SIMULATION OF THE INTERACTION BETWEEN SILICA SURFACE AND ACID OR ALKALINE AQUEOUS MEDIA

**A.A. Kravchenko, E.M. Demianenko, O.M. Tsendra, V.V. Lobanov,
A.G. Grebenyuk , M.I. Terets**

*Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine,
17 General Naumov Str., Kyiv 03164, Ukraine*

A quantum chemical analysis has been carried out of the equilibrium structure of hydrated HCl and HBr acid complexes and alkaline metal hydroxides on silica surface by means of density functional theory method with extended basis set 6-31++G(d,p) and exchange-correlation functional B3LYP. Deprotonation constants of silica surface hydroxyl group and of its cationic form have been calculated.

Introduction

Highly dispersed silica due to its exceptional physical and chemical properties, including the well-developed surface, chemical inertness, good adsorption capacity, is used as a sorbent and a carrier of drugs and pharmaceutical compositions in various fields of medicine, pharmacy, veterinary, biotechnology *etc.* [1]. Silica surface properties at the adsorption from aqueous solutions depend on many factors such as energy of interaction between surface functional groups and some segments of adsorbate molecule, surface charge, ionic strength and acidity of the solution. Knowledge about the mechanism of acid-base balance at silica surface–solution interface at atomic level is necessary for creation of new silica-based sorbents and for their effective use.

Information about the structural parameters and thermodynamic values such as the change ΔG in Gibbs free energy of dissociation of neutral and protonated surface silanol groups, dissociation constant of the both hydroxyl group (pK_a) and surface silanol group in a cationic form (pK_b), as well as the point of zero charge (pzc) can be provided by methods of quantum chemistry.

Since pzc is an arithmetic mean of the pK_a and pK_b values, firstly the pK_a value (deprotonation constant of the $\equiv$Si-OH groups) was calculated according to the equation:

$$\equiv\text{Si–OH} \rightleftharpoons \equiv\text{Si–O}^- + \text{H}^+. \tag{1}$$

The constant of deprotonation (pK_b) of cationic form of silanol groups was found from the equation:

$$\equiv\text{Si–OH}_2^+ \rightleftharpoons \equiv\text{Si–OH} + \text{H}^+. \tag{2}$$
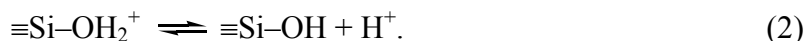
It is known [2], that the surface of SiO_2 particles may acquire negative charge when the pH of solution increases. The value of the negative charge is determined by the degree of ionization of surface hydroxyl groups which can also interact with alkali metal cations according to the equation:

$$\equiv\text{SiOH} + \text{Me}^+ + \text{OH}^- \rightleftharpoons \equiv\text{SiO}^-\text{Me}^+ + \text{H}_2\text{O}. \tag{3}$$

It has been shown [3] that adsorption of lithium, sodium and potassium cations on silica surface decreases in a series $Li^+>Na^+>K^+$ at pH> 9.5, in contrast to the average values of pH (6-8). Nevertheless some parameters of elementary stages of the interaction between silica surface and alkaline aqueous solution cannot be determined by experimental methods.

Therefore it is necessary to study the interaction of hydrated HCl and HBr acid complexes and alkaline metal hydroxides with silica surface by means of quantum chemical methods. Simulation of acid-base properties of the silica surface, according to the equations (1) and (2), as well as its sorption properties in relation to the alkaline metal cations (according to the equation (3)) is the subject of this study.

Objects and methods

Calculations have been performed by density functional theory method [4] using exchange-correlation functional B3LYP [5,6] and 6-31++G(d,p) valence-split basis set. The effect of the aqueous medium was taken into account using polarizable continuum solvent model (CPCM) [7, 8]. A cubic-like structure $(Si_8O_{12}(OH)_8)$ was chosen as the model of silica surface. The deprotonation constants for cationic forms of silanol group pK_a and pK_b were found after the formula:

$$pK = \Delta G/2.303RT \qquad (4)$$

where R – universal gas constant, T – temperature, ΔG – change in Gibbs free energy of deprotonation reaction. The pzc value (point of zero charge) was calculated according to the formula:

$$pzc = (pK_a + pK_b)/2. \qquad (5)$$

All the calculations were performed using the software package US GAMESS [9].

