the precursor for silica modification. The chemical grafting of (CH₃)₃Si-groups was carried out as a result of contacting a modifier vapour with SiO₂ surface at 150-160°C. Small amount of acetic acid (as a catalyst) was added to the reactor to reduce the temperature of the chemisorption process.

The adsorbent mass was 20-30 mg and the BaCl₂ volume solution was 10 ml at measuring the adsorption value A_{eq} at adsorption-desorption equilibrium. The duration of interaction of the adsorbent with the electrolyte solution was 180 min. The initial concentration of Ba²⁺ ions in the solutions varied from 0.0025 to 0.1 mol·l⁻¹. The pH value of the electrolyte was ~ 7.0 at those concentrations.

The BaCl₂ solution concentration was 0.01 mol·l⁻¹ and the sorption duration varied from 1 to 180 min at studies of kinetics of Ba²⁺ ion binding.

The number of silanols and TMS-groups on SiO₂ surface was controlled by IR-spectroscopy using the Specord M-80 spectrometer (Carl Zeiss, Yena, Germany). The degree of SiO₂ modification θ (in percentages) was determined by the ratio of the optical density of the absorption band of free silanol groups 3750 cm⁻¹ in the spectrum of modified and basic silica using the formula:

$$q = 100 \left(1 - \frac{D}{D_0} \right), \quad (1)$$

where D_0 and D – the area of the absorption band 3750 cm⁻¹ in initial and modified SiO₂, respectively,

The hydrophilicity of basic and modified silica was determined by P. Rebinder's method. For this purpose, the specific heat of wetting of the material surface by polar and nonpolar solvents was measured [7] and the hydrophilicity coefficient β was calculated analytically by the formula:

$$b = \frac{Q_w}{Q_d}, \quad (2)$$

where Q_w and Q_d – heat of wetting of surface by water and decane, respectively. The heat of wetting of materials was measured using differential calorimeter DAC1.1A (EPSE, Chernogolovka). Calibration of the device was carried out by the thermal effect of KCl dissolving in an aqueous medium (18.6 ± 0.012 kJ·mol) at 20°C.

The adsorption ability of trimethylsilylated and basic silicas for binding of Ba²⁺ ions was determined by a method that involves mixing the material with the electrolyte solution of the appropriate concentration, keeping the mixture in a static mode at 20°C for 4 hours, and removing of the adsorbent from the solution by centrifugation. The equilibrium concentration of cations in the overprecipitate solution C_{eq} (mmol·l⁻¹) was determined by the method of complexometric titration [10, 11]. For this purpose, an ammonium buffer mixture NH₄Cl + NH₄OH and a few drops of 5 % alcohol

solution of eriochrome black T were added to the solution, then titration was performed by sodium edetate solution. The adsorption value A (mmol·g⁻¹) was calculated by the formula:

$$A = \frac{(C_{in} - C_{res})V}{m}, \quad (3)$$

where C_{in} and C_{res} – concentration of ions in the initial and residual solution, respectively; m – adsorbent mass, V – solution volume.

The distribution coefficient K_d (l·g⁻¹) of adsorbents was determined by the formula:

$$K_d = \frac{A}{C_{res}}. \quad (4)$$

The value of the distribution coefficient indicates the volume of solution from which 1 g of adsorbent is able to remove (bind) the entire amount of dissolved adsorbate.

II. Results and discussion

Complete substitution of silanols of pyrogenic silica surface on TMS-groups is used to obtain an organophilic product that is not wetted by water [5]. Experimental standards of modified silica containing 27.2, 37.2, and 48.3 % of chemisorbed (CH₃)₂Si-groups are denoted as M30, M40, and M50, respectively (Table 1).

Table 1

The hydrophilicity coefficient β and substitution degree of silanols on TMS-groups for explored standards

Standard	Substitution degree of silanols on TMS-groups, %	β
A-300	0	2.0
M30	27.2	1.6
M40	37.2	1.5
M50	48.3	1.4

The modified silica retains its hydrophilicity when replacing almost half of the SiO₂ particles' silanols on TMS-groups (standard M50). The hydrophilicity coefficient of this standard decreases from 2.0 to 1.4 compared with the basis silica A-300. The extrapolation of $\beta = f(\theta)$ dependence to the value $\beta = 1.0$ allows to determine that complete non-wetting of the silica surface takes place at ~ 80 % substitution of silanols on TMS-groups.

