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A Quantum Chemistry Study on the Interaction Between Silica Surface and Aqueous Alkaline Solutions

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A quantum chemical analysis has been carried out of the equilibrium structure and energy parameters of hydrated Li^+, Na^+, and K^+ cations interacting with ionized silica surface by means of density functional theory method with extended basis set 6-31++G(d,p) and exchange-correlation functional B3LYP. The calculated adsorption energy values related to those cations reproduce the experimental adsorption row of alkali metal cations at pH = 10.

Key words: silica, alkali metal hydroxides, density functional theory.

Introduction

High-disperse silica, due to its exceptional physical and chemical properties, in particular, well-developed surface, chemical inertness, significant adsorption capacity, is used as a sorbent and carrier of drugs in many branches of medicine, biotechnology, etc. [1]. The adsorption properties of silica surface from aqueous solutions depend on many factors, such as: the energy of the interaction between the surface functional groups and the segments of adsorbate molecules, the surface charge, the ionic strength and the acidity of the solution. For the creation and effective application of new silica-based sorbents it is necessary to understand at the molecular level the mechanisms for achieving the acid-base equilibrium within its near-surface layer.

It is known [2] that with increasing pH of the solution, the SiO_2 particles surface can get a negative charge, its value being determined by the ionization degree of surface hydroxyl groups, which, in turn, can interact with cations of alkali metals according to the equation:

$$\equiv SiOH + Me^+ + OH^- \rightleftarrows \equiv SiO^- Me^+ + H_2O. \qquad (1)$$
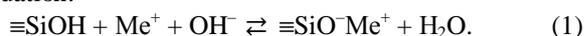
In Fig. 1 experimentally obtained curves are shown of sorption by silica gel of cations Li^+, Na^+ and K^+ from 0.1 N solutions of relative perchlorates [3]. They testify that in absence of silica dissolution, an inversion takes place of a row of sorption of cations in strongly alkaline media. If at pH 7-8 the sorption of alkaline cations increases in the row $Li^+ < Na^+ < K^+$, then with increasing pH of the solution to 10.5 this series has an inverse form

$K^+ < Na^+ < Li^+$. This fact needs to be analyzed at a molecular level.

Since in acidic and weakly acidic media on the surface of silica particles there are soluble forms of polysilic acid oligomers characterized by a ratio of oxygen atoms to silicon atoms of more than two (in an orthosilicate acid molecule the ratio O/Si = 4), it prompted us to investigate the interaction of hydrated complexes of alkali metal hydroxides with orthosilic acid molecule [4]. In particular, it has been shown that the dissociation constant (pK_{Me}) of the $\equiv SiOMe$ group of $Si(OH)_4$ molecule changes symbathically with the value
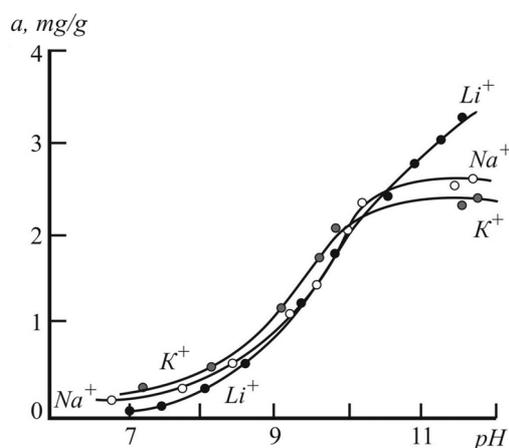
Fig. 1. Adsorption of cations of alkali metals in the region of high pH values for titration of silica gel by LiOH, NaOH, KOH solutions [3].
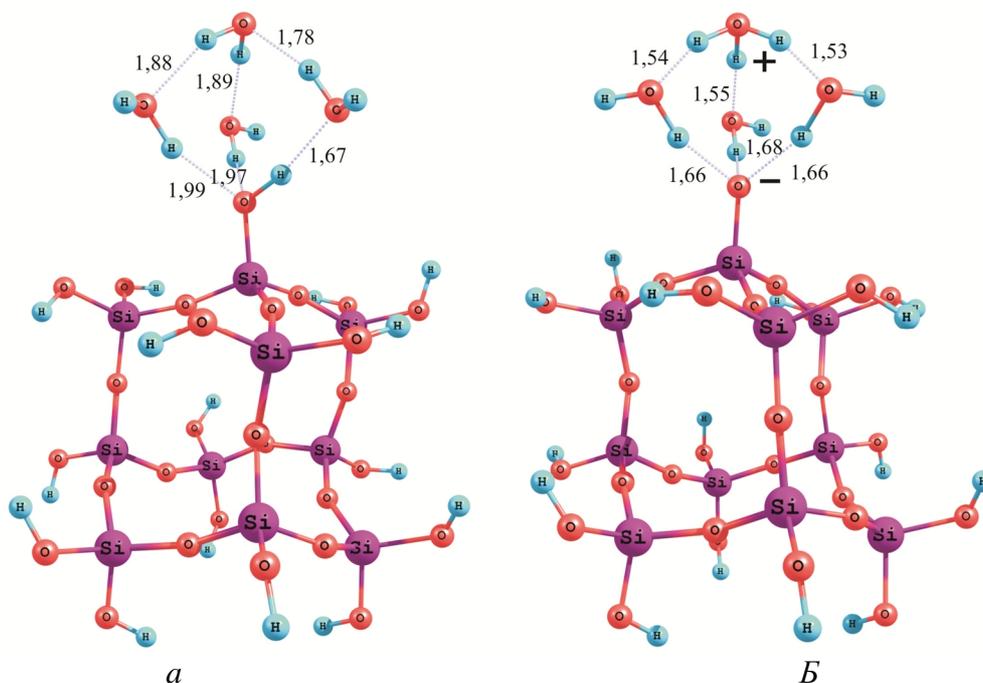
Fig. 2. Equilibrium structure of the complex of the $Si_{10}O_{12}(OH)_{16}$ molecule and four water molecules: *a* is the molecular state; *b* - a state with separated charges

