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Electrical Double Layer at Zirconium Silicate/Electrolyte Solution Interface

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Parameters of the electrical double layer at zirconium silicate/aqueous sodium chloride interface were estimated from potentiometric titrations, background electrolyte ions adsorption and electrophoretic measurements data. Using numerical optimization the ionization and complexation constants of surface hydroxyl groups were determined. The best fit of calculations to the experimental data was achieved by assuming two kinds of surface hydroxyl groups that differ in acid-base properties.

Key words: zirconium silicate, electrical double layer, pzc, iep

Zirconium silicate ($ZrSiO_4$), beside baddeleyite, is the main parent mineral of zircon and in production of its compounds [1]. The stability of $ZrSiO_4$ dispersions depends among other things on electrical double layer (edl) interactions at solid/solution interface.

The surface charge at metal oxide/electrolyte interface results from the reaction between surface hydroxyl groups and electrolyte ions. For aqueous solutions, hydrogen and background electrolyte (denoted as *AnCt*) ions are able to create surface charge through the following reactions [2]:

$$\equiv SOH_2^+ \rightleftarrows \equiv SOH + H^+ \quad (1) \qquad \equiv SOH \rightleftarrows \equiv SO^- + H^+ \quad (2)$$

$$\equiv SOH_2^+An^- \rightleftarrows \equiv SOH + H^+ + An^- \quad (3) \qquad \equiv SOH + Ct^+ \rightleftarrows \equiv SO^-Ct^+ + H^+ \quad (4)$$

These reactions explain the changes of surface charge density and the dzeta potential with changes of solution pH and background electrolyte concentration [2].

The edl model that, beside the ionization reactions (1) and (2), considers also the complexation reactions (3) and (4) as forming surface charge is called Triple Layer Model (TLM). The equilibrium constants of the reactions (1) and (2) are denoted as K_{a1} and K_{a2}, whereas those of the reactions (3) and (4) as K_{An} and K_{Ct}. These constants may be calculated from experimental data (*e.g.* surface charge, adsorption of ions and ζ potential *vs* pH and background electrolyte concentration) using different methods [3].

Another approach to the calculation of the protonation constants of the surface hydroxyl- or oxyl- groups, developed by Hiemstra *et al.*, is MUSIC (MUltiSIte Complexation) model [4]. According to this model, the surface charge at metal oxide/electrolyte interface is the result of protonation of the surface hydroxyl- or oxyl-groups:

$$(\equiv Me_kOH_m((OH)_{1/2})_n)^{s_{init}} + H^+ \rightleftarrows (\equiv Me_kOH_{m+1}((OH)_{1/2})_{n-1})^{s_{fin}} \tag{5}$$

where: $k = 1 \rightarrow m + n = 2,\ k = 2 \rightarrow m + n = 2$ or $m + n = 1,\ k = 3 \rightarrow m + n = 1$, s_{init} – initial charge of the surface groups (before hydrogen ions adsorption), s_{fin} – final charge of the surface groups (after hydrogen ions adsorption).

Neutralization of the local charge of the surface oxygen atom (Σs_j) may be calculated according to equation (6) [4]:

$$\sum_j s_j = s_{Me} + m \times s_H + n \times (1 - s_H) \qquad (6) \qquad s = \exp\left(\frac{R - R_0}{b}\right) \qquad s = (R/R_0)^N \qquad (7)$$

where: m – the number of sp^3 oxygen orbitals bounded by H, n – the number of free orbitals of the oxygen, s_H – the actual bond valence of H = 0.8 valence unit (v.u.), s_{Me} – the effective metal atom charge that is calculated according to Brown's theory [5] from one of the equations (7), R – the distance between metal and oxygen atoms, R_0 – Me–O the distance characteristic of the metal atom (tabulated in [5]), and N, b – the constants (tabulated in [5]).

The protonation constants of the surface groups (5) may be calculated using the equation:

$$\log K = -A(\Sigma s_j + V) \tag{8}$$

where: A – the constant = 19.8, V – oxygen charge = –2.