The adsorption indices of Ba²⁺ ions from 0.01 M BaCl₂ solution by explored standards of basic and modified silica are given in Table 2. The results of the studies confirm that the adsorption of Ba²⁺ ions increases with increasing of number of grafted TMS-groups.

The standard M50 adsorbs 1.8 mmol·g⁻¹ of Ba²⁺ cations, that in three times exceeds the adsorption rate of these ions by the unmodified standard A-300. Characteristically, the modification of silica also improves the distribution coefficient of the adsorbent. In particular, 1 g of the standard M50 is capable of

Table 2

Adsorption of Ba²⁺ ions from 0.01 M BaCl₂ solution by basic and modified adsorbents

Adsorbent	Adsorbate	Electrolyte	Adsorption, mmol·g ⁻¹	Distribution coefficient, l·g ⁻¹
A-300	Ba ²⁺	0.01 M BaCl ₂	0.59 ± 0.05	0.07
M30			1.2 ± 0.17	0.24
M40			1.7 ± 0.35	0.45
M50			1.8 ± 0.06	0.46

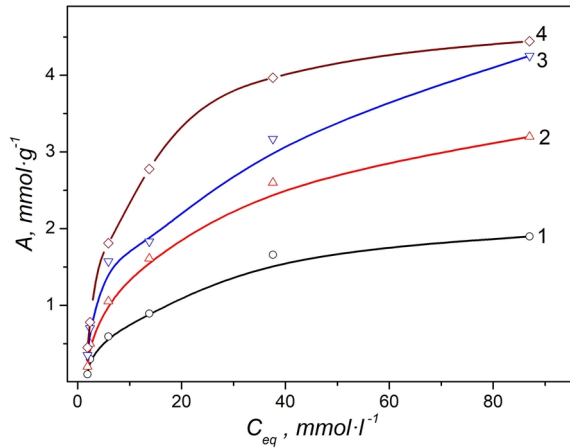


Fig. 1. Isotherms of adsorption of Ba²⁺ cations by basic silica A-300 (1) and modified silica M30 (2), M40 (3) and M50 (4).

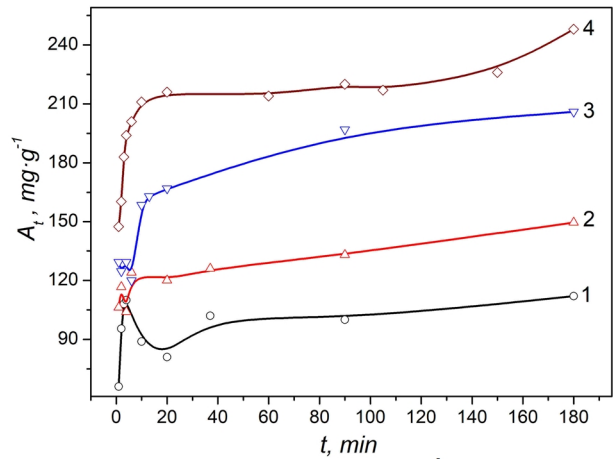


Fig. 2. The adsorption kinetics of Ba²⁺ ions by basic silica A-300 (1) and modified silica M30 (2), M40 (3) and M50 (4).