of the Gibbs free energy and increases in a row $Li^+>Na^+>K^+$, and is -2.5, -3.4 and –4.8 respectively. However, with increasing dimensions to $Si_8O_{12}(OH)_8$ molecule (ratio O/Si = 2.5), the pK_{Me} values for complexes containing Li^+, Na^+ and K^+ cations were 6.5, -2.4 and -0.4 respectively [5]. Naturally a question arises, which of the factors, structural or component, are responsible for changing the ion-exchange properties of the model. To find out this question model $Si_{10}O_{12}(OH)_{16}$ was applied, which is characterized by the ratio of O/Si = 2.8.

I.   Objects and methods

The calculations were performed by the method of density functional theory [6] using the correlation-exchange functional B3LYP [7, 8] and the valence-split basis set 6-31++G (d, p). The influence of the aqueous medium was taken into account in the framework of the continuum solvent model (CPCM) [9, 10]. The model of the surface of silica was an adamantane-like cell of $Si_{10}O_{12}(OH)_{16}$. The deprotonation constant (pK_a) and that of ion exchange (pK_{Me}) of the silanol group were as follows:

$$pK= \Delta G/2,303RT, \qquad (2)$$

where R is the universal gas constant, T is the temperature, ΔG is the free Gibbs energy of the deprotonation reaction. All calculations have been made using the US GAMESS software package [11].

II.   Results and their discussion

According to the experimental data, the pK_a of orthosilic acid is 9.3 [12]. The chosen calculation method used in this paper allows a quantitative reproduction of

this value [13]. To evaluate the protolytic properties of the selected model, we first obtained the equilibrium geometric parameters of the $Si_{10}O_{12}(OH)_{16}$ molecule and of its complexes with four water molecules in two states: the molecular state and the state with separated charges (Fig. 2). The results of the calculation show that the pK_a value for dissociation of the silanol group is 9.8, which in turn allows us to expect somewhat higher values of pK_{Me} than that obtained in [4].

When simulating the interaction of an aqueous solution of alkalis with a silica surface, it is assumed that the proton of a silanol group is neutralized by a hydroxide ion of alkali to form a water molecule. In this connection, the electroneutral interspheric and exterior spherical complexes consisting of hydrated Li^+, Na^+, and K^+ cations and $Si_{10}O_{12}(OH)_{16}$ molecule with a deprotonated silanol group are considered. The interior complexes include those where the oxygen atom of a deprotonated silanol group is included in the first hydatic shell of a cation (Fig. 3a), whereas in the exterior-spheric complexes the hydrated cation and the silanol group are separated by water molecules (Fig. 3, b). So, it is clear from Fig. 3, a that between the oxygen atom of deprotonated silanol group and the Li^+ cation, a slightly shorter bond (1.86 Å) is formed, in comparison with the bonds between the Li^+ cation and the oxygen atoms of the water molecules of its first hydrated shell.