The silicates are considered as composite oxides, and an attempt was made to analyze their pzc and surface charge density relationships [6,7]. However, a better comparison of the properties of surface hydroxyl groups may be performed by characterization of the ionization and complexation properties of these groups for the systems with simple and composite oxides. According to Parks' idea [6], $ZrSiO_4$ properties should be a combination of the acid-base properties of surface hydroxyl groups, characteristic of SiO_2 and ZrO_2. However, such simplification according to MUSIC model may be related only to the groups coordinated by one atom of the metal [4]. For hydroxyl groups, coordinated by more atoms, the acid-base properties of hydroxyl groups will result from the polarity of all oxygen-metal bonds. The crystal structure of $ZrSiO_4$ indicated that double coordinated groups might be coordinated either by two Si or by Si and Zr atoms. The protonation constants of oxyl and hydroxyl groups, presented in Table 1, were calculated from Eqs. (6–8), taking into account the characteristic parameters of $ZrSiO_4$ crystal cell [8]. The expected pzc value, calculated from all log$K$ values of singly coordinated oxo- and hydroxo-groups, was 11.95. When we used only the log$K$ values of the oxo- and hydroxo-groups of Si atoms then the calculated value of pzc was 7.92. The drawback of this approach is caused by taking into account the parameters of crystal of solid phase in calculation of the actual valence bond of the surface groups, whereas in the surface region the distances between atoms are different than in the solid phase bulk.

Table 1. MUSIC calculation of the protonation constants of oxyl and hydroxyl groups.

Group	oxyl groups		hydroxyl groups	
	$V + \Sigma s_j$	pK_{oxo}	$V + \Sigma s_j$	$pK_{hydroxo}$
$\equiv$SiO	–0.6	11.88	0.2	3.96
$\equiv Si_2O$	0.2	–3.96		
$\equiv$ZrO	–1.1	21.79	–0.5	9.91
$\equiv$(Zr,Si)O	–0.3	5.95		

On the other hand, applications of TLM model to the zirconium silicate/electrolyte system will be connected with introducing a few kinds of hydroxyl groups having different acid-base properties. Such a surface has heterogeneous properties, where these groups are mixed. For each kind of the groups the reactions (1)–(4) may occur.

In this paper a description of some properties of surface hydroxyl groups of composite oxide as additive properties of simple oxides has been presented by comparing the surface reaction constants of hydroxyl groups of simple oxides with composite ones. The comparison of the experimental and theoretical parameters estimated by using the MUSIC and TLM (with two kinds of hydroxyl groups differ in acid-base properties) models is presented.

EXPERIMENTAL

Experiments were performed on a commercial zirconium silicate sample purchased from Aldrich Chemical Company. Roentgen diffraction analysis revealed a tetragonal structure of the silicate studied. Size distribution analysis by PCS method showed that particles size is ranged from 20 nm to >3000 nm and the mean diameter of the particles was 1.24 μm. The other characteristic parameters of the particle size distribution were $d_{10\%} = 400$ nm and $d_{90\%} \sim 3000$ nm. XRF analysis of the sample showed the presence of the following elements: 1.98% ± 0.035% Hf, 0.0925% ± 0.003% Y, and trace amounts of Ca, Ti and Sc. The specific surface of the $ZrSiO_4$ sample, determined by nitrogen desorption, was 3.24 m^2/g. BJH analysis of the isotherm obtained by adsorption-desorption of nitrogen did not reveal micropores in the examined $ZrSiO_4$ sample. Sodium ions adsorption was performed with ^{22}Na isotope as tracer. The adsorption on the surface of the zirconium silicate was determined from the loss of the activity in the solution after contact with the solid.

To remove ionic type contaminations, which might influence the ions adsorption measurements, $ZrSiO_4$ was washed with double distilled water until constant conductivity about 2 μS/cm was achieved. Adsorption and surface charge measurements were performed simultaneously in the suspension of the same solid content, to keep the identical conditions of the experiments in a thermostated Teflon vessel in 25°C. To eliminate the influence of CO_2 all potentiometric measurements were performed under nitrogen atmosphere. pH values were measured using a set of glass and calomel electrodes with Beckman assembly. Surface charge density was calculated from the difference of the amounts of added acid or base to obtain the same pH value of suspension as for the background electrolyte.

The ζ potential of the zirconium silicate dispersions was determined by electrophoresis with Zetasizer 3000 by Malvern. The measurements were performed at 100 p.p.m. solid concentration after ultrasonication of the suspension.