Table 3

Nonlinear and linear forms of analytic equations of kinetic adsorption models

Kinetic model	Nonlinear equation	Linear equation
Elovich	$\frac{dA_t}{dt} = a e^{-bt}$	$A_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t)$
Absorption binding	–	$A_t = K_1 t^{\frac{1}{2}} + K_0$
Pseudo-first order	$\frac{dA_t}{dt} = K_2 (A_{eq} - A_t)$	$\lg(A_{eq} - A_t) = \lg A_{eq} - \frac{K_2}{2.303} t$
Pseudo-second order	$\frac{dA_t}{dt} = K_3 (A_{eq} - A_t)^2$	$\frac{t}{A_t} = \frac{1}{K_3 A_{eq}^2} + \frac{t}{A_{eq}}$

A_t, A_{eq} – adsorption value at the time t and the state of adsorption-desorption equilibrium, respectively [mg·g⁻¹]; a – initial value of adsorption [mg·g⁻¹·min⁻¹]; b – binding degree of adsorbent due to chemisorption [g·mg⁻¹]; K_1 – the constant of diffusion insertion of the adsorbent [mg·g⁻¹·min^{-0.5}]; K_0 – mass fraction of the boundary layer [mg·g⁻¹]; K_2 – coefficient [min⁻¹]; K_3 – coefficient [g·mg⁻¹·min⁻¹].

removing all Ba²⁺ cations from 0.46 l of 0.01 M BaCl₂ solution, while the same amount of basic adsorbent is able to bind all cations only with 0.07 l of this solution. The isotherms of adsorption of Ba²⁺ cations by basic and modified silica (Fig. 1) are typical for the case of Langmuir’s monomolecular adsorption [12].

For the practical use of adsorbents, information is needed about their maximum sorption capacity in the state of equilibrium and on the kinetics of the process itself. The adsorption results within the framework of the appropriate kinetic model allow to predict the results of adsorption processes and ensure their maximum efficiency.

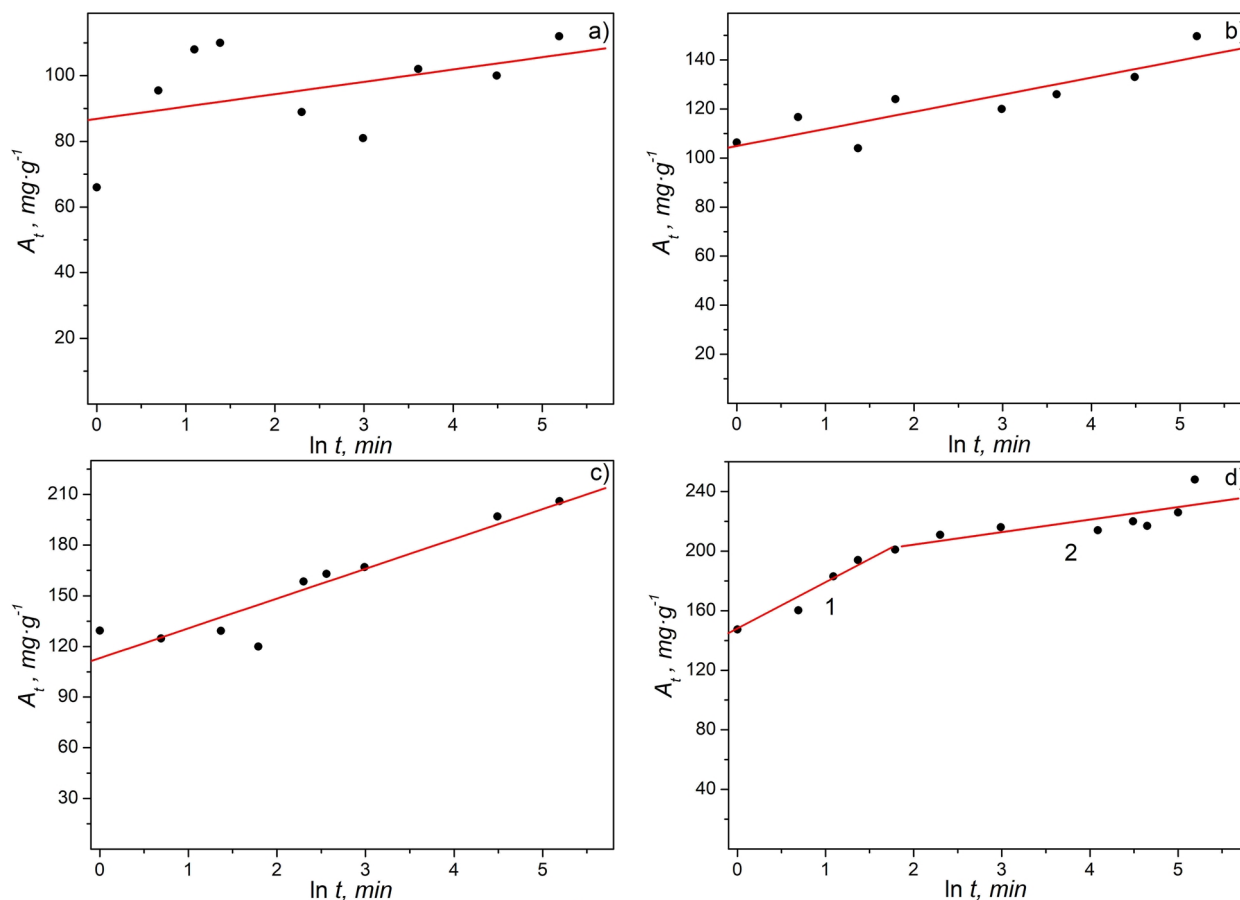
The common kinetic models of adsorption processes are the absorption (diffusion) model and the Elovich kinematic model [13-16]. In the last two decades, researchers have used the Lagergren equation of the pseudo-first or pseudo-second order for an analytical description of the kinetics of adsorption processes [15-19].