As in the intra-spheric complex containing lithium cations, in the intra-spherical complex with sodium cation, the distance between the oxygen atom of the deprotonated silanol group and the Na^+ cation is slightly lower (2.21 Å) than the distance between the cation Na^+ and the oxygen atoms of the water molecules of the first hydrated shell (Fig. 4, a). This dependence corresponds to the experimental data obtained in [14] concerning the crystalline structure of sodium hydrosilicate $Na_3HSiO_4·5H_2O$, where the length of O-Na bond in the
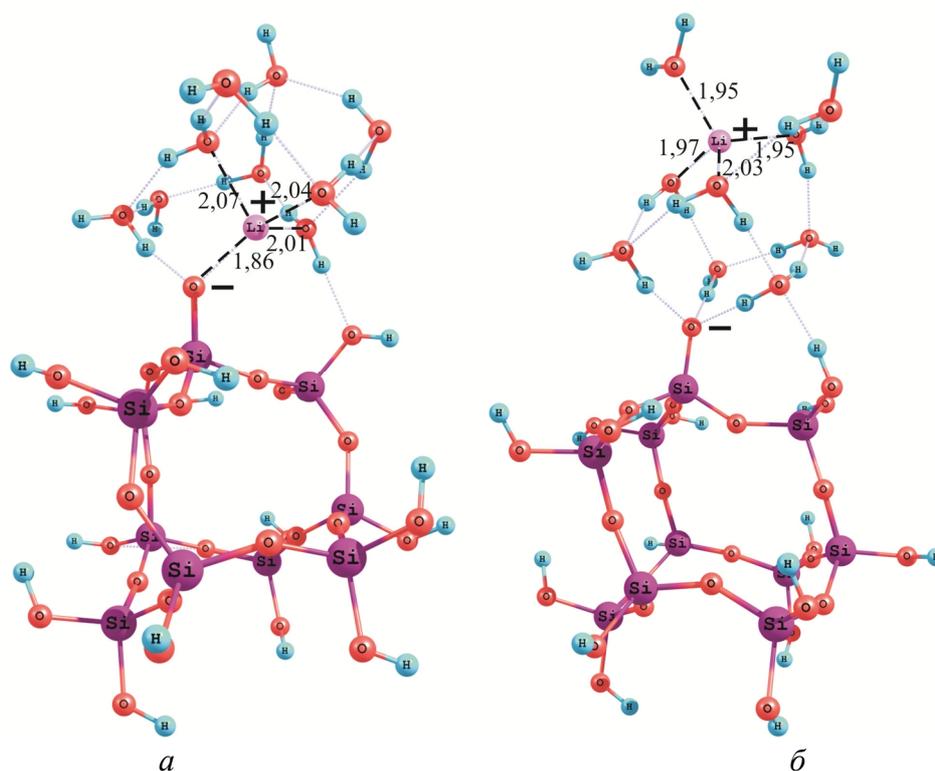
Fig. 3. Equilibrium structure of the complex containing anion $Si_{10}O_{12}(OH)_{15}O^-$, nine water molecules and lithium cation: *a* - intra-spherical complex; b - the external sphere complex.
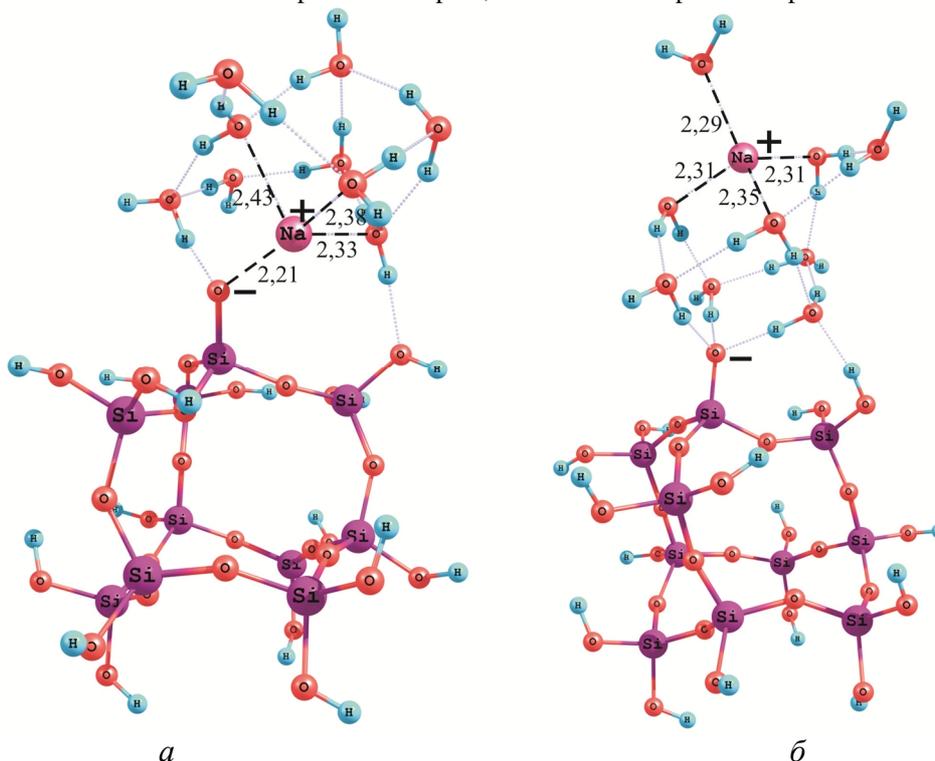
Fig. 4. Equilibrium structure of the complex containing an anion $Si_{10}O_{12}(OH)_{15}O^-$, nine water molecules and a sodium cation: *a* - intra-spherical complex; b - the external sphere complex