Results and discussion

To study the reaction of silanol group deprotonation, we have obtained equilibrium geometrical parameters of molecules $Si_8O_{12}(OH)_8$, which interacts with four water molecules in both molecular state and charge separation state which contains dissociated silanol group and hydronium cation (Figure 1).
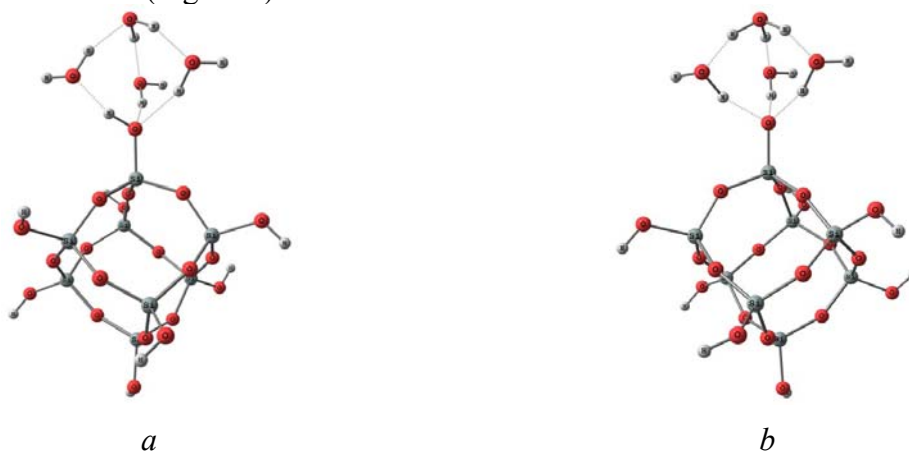

a   *b*

Fig. 1. The equilibrium structure of the complexes with (*a*) undissociated silanol group and wa-ter molecules; (*b*) dissociated silanol group, water molecules and a hydronium cation

The calculated results show that pK_a of dissociation of silanol groups is a positive value of 7.2, which is consistent with experimental values for silica acidity (close to 8) [10]. It proves this model for silica surface to be appropriate for modeling further acid-base processes.

The reaction of deprotonation for cationic form silanol groups according to equation (2) in the presence of Cl⁻ and Br⁻ anions is the proton transfer reaction from a positively charged group $\equiv Si-OH_2^+$ (Fig. 2, *a, b*) to corresponding halogen anion (Fig. 2, *b, d*). As can be seen from the Table 1, for complexes containing Cl⁻ or Br⁻ anions, the change in total energy of deprotonation reaction of positively charged silanol groups ($\Delta E_{react.}$) is almost the