Analyzing graphic dependences $A_t = f(t)$ (Fig. 2), it can be found that the adsorption value is different for each standard during first minutes of contacting the materials with the electrolyte solution. The smallest value is characteristic for basic silica – 66 mg·g⁻¹. When the number of grafted TMS-groups increases, the initial

Table 4

 The adsorption equations of Ba²⁺ ions for experimental adsorbents in the approximation of the Elovich model and their corresponding correlation coefficients R^2

Adsorbent	Process duration, min	Adsorption equation	R^2
A-300	1-180	$A_t = 3.75 \ln t + 86.86$	0.196
M30	1-140	$A_t = 6.96 \ln t + 104.98$	0.774
M40	1-180	$A_t = 17.66 \ln t + 118$	0.876
M50	1-10	$A_t = 29.6 \ln t + 147.7$	0.959
	10-180	$A_t = 10.33 \ln t + 178$	0.415


Fig. 3. The linear dependences of adsorption of Ba²⁺ ions by basic silica A-300 (a) and modified silica M30 (b), M40 (c) and M50 (d) in Elovich model approximation.

adsorption of Ba²⁺ ions also increases for samples M30, M40, and M50 and is 106, 129, and 148 mg·g⁻¹, respectively.

The curves of the kinetic process for A-300, M30 and M40 standards exhibit slight deviations from the parabolic dependence in the direction of A_t values decreasing in the time interval of 20–40 min. This indicates on instability of the adsorption-desorption equilibrium in the system oxide material-electrolyte solution in this time period.

For the search analytic equations describing the kinetic process of Ba²⁺ ions binding by basic and modified silica, known mathematical models were used (Table 3).

The adequacy of the equation of the kinetic model of adsorption with experimental data was estimated by the

correlation coefficient R^2 [20–21]. In particular, Table 4 shows the adsorption equations of Ba²⁺ ions for experimental adsorbents in the approximation of the Elovich model and their corresponding correlation coefficients R^2 .

The adequacy of the analytic equations to the experimental values of adsorption is also illustrated by Fig. 3. The correlation coefficient R^2 of the Elovich equation for adsorption of cations by basic silica is 0.196. The growth of the number of grafted TMS-groups on the surface of adsorbents improves the accuracy of analytic equations. For example, R^2 value increases for standards M30 and M40, i.e. equal to 0.774 and 0.876, respectively. The constant magnitude of the inclination angle of the linear dependences $A_t = f(\ln t)$ for standards A-300, M30 and M40 indicates the invariability of the

Table 5

The adsorption equation for Ba²⁺ ions by modified silica M50 in the approximation of absorption and the pseudo-first order models and their correlation coefficients R²