group ≡Si-O-Na is 2.38 Å, whereas for a similar bond with the oxygen atom of water molecule it is equal to 2.58 Å. Also, the value of the Si-O bond length in the ≡Si-O-Na group (1.59 Å), which is close to the experimental value of 1.62 Å, is almost quantitatively reproduced. The mentioned interatomic distances completely coincide with the similar quantities obtained in [15].

The distance between the cation K^+ and the oxygen atom of a deprotonated silanol group is 2.59 Å (Fig. 5), i.e., with the increase in the radius of the cation, the mentioned value increases.

A somewhat more complex character has the dependence of the Mulliken charge on the oxygen atom
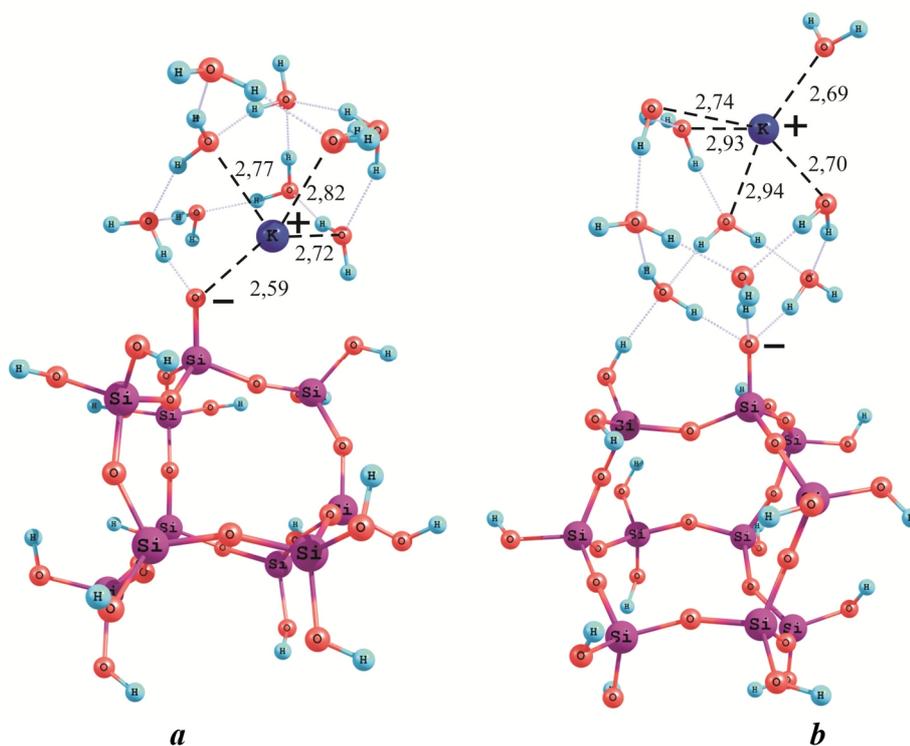
Fig. 5. Equilibrium structure of the complex containing an anion $Si_{10}O_{12}(OH)_{15}O^-$, nine water molecules and a potassium cation: *a* - intra-spherical complex; *b* - the external sphere complex.
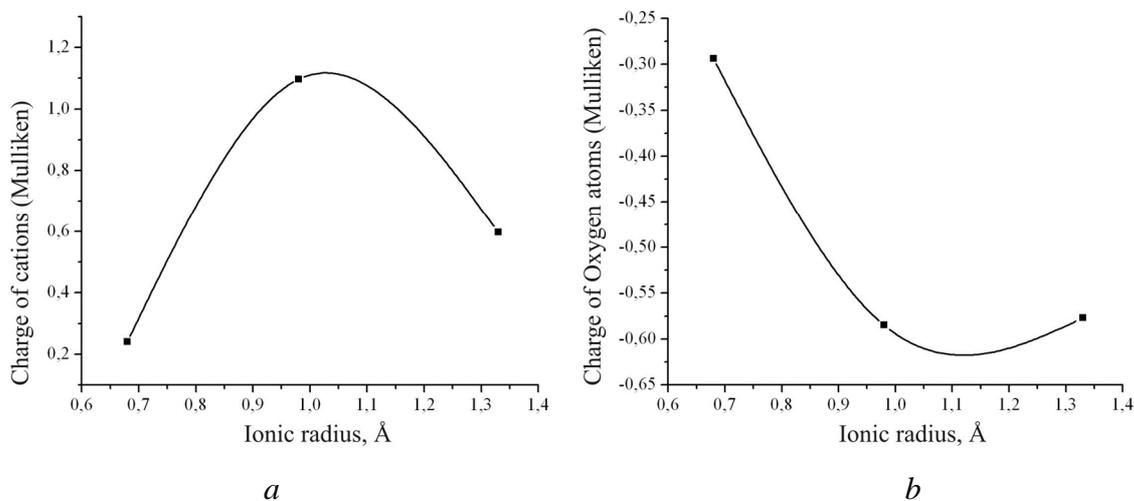
Fig. 6. A dependence of the Mulliken charge on the cation size: *a* – the charges on cations Li^+, Na^+ and K^+; *b* – is the charge on the oxygen atom of the group $\equiv SiO^-$.