RESULTS AND DISCUSSION

Fig. 1 presents the surface charge density of zirconium silicate as a function of pH in NaCl solutions concentrations: 0.1; 0.01; 0.001 and 0.0001 mol/dm^3. As can be seen, all curves charge densities *versus* pH intersect in one point $\sigma_0 = 0$. This point determines the point of zero charge ($pH_{pzc} = 7.2$) and is also treated as *Common Intersection Point* (CIP). The same value of pH_{pzc} and CIP means that in pzc the adsorption density of cations and anions is the same, therefore, the isoelectric point pH_{iep} should also be in the same place. The ζ potential *versus* pH dependence is presented in Fig. 2, where, as can be seen, pH_{iep} equals to 5.5. A similar relation between pH_{pzc} and pH_{iep} for $ZrSiO_4$/ KNO_3 solution systems was obtained by Mao *et al.* [9]. Their studies concerned the electrical double layer of natural and synthetic zirconium silicate in KNO_3 solutions. The authors obtained $pH_{pzc} = 6.1$ and 5.9, whereas pH_{iep} equal to 5.5 and 5.7 for natural and commercial samples, respectively. Mao *et al.* suppose that the difference between pH_{pzc} and pH_{iep} may be due to the contamination of the surface by base type substances; however, the described procedure of surface purification should re-

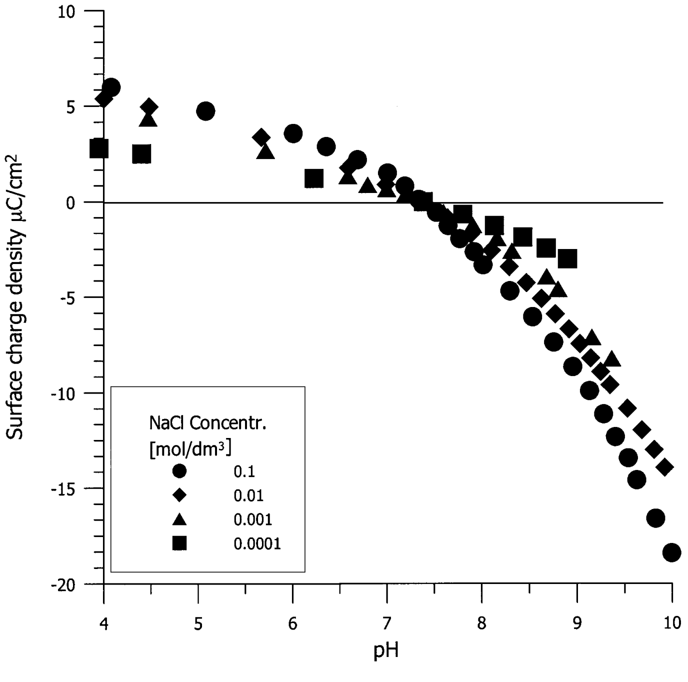

Figure 1. Surface charge density at the zirconium silicate/aqueous solutions of NaCl interface as a function of pH.

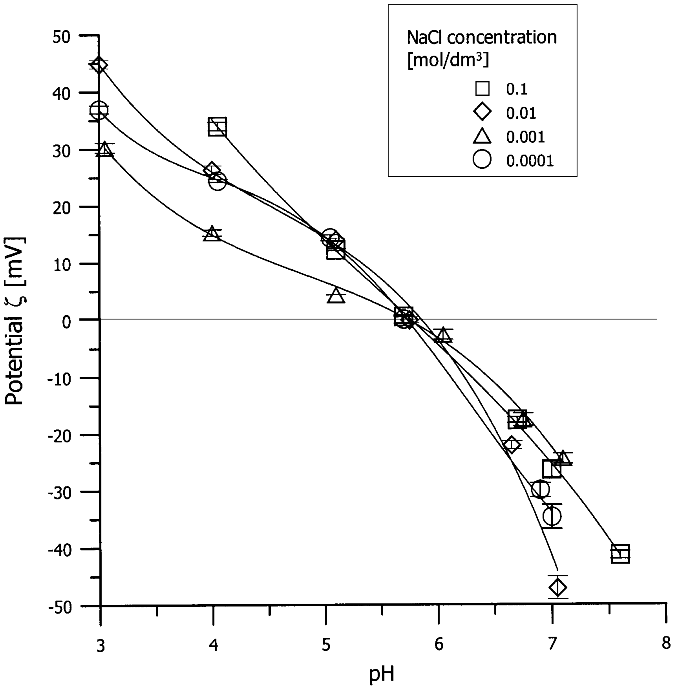

Figure 2. The ζ potential of the zirconium silicate particles in solutions of NaCl as a function of pH.