Kinetic model	Adsorption equation and correlation coefficient			
	First stage	R ²	Second stage	R ²
Absorption model	$A_t = 30.3t^{\frac{1}{2}} + 123.6$	0.899	$A_t = 2.94t^{\frac{1}{2}} + 195$	0.556
Pseudo-first order model	$\lg(A_{eq} - A_t) = -0.7t + 2.0$	0.949	$\lg(A_{eq} - A_t) = -t + 1.6$	0.736

mechanism of cation binding during whole time of the contact of adsorbents with the electrolyte (Fig. 3, a-c). However, the nature of the adsorption process with the modified silica M50 changes over time (Fig. 3, d). Linear dependence reduces the inclination angle to the abscissa axis at 10 min from the beginning of the adsorption process. The adsorptive binding takes place with the participation of less active centers at this stage of adsorption process. The first and second stages of the process are indicated as 1 and 2, respectively (Fig. 3, d).

Characteristically, the equations of cation adsorption by modified silica M50 also indicate a two-stage process of cation binding in the approximation of absorption and pseudo-first order models (Table 5). The equation of these models describes the adsorption of Ba²⁺ ions quite accurately at the first stage of the adsorption process, since their correlation coefficients are close to 1 and are

Table 6

The adsorption equation for Ba²⁺ ions by adsorbents M50 in the approximation of the pseudo-second order model and their correlation coefficients R²

Adsorbent	Adsorption equation	R ²
A-300	$\frac{t}{A_t} = 0.009t + 0.016$	0.996
M30	$\frac{t}{A_t} = 0.007t + 0.020$	0.996
M40	$\frac{t}{A_t} = 0.005t + 0.014$	0.999
M50	$\frac{t}{A_t} = 0.004t + 0.012$	0.94

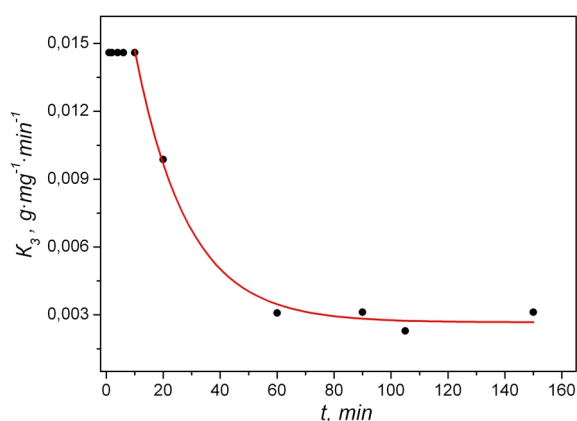


Fig. 4. The dependence of K₃ value in the pseudo-second order equation from the contact time with the electrolyte solution for modified silica M50.

equal to 0.899 and 0.949, respectively. However, the correlation coefficients of these equations in the second stage of adsorption binding of cations are low – their value is 0.556 and 0.736, respectively.

The pseudo-second order equations describe the most adequately the process of adsorption binding of Ba²⁺ ions (Table 6). Correlation coefficients of linear equations are close to 1 (0.995-0.999).

The dependencies $\frac{t}{A_t} = f(t)$ represent a straight

line for all investigated adsorbents. A sharp decreasing in K₃ value after 10 min of its contact with the electrolyte indicates on the two-stage adsorption of cations by adsorbent M50 (Fig. 4).

The coefficient K₃ in the pseudo-second order equation is constant and its average value is $0.014 \pm 0.001 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ for 1 ÷ 10 min of the adsorption process. However, its value decreases to $0.003 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ with further adsorption. The change in its value is described by the equation $K_2 = 0,06t^{-0,64}$, for which the correlation coefficient is 0.915. The coefficient K₃ in the equations, describing the binding process of barium ions by M30 and M40 adsorbents in one-stage process, are $0.026 \pm 0.008 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ and $0.010 \pm 0.003 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$, respectively.

The coefficient K₃ indicates the rate of mass consumption of the adsorbent on the binding of 1 mg of adsorptive. The stability of this coefficient for 10 min from the beginning of the contact of the modified silica M50 with the electrolyte solution indicates that the cation binding in these conditions is carried out with the participation of available active centers. In fact, a monomolecular layer of an adsorptive is formed in this time interval. Since the formation of a monomolecular layer does not compensate an excess surface energy, therefore, less active adsorption centers contribute to the formation of a polymolecular layer over the specified time. The growth of the adsorption capacity of modified silica in relation to Ba²⁺ ions is due to structural changes that occur in the oxide material as a result of TMS-groups grafting.