same; the change in Gibbs free energy of deprotonation reactions ($\Delta G_{react.}$) differs for 6.4 kJ/mol. Dissociation constants (pK_b), for cationic form of silanol groups in complexes containing Cl^- and Br^- are calculated according to the equation (4); they are -0.3 and 0.9 respectively.
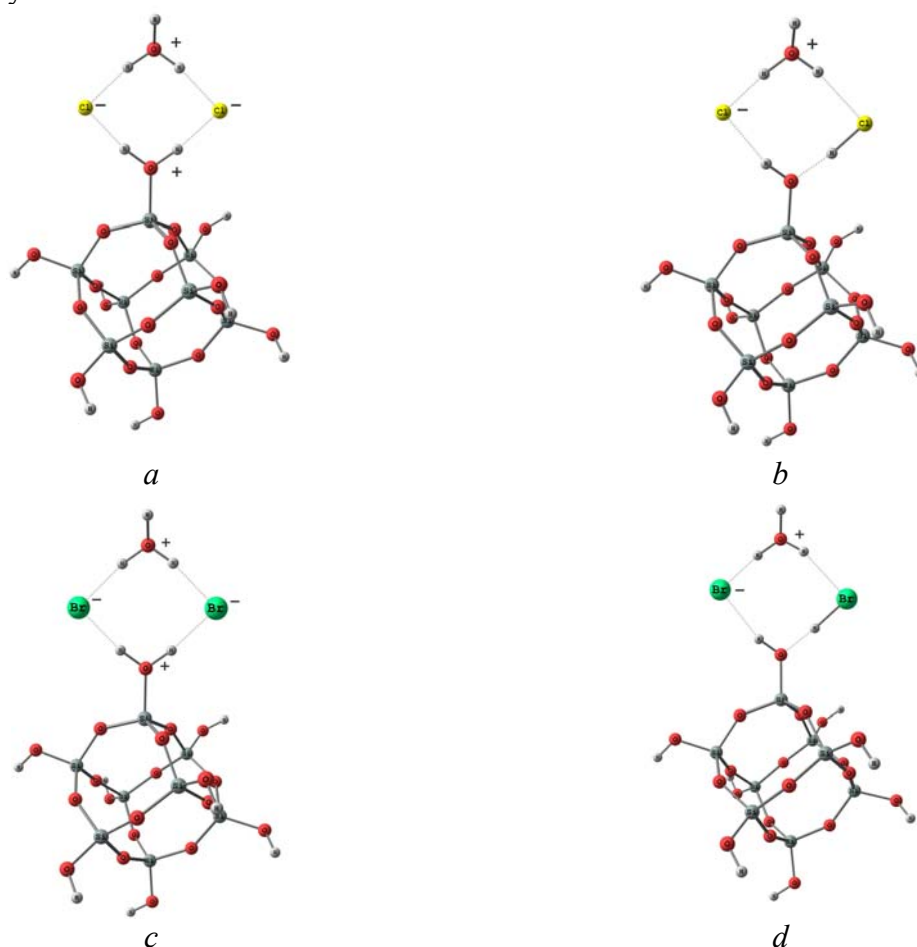

Fig. 2. Equilibrium structures for complexes consisting of a cluster $Si_8O_{12}(OH)_8$, two anions Cl^- (*a, b*) or Br^- (*c, d*) and hydronium ion: cationic forms of silanol groups (*a, c*); ordinary forms of silanol group (*b, d*)

The values of dissociation constant (pK_b) for cationic forms of silanol groups along with deprotonation constant of neutral form of silanol groups (pK_a) make it possible to calculate the value of pzc, this is about 3 and agree well with experimental data [10].

Table 1. The total energy changes value for deprotonation reaction ($\Delta E_{react.}$), the value of Gibbs free energy change in deprotonation reactions ($\Delta G_{react.}$), and the deprotonation constant (pK_b) of cationic form of silanol groups

Complex	ΔE_{react}, kJ/mol	ΔG_{react}, kJ/mol	pK_b
$2Cl^- \cdots H_2O \cdots {}^+H_2OSi_8O_{12}(OH)_7$	3.7	-1.5	-0.3
$2Br^- \cdots H_2O \cdots {}^+H_2OSi_8O_{12}(OH)_7$	10.1	4.9	0.9