move this phase. This effect may result also from finer fraction of the solid that is used for ζ potential measurements than for potentiometric titration. Analyzing the size distribution, one can notice, besides 40% of particles of diameter <1 μm, also some amount of particles bigger than 3 μm. The pH_{pzc} value obtained for the examined sample is close to that one obtained by Cases [10]. The pH_{pzc} value calculated by Parks was 6.0, whereas Sverjensky claimed that it should be higher, namely $pH_{pzc} = 9.1$ [6,11]. It should be noted that both predicted values of pH_{pzc} are fairly different from the experimental ones. Similarly, pH_{pzc} value calculated from the data from Table 1 is far from that obtained from the potentiometric titrations of the suspension.

Another difficult to explain the property, shown in Fig. 2, is the ζ potential *vs* pH and the concentration of background electrolyte dependences. As it is seen, the sequence of ζ potential values does not decrease with increasing of the background electrolyte concentration. A small dependence of ζ potential *vs* electrolyte concentration for this system was observed by Mao *et al.* [9]. The ζ potential as a function of electrolyte concentration had a maximum, which is usually observed for large particles and high values of $\zeta \cong 125–175$ mV [12]. Such maximum was also observed for particles with a hairy structure of surfaces at lower values of ζ potential, but as it was mentioned above the examined sample had no micropores. The most probable reason of such relationship seems to be nonuniformity of particle sizes caused by their various aggregation for increasing electrolyte concentration.

When one assumes that the surface charge is formed as a result of proton exchange between ≡SiO and ≡SiOH groups then pH_{pzc} should be equal to 7.92. The ionization and complexation constants were calculated according to the method of Davies *et al.* [13], Sprycha [14], Schwarzenbach modified by Janusz [15] and numerically, using surface charge density *versus* pH and electrolyte concentration dependency [16]. The concentration of the surface hydroxyl groups, assumed after Mao *et al.* [9], was 3.6 OH groups/nm^2. The obtained values of the constants of the reactions (1)–(4) are presented in Table 2.

Table 2. The values of surface ionization and complexation constants for $ZrSiO_4$/NaCl system (s denotes relative standard deviation of surface charge value).

	Method			
	Davis *et al.* [13]	Sprycha [14]	Modified Schwarzenbach's [15]	Numerical optimization [16]
pK_{a1}	5.83±0.3	0.25	5.93±0.55	4.91
pK_{a2}	9.08±0.20	9.34	9.07±0.37	8.45
pK_{Cl}	8.07±0.39		7.61±0.26	1.00
pK_{Na}	8.44±0.12		7.82±0.46	7.45
s	10.15		9.23	0.08

In determination of the surface reactions constants, by the numerical method, we sought the minimum of function that is the sum of squares of differences between the theoretically calculated values of surface charge and experimental ones [16]. To determine the concentration of the surface groups and surface charge density *vs* pH and background electrolyte concentration (according to reactions (1)–(4)), the surface potential as well as potential of Inner Helmholtz Plane were calculated from ζ potential, using the following relation:

$$\psi_\beta = \psi_d - \frac{\sigma_d}{C_2} \tag{9}$$

where: ψ_β stands for the potential of Outer Helmholtz Plane (OHP); ψ_d denotes the potential of Inner Helmholtz Plane (IHP) (calculated from ζ potential); C_2 denotes the capacity between IHP and OHP.

Assuming that the separation distance of the shear plane from OHP is 0.7 nm, the charge density in OHP (calculated from ζ potential) σ_d may be calculated from the Gouy-Champman theory, and finally ψ_β from equation (9).

Having ψ_β, the surface potential ψ_0 may be calculated using the following equation:

$$\psi_0 = \psi_\beta + \frac{\sigma_0}{C_1} \tag{10}$$

where: ψ_0 denotes the surface potential, and C_1 is the capacity between surface and IHP. The calculation of the surface charge density *vs* pH and electrolyte concentration, using the constants from Table 2, indicates that the numerically determined set gives values of the surface charge close to experimental ones. The standard deviation is smaller than for other sets. Additionally, the advantage of this method is prediction of the concentration of the surface groups as a function of pH. However, the values of surface charge density *versus* pH calculated in this way lead to unsatisfactory fitting of the experimental data. On the other hand, such fitting was better than that presented by Mao *et al.* [9].