Chemisorbed TMS-groups reduce a surface tension and Laplace pressure in SiO₂ particles [22]. This, in turn, leads to an increase in the valence angle in Si – O – Si bridges and a reduction in the siloxane bond length in SiO₄ tetrahedra. Reducing the particles' size and increasing their density provides an increase in the number of atoms per unit area of the particles' surface, and the number of adsorption centers in the surface layer. This dimensional effect is manifested by displacement in

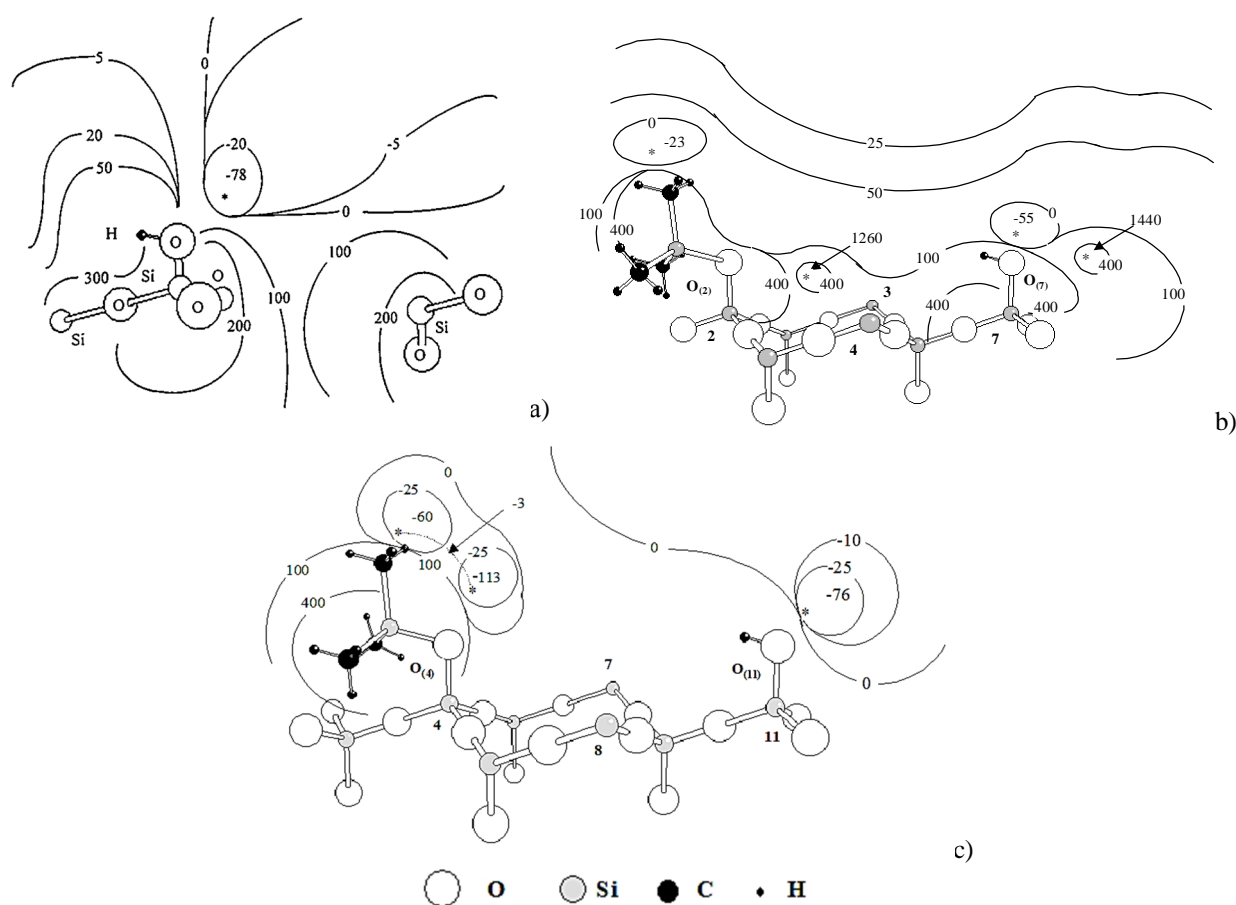


Fig. 5. The profiles of electrostatic potentials (in kJ·mol⁻¹) of clusters that simulate the hydroxylated surface of silica (a), a silica surface with small (b) and relatively high (c) degree of silanol substitution on TMS-groups [23, 24].

the short-wave region of absorption bands in the infrared spectra of modified silica, associated with asymmetric oscillations of tetrahedra SiO₄ (ν_a) and deformation oscillations of siloxane bridges (ν_{OSiO}) [22].

Simulation of the structure of a number clusters of silica surface by quantum chemistry methods revealed that there is significant change in the electrostatic potential distribution during the consistent substitution of surface silanols by the TMS-groups [23, 24]. The regions with negative potential (-60 and -113 kJ·mol⁻¹) are formed close to the silicon atom of the grafted group at the initial stages of trimethylsilylation (Fig. 5, b). An increase in the number of TMS-groups relative to a certain value is accompanied by a decrease in the negative potential region and the appearance of positive potential areas (~1260 and 1440 kJ·mol⁻¹) localized at the entrance to the hexagonal cavity (Fig. 5, c), which is also characteristic for fully trimethylsilylation SiO₂ surface.

The results of modeling of the structure of the modified silica surface and the study of the electrostatic potential distribution allow predicting that incomplete trimethylsilylation of the SiO₂ surface may also increase significantly the adsorption activity of the oxide material relative to negatively charged ions of Cl⁻, Br⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻, etc.

Conclusions