When modeling the interaction between an alkaline aqueous solution and silica surface, it is assumed (equation 3), that protons of silanol groups are neutralized by hydroxide anions to form water molecules. In this regard, considered electroneutral complexes (innerspheric complexes), consisting of the cations Li^+, Na^+ and K^+ (hydrated nine water molecules) and the molecules $Si_8O_{12}(OH)_8$ with deprotonated silanol groups (Fig. 3).
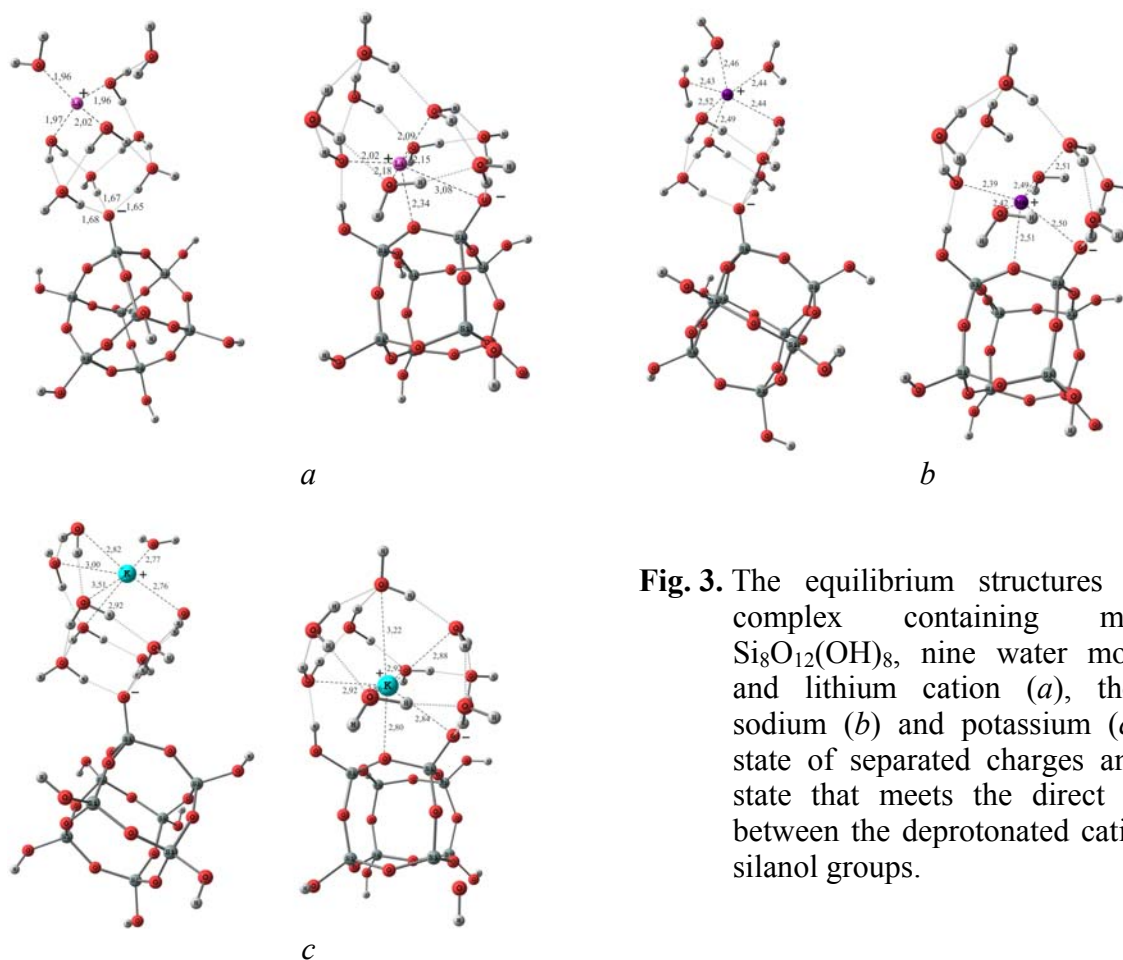
Fig. 3. The equilibrium structures of the complex containing molecule $Si_8O_{12}(OH)_8$, nine water molecules and lithium cation (*a*), those of sodium (*b*) and potassium (*c*) in a state of separated charges and in a state that meets the direct contact between the deprotonated cation and silanol groups.

The calculated results have shown that the greatest impact on the energy of siloxane bond relates to the smallest radius of cations. As it is well known [11], potassium cations in solution can have a hydration number up to eight. That is why to model the hydration of alkali metal cations we used nine water molecules – enough to saturate the first hydration shell of a cation, some of them being included into the second hydration shell.