To achieve a better fitting of model calculations to experimental data, equilibrium constants of surface reactions were calculated again assuming two types of hydroxyl groups denoted as $\equiv$S(1)OH and $\equiv$S(2)OH that randomly mixed on the surface of zirconium silicate. This distribution of the hydroxyl groups allowed us to describe the dissociation reactions or adsorption of ions at the same surface potential ψ_0.

Constants $pK_{a1}(1) = 5.76$, $pK_{a1}(2) = 3.55$, $pK_{a2}(1) = 9.86$, $pK_{a2}(2) = 8.31$, $pK_{An}(1) = 7.87$, $pK_{An}(2) = 4.21$, $pK_{Ct}(1) = 6.77$, $pK_{Ct}(2) = 7.90$ obtained for such model allow charge densities fitting to the experimental data with about 4% accuracy (see Fig. 3). The participation of the second type of groups was smaller about (18.1%) than the first ones, but the former revealed higher tendency to dissociate out H^+ ions.

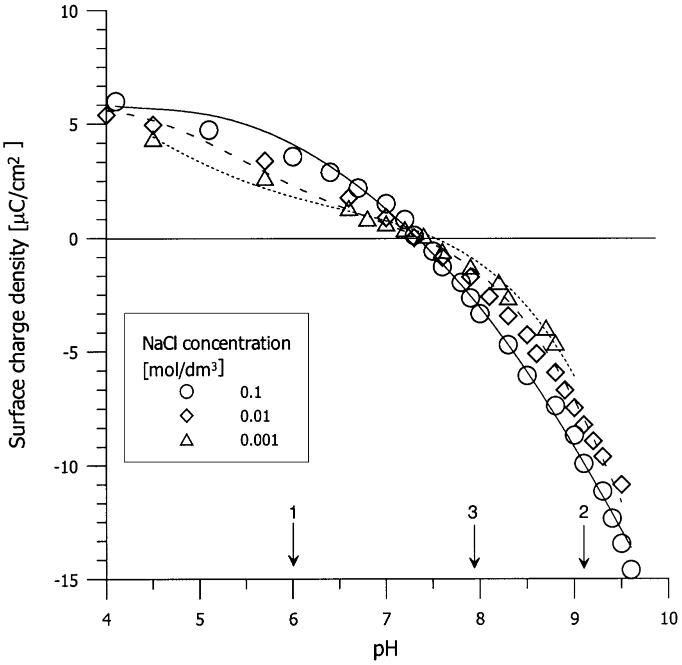

Figure 3. Comparison of model calculations of surface charge density as a function of pH at the $ZrSiO_4$/NaCl solutions interface (lines) with experimental ones (points). Arrows represent the pzc predicted by theory of: 1 – Parks, 2 – Sverjensky *et al.*, 3 – MUSIC.

The share of the particular surface forms in the charge on the surface of zirconium silicate is presented in Fig. 4. It can be noticed that at this electrolyte concentration the participation of the complexed forms in the charge formation is very small. In the range pH < pH_{pzc} the surface charge is formed mainly by the form connected with type 1 hydroxyl groups. The participation of type 2 groups is smaller, whereas in the range pH > pH_{pzc} these groups dissociate more easily. At higher concentrations of the electrolyte the magnitude of the surface charge is determined by complexed forms, and in the range pH > pH_{pzc} the participation of both forms is comparable.