It is found that the substitution of 30-50 % of free silanols of fumed silica surface on (CH₃)₃Si-groups leads to an increase in the ability of modified SiO₂ to adsorb Ba²⁺ cations from the electrolyte solution. In particular, modified silica with 48.3 % of TMS-groups adsorbs 1.8 mmol·g⁻¹ Ba²⁺ cations from 0.01 M BaCl₂ solution, that in 3 times more then the adsorption of these cations by unmodified silica.

It is show that the adsorption of Ba²⁺ ions by basic and modified silica is well described by the pseudo-second order Lagergren equation. The process of cation binding by adsorbents A-300, M30 and M40 is carried out in one stage and ends with the formation of monomolecular layer of adsorptive.

The adsorption process by modified silica M50 takes place in two stages, i.e. a monomolecular layer of the adsorptive is formed on the adsorbent surface for 10 min from the beginning of contact of trimethylsilylated silica with an electrolyte solution, and a polymolecular layer is formed over the specified time. The fraction of Ba²⁺ ions in its monomolecular layer is almost 85 % of the equilibrium amount of the bound adsorptive.

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Кінетика адсорбційного зв'язування йонів Ва²⁺ триметилсилільованими кремнеземами

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Встановлено, що неповне заміщення вільних силанолів поверхні пірогенного кремнезему на (СН₃)₃Si-групи призводить до зростання спроможності модифікованого SiO₂ адсорбційно зв'язувати катіони Ва²⁺ із розчину електроліту. Зокрема, кремнезем із 48,3 % триметилсилільних груп адсорбує 1,8 ммоль·г⁻¹ катіонів Ва²⁺ із 0,01 М розчину ВаСl₂, що в 3 рази перевищує адсорбцію цих катіонів не модифікованим кремнеземом. З'ясовано, що адсорбція катіонів базовим та модифікованими кремнеземами добре описується рівнянням Лагергрена псевдодругого порядку. Висока адсорбційна активність кремнезему з хемосорбованими триметилсилільними групами обумовлена утворенням в околі прищеплених груп локальних областей із відносно великими значеннями негативного і позитивного електростатичних потенціалів.

Ключові слова: кремнезем, силанолі, хемосорбція, триметилсилільні групи, адсорбційне зв'язування йонів.