Hydrated lithium cation has no direct contact with oxygen atoms of deprotonated silanol groups (Fig. 3, *a*), what can be explained by its small radius and large polarization capability with respect to water molecules of its own hydration shell. The latters in turn form strong hydrogen bonds with oxygen atoms of deprotonated silanol groups and therefore sterically hinder direct contact with its Li^+ cation. It should be noted that the distance between the oxygen atom of undissociated silanol group and alkali metal cations increases proportionally to the radius of the hydrated cation. Thus, the hydration shell of lithium cation contains five water molecules (Fig. 3, *a*), and those of sodium and potassium contain six water molecules (Fig. 3, *b, c*).

The energy of interaction of alkali metal cations (ΔE) (see Table 2) with silica acid oligomer is calculated as the total energy difference between the values for outerspheric and of inner-spheric systems, the transformations occurring due to following scheme:

$$\equiv Si\,O^- \cdots (H_2O)_9 \cdots Me^+ \rightleftharpoons \equiv SiO^-Me^+ \cdots (H_2O)_9.$$
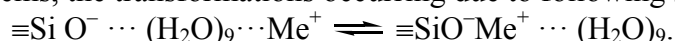
The Gibbs free energy of interaction (see Table 2) increases with growth of radii of hydrated alkali metal cations in the series Li <Na <K, what correlates with the experimental adsorption values (*A*) found in [6] at pH > 9.5. The calculated ΔG values indicate a relatively negligible adsorption capability of silica surface concerning alkali metal cations. The total energy changes due to transition from outerspheric complex to inner-spheric ones indicate greater probability of formation of the formers relative to the latters. This conclusion is

consistent with the data from [12], where the dependences were examined of the surface charge value pH within solutions of LiCl, NaCl, KCl, RbCl, CaCl$_2$, SrCl$_2$ and BaCl$_2$ electrolytes in order to evaluate their effect on the rate of silica dissolution. The authors presented models based on the idea that the alkali metal ions affect the proton donor properties of the surface via formation of outerspheric complexes resulting in moving off charged surface active centers. The authors believe the surface charge density to depend on the radii and charge of counter- ions. Within this model, the rate of silica dissolution depends on the electrolyte nature and content, due to its effect on the surface electrostatic properties. Thus, the greater charge should be accumulated on silica surface containing weak-hydrated ions of large size, as compared with strong hydrated ions.

Table 2. Changes in the total energy (ΔE) and Gibbs free energy (ΔG) for interaction between hydrated alkali metal cations and negatively charged silica surface, and experimental values of their adsorption (A).

Reaction scheme	ΔE, kJ/mol	ΔG, kJ/mol	A, mg-eq/g, [6]
$\equiv SiO^- \cdots (H_2O)_9 \cdots Li^+ \rightleftharpoons \equiv SiO^- Li^+ \cdots (H_2O)_9$	-16.9	-36.8	-6.5
$\equiv Si\,O^- \cdots (H_2O)_9 \cdots Na^+ \rightleftharpoons \equiv SiO^- Na^+ \cdots (H_2O)_9$	26.4	13.5	2.4
$\equiv Si\,O^- \cdots (H_2O)_9 \cdots K^+ \rightleftharpoons \equiv SiO^- K^+ \cdots (H_2O)_9$	19.1	2.2	0.4

Conclusions

A proton transfer is probable from hydronium ion to the oxygen atoms of silanol groups with formation of their cationic form due to interaction of hydrated ion pairs of HCl and HBr with silica surface in aqueous solutions. Deprotonation constant of cationic form of silanol group depends on the nature of an anion and increases in magnitude with increasing anion radius.

The increase in adsorption of alkali metal cations with decreasing cation radius (observed in the experiment at high pH) is due to the formation of inside-sphere complexes and is defined by polarization capability of cations. Smaller values of the Gibbs free energy changes in complexes containing lithium cation, compared with those in complexes with sodium and potassium cations, can be explained by the presence of lithium cations resulting in to decreasing the electron density on the oxygen atom of deprotonated silanol group and so in reducing the ionicity of the $\equiv Si\,O^- \cdots Me^+$ bond (between the oxygen atom of silanol group and corresponding alkali metal atom).