Table

The changes in total energy (ΔE) and Gibbs free energy (ΔG) of interaction of hydrated alkali metal cations with a negatively charged silica surface

Scheme of reaction	ΔE, kJ/mol	ΔG, kJ/mol	pK_{Me}
$\equiv SiO^- \cdots (H_2O)_9 \cdots Li^+ \rightleftharpoons \equiv SiO^- Li^+ \cdots (H_2O)_9$	-16.2	-3.9	-0.7
$\equiv Si O^- \cdots (H_2O)_9 \cdots Na^+ \rightleftharpoons \equiv SiO^- Na^+ \cdots (H_2O)_9$	-21.8	-9.1	-1.6
$\equiv Si O^- \cdots (H_2O)_9 \cdots K^+ \rightleftharpoons \equiv SiO^- K^+ \cdots (H_2O)_9$	-16.7	7.2	1.3

of the deprotonated silanol group on the size of the cation. For example, in the intra-sphere complexes containing Li^+, Na^+, and K^+ cations, the charge value on the oxygen atom is -0.294, -0.585, and -0.577, respectively, while the charge on the cations themselves are 0.241, 1.091, and 0.597 (Fig. 6).

The energy of adsorption of cations (ΔE) of alkali metals from the aqueous solution (see Table) on the silica surface was calculated as the difference between the values of the total energies of the intra-spheric and external-sphere complexes. It can be seen from the Table that the Gibbs free energy of the interaction is negative

for the complexes containing Li$^+$ and Na$^+$ cations, and is positive for the complex with cation K$^+$, that is, the silica surface exhibits insignificant adsorption capacity for potassium cations. The changes in the total energy during the transition from the outer-sphere complex to the internal one indicate a greater likelihood of the formation of the latter.

Conclusions

According to the data obtained, the adsorption value of sodium cation is the highest compared with cations of lithium and potassium, which agrees well with the experimental data at pH = 10. This can be explained by the most effective charge of sodium cation, considering that lithium cation (which has the highest polarization power) is more strongly polarized by the water molecules of the first hydrated sphere, which, in turn, hinder its contacts with the deprotonated oxygen atom of a silanol group.

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Моделювання взаємодії поверхні кремнезему з лугами у водному середовищі

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Методом функціоналу густини з використанням розширеного базисного набору 6-31++G(d,p) та обмінно-кореляційного функціоналу B3LYP проведено квантовохімічний аналіз будови гідратованих комплексів гідроксидів лужних металів на поверхні кремнезему. Розраховані значення pK$_{Me}$ іонного обміну поверхні кремнезему при взаємодії з катіонами Li$^+$, Na$^+$ та K$^+$.
Ключові слова: кремнезем, гідроксиди лужних металів, теорія функціоналу густини.