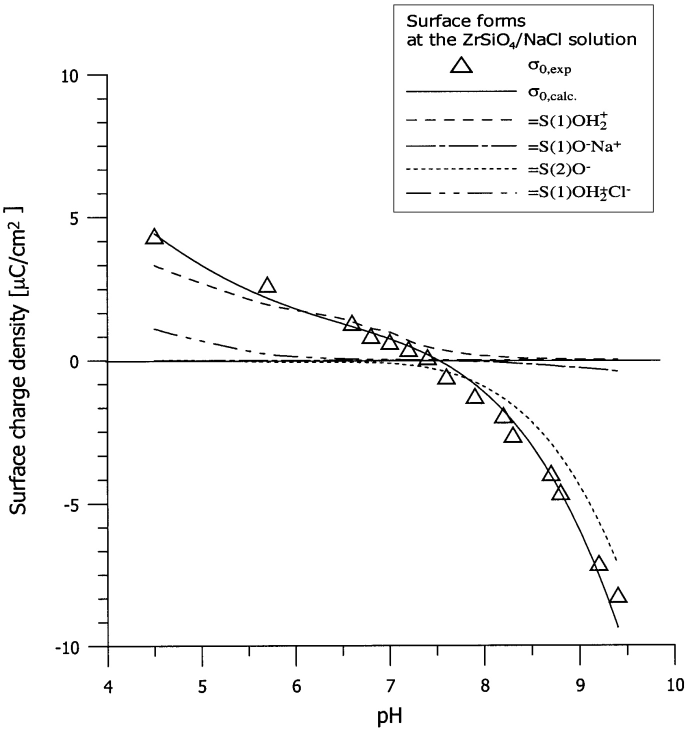

Figure 4. Model calculation of surface charged forms at the $ZrSiO_4$ surface in the 0.001 mol/dm^3 solution of NaCl of concentration.

The dependence of adsorption density of Na^+ ions on pH for the $ZrSiO_4$/NaCl solution system is presented in Fig. 5. It can be noticed that adsorption of Na^+ ions runs in the way characteristic of the metal oxide/electrolyte solution systems. For pH < pH_{pzc} a negative adsorption was observed, caused by electrostatic interaction between positive charge of the surface and Na^+ ions, whereas in the range pH > pH_{pzc} the adsorption density increases according to the equation (4).

As it is seen, the calculated concentration of the surface groups and complexing sodium cations (Fig. 4) with the adsorption data obtained experimentally (Fig. 5) shows acceptable consistence of both values. Comparison of the reaction equilibrium constants of the surface hydroxyl groups, obtained for the studied $ZrSiO_4$ system with

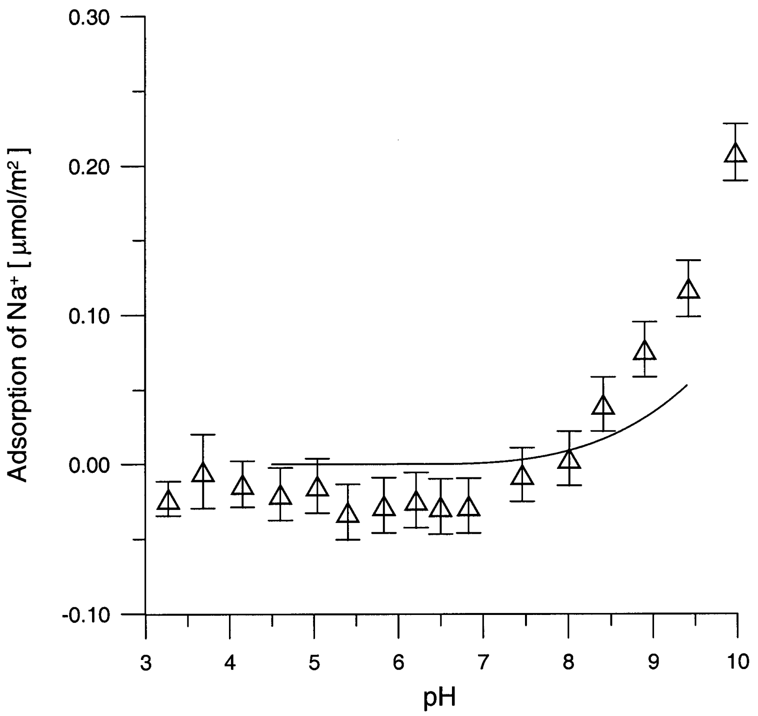

Figure 5. Adsorption density of Na^+ ions at zirconium silicate/aqueous solution of 0.001 mol/dm^3 NaCl interface.

the literature data for SiO_2/NaCl solutions ($pK_{a2} = 6.13–6.52$; $pK_{Na} = –1.32$) [17] and for ZrO_2/NaCl solutions ($pK_{a1} = 5.5$, $pK_{a2} = 10.9$, $pK_{Cl} = 7.0$, $pK_{Na} = 9.45$) [18], shows that the individual acid-base character of the surface hydroxyl groups bonded with silicon or zirconium atoms in zirconium silicate is different than that in pure silica or crystal zirconium dioxide.

The presence of other ions in metal atom surroundings produces indirectly a change of the polarity of the bonds in the hydroxyl group, which results in changes of acid-base character of the group. In consequence, even for zirconium silicate the surface properties of the interface silicate/electrolyte solution cannot be described by simple summarizing of the properties of silica and zirconia groups.

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