References

1. Medical chemistry and clinical application of silicon dioxide / A.A. Chuiko, Ed. – Kyiv: Nauk. Dumka, 2003. – 415 p. (in Russian).
2. Zuyi T., Hongxia Z. Acidity and Alkali Metal Adsorption on the SiO$_2$–Aqueous Solution Interface // J. Colloid Interface Sci. – 2002. – V. 252, N 1. – P. 15-20.
3. Silica gel based sorbents in radiochemistry / B.N. Laskorin, Ed. – Moskow: Atomiydat, 1977. – 304 p. (in Russian).
4. Baerends E.J., Gritsenco O.V. A quantum chemical view of density functional theory // J. Phys. Chem. A. – 1997. – V. 101, N 30. – P. 5383-5403.
5. Becke A.D. Density functional thermochemistry. III. The role of exact exchange // J. Chem. Phys. – 1993. – V. 98, N 7. – P. 5648-5653.
6. Lee C., Yang W., Parr R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density // Phys. Rev. B. – 1988. – V. 37, N 2. – P. 785-789.
7. Cossi M., Barone V., Cammi R., Tomasi J. Ab initio study of solvated molecules: a new implementation of the polarizable continuum model // Chem. Phys. Lett. – 1996. – V. 255, N 4-6. – P. 327-335.

8. Fortunelli A., Tomasi J. The implementation of density functional theory within the polarizable continuum model for salvation // Chem. Phys. Lett. – 1994. – V. 231, N 1. – P. 34-39.

9. Schmidt M.W., Baldridge K.K., Boatz J.A., Elbert S.T., Gordon M.S., Jensen J.H., Koseki S., Matsunaga N., Nguen K.A., Su S.J., Windus T.L., Dupuis M., Montgomery J.A.. General atomic and molecular electronic-structure system: Review // J. Comput. Chem. – 1993. – V. 14, N 11. – P. 1347-1363.

10. R.K. Iler The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica. - Published by John Wiley Sons Inc, United States (1979).

11. Enderby J.E. Ion Solvation via Neutron Scattering // Chem. Soc. Rev. – 1995. – V. 23, N 3. – P. 159-168.

12. Karlsson M., Craven C., Dove P M., Casey W.H. Surface Charge Concentrations on Silica in Different 1.0 M Metal-Chloride Background Electrolytes and Implications for Dissolution Rates // Aquatic Geochemistry. – 2001. – V. 7, N1. – P. 13-32.

МОДЕЛИРОВАННЯ ВЗАИМОДЕЙСТВИЯ ПОВЕРХНОСТИ КРЕМНЕЗЕМА С КИСЛОТАМИ И ОСНОВАНИЯМИ В ВОДНОЙ СРЕДЕ

**А.А. Кравченко, Е.Н. Демяненко, О.М. Цендра, В.В. Лобанов,
А.Г. Гребенюк, М.И. Терец**

*Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины
ул. Генерала Наумова, 17, Киев, 03164, Украина*

Методом функционала плотности с использованием расширенного базисного набора $6-31++G(d,p)$ и обменно-корреляцийного функционала B3LYP проведен квантовохимический анализ строения гидратированных комплексов кислот HCl и HBr и гидроксидов щелочных металлов на поверхности кремнезема. Рассчитаны константы депротонирования гидроксильной группы поверхности кремнезема и её катионной формы.

МОДЕЛЮВАННЯ ВЗАЄМОДІЇ ПОВЕРХНІ КРЕМНЕЗЕМУ З КИСЛОТАМИ ТА ЛУГАМИ У ВОДНОМУ СЕРЕДОВИЩІ

**А.А. Кравченко, Є.М. Дем'яненко, О.М. Цендра, В.В. Лобанов,
А.Г. Гребенюк, М.І. Терець**

*Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна*

Методом функціоналу густини з використанням розширеного базисного набору $6-31++G(d,p)$ та обмінно-корреляційного функціоналу B3LYP проведено квантовохімічний аналіз будови гідратованих комплексів кислот HCl і HBr та гідроксидів лужних металів на поверхні кремнезему. Розраховані константи депротонування гідроксильної групи групи поверхні кремнезему і її катіонної форми.