Physicochemical Problems of Mineral Processing, 41 (2007), 215-225
Fizykochemiczne Problemy Mineralurgii, 41 (2007), 215-225

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STRUCTURE OF ELECTRICAL DOUBLE LAYER AT THE Al_2O_3-SiO_2/ELECTROLYTE SOLUTION INTERFACE

Received March 15, 2007; reviewed; accepted June 4, 2007

The structures of the electrical double layer at the Al_2O_3-SiO_2/$NaClO_4$ interface with different alumina-to-silica ratios were interpreted using the surface complexation model. The surface charge and potential ζ of the system has been determined as a function of pH for 0.1, 0.01, and 0.001 mol/dm^3 solutions of $NaClO_4$. A significant difference in the pH values of IEP and point of zero charge was observed for Al_2O_3-SiO_2 samples. The ionization and complexation constants have also been determined.

Key words: alumina, silica, electrical double layer, surface charge, zeta potential

INTRUDUCTION

The studies of the surface properties of mixed oxides are important for theoretical and practical reasons, because they imitate better systems that occur in nature (like soils) and technology, than the individual metal oxides. Especially, such mixed oxides are important in catalysis.

The surface charge at a metal oxide/electrolyte interface is formed as result of acid-base reactions of surface hydroxyl groups (-SOH) according to equations:

$$SOH_2^+ \leftrightarrow SOH^0 + H^+ \tag{1}$$

$$SOH^0 \leftrightarrow SO^- + H^+ \tag{2}$$

The site–binding theory of the electrical interfacial layer (eil) assumes that the background electrolyte ions play a very important role in the formation of surface

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charge due to their specific interactions with surface hydroxyl groups of metal oxide (James and Parks, 1989). This process can be described as follows:

$$\mathrm{SOH_2^+An^-} \leftrightarrow \mathrm{SOH^0} + \mathrm{H^+} + \mathrm{An^-} \tag{3}$$

$$\mathrm{SOH^0} + \mathrm{Ct^+} \leftrightarrow \mathrm{SO^-Ct^+} + \mathrm{H^+} \tag{4}$$

The equilibrium constants of reactions 1 and 2 are denoted as K_{a1} and K_{a2}, whereas those of reactions 3 and 4 as K_{An} and K_{Ct}. These constants may be calculated from the surface charge density or electrokinetic data using different methods.

Structural characteristics of Al_2O_3-SiO_2 depends on a synthesis method and composition of the mixed oxide. A different condition of synthesis of mixed oxides leads to changes in distribution of Al_2O_3 across particles and structure. These changes influence chemical properties of mixed oxide surface and consequently adsorption affinity of surface groups to ions from solution. Adsorption of cations on these groups will proceed as follows:

$$\equiv \mathrm{Si-O(H)-Al} = +\mathrm{Ct^{n+}} \Rightarrow \equiv \mathrm{Si-O(Ct^{n+})Al} = +\mathrm{H^+} \tag{5}$$

$$= \mathrm{AlOH} + \mathrm{Ct^{n+}} \Rightarrow = \mathrm{AlO(H)Ct^{n+}} \tag{6}$$

The properties of surface groups at these mixed oxides are not well described because of effect of electrostatic charge accumulation in electron spectroscopic study. For the Al_2O_3 - SiO_2 system where Al_2O_3 has been deposited by evaporation on a flat SiO_2 surface, electron photoemission parameters such as binding energy (BE) and modified Auger parameter (α) has been analyzed by X-ray Photoemission Spectroscopy (XPS) and Reflection Electron Energy Loss Spectroscopy (REELS) (Reiche et. al., 2000).

Studies of the electrical double layer at the Al_2O_3-SiO_2/$NaClO_4$ interface and adsorption properties of such system in reference to pure, mixed and composite oxides were reported in literature (Kosmulski, 2001; Schwarz et al., 1983). A comprehensive review of the pH_{PZC} and pH_{IEP} values for such systems was presented by Kosmulski (2001). Schwarz et al. (1983) studied the surface charge density of composite SiO_2 and Al_2O_3 oxides in wide range of composition of solid phase. Their results agree with calculation by means a method suggested by Parks for calculation of the pH_{PZC} of mixed oxide system. The model assumed that each component of the binary oxide system behaves independently and the pH_{pzc} of such a mixed oxide is a linear function of amount of pure oxides. However, to achieve good agreement of calculated values and experimental pH_{pzc} for mixed oxides containing silica, the values of pH_{pzc} of silica has to be taken for calculation is too high. A similar study of the silica alumina system were carried out by Reymond and Kolenda (1999). They found that only when silica content increases from 0 to 85 wt.%, the mixture pH_{PZC} value changes linearly with silica content. Above this value, the dependence varies as linear extrapolation of pH_{pzc} for pure oxides. Reymond and Kolenda (1999) suggest that in natural and acidic environment, aluminum oxide may dissolve, creating small particles of AlOOH, which precipitate on the SiO_2 surface. When SiO_2 concentration is high (>90%), the surface coverage by AlOOH particles is low and the particle charge is determined by the SiO_2 face. The difference in behavior in both described above systems seems to arise from the difference in the equilibration time of the system. Schwarz et al. (1992) assumed it as 10 min., but Reymond and Kolenda (1999) carried out pH measurements after 24 hours. In such studies, during a long time of equilibration the subsequent dissolution and precipitation of AlOOH process took place in the system. The aim of the paper was to characterize the electrical double layer parameters at the Al_2O_3-SiO_2/$NaClO_4$. In both papers, the authors in their experiments used magnetic stirrer during titration and this device may grind solid particles, so it is not recommended for potentiometric titration purposes (Janusz, 2000).

The pH_{PZC} measurements for the mixed oxides Al_2O_3–SiO_2 which were prepared by a co-precipitation of Na_2SiO_3 + $Al(NO_3)_3$ in $NaNO_3$ solution showed, that the pH_{PZC} point shifts to the lower pH value with increase of the SiO_2 concentration in the mixed oxide. For mixed oxide with composition of 50-60% Al_2O_3 the pH_{pzc} =4.5. For 70% Al_2O_3 pH_{pzc} =5.8 and for 80% Al_2O_3 the pH_{PZC} =7 (Kuo and Yen, 1988).

In this paper, some studies on the electrical double layer at mixed silica-alumina oxides/electrolyte solution are presented. Measurements comprise surface charge and zeta potential in the $NaClO_4$ solutions. The experimental data were used for theoretical calculations of the ionization and complexion constants of reactions of the surface hydroxyl groups. The results of these calculations allowed to estimate the shares of respective surface groups in the surface charge at the mixed silica-alumina oxides/electrolyte solution interface.

EXPERIMENTAL

MATERIALS AND METHODS

The Al_2O_3-SiO_2 systems were prepared using the fumed method. The samples of mixed oxide of silica-alumina contain the following amount of Al_2O_3: 30, 23, 8, 3 and 1% and was described as AS30, AS23, AS8, AS3, AS1, respectively. By means of the nitrogen adsorption–desorption isotherms using a Micrometrics ASAP, the structural characteristics of studied materials were obtained and are collected in Table 1.

S_{BET} (the specific surface area) was calculated according to the BET method (Adamson and Gast, 1997) using adsorption data at relative pressures p/p_o between 0.05 and 0.25, where p and p_o denote the equilibrium pressure. The pore volume V_p was evaluated from the adsorption data using the BJH (Barrett-Joyner-Halenda) method. The $R_{p.}$ (pore radius), S_{BET}, and V_p were utilized to estimate the average specific surface area of mesopores S_K was calculated using the Kiselev equation. The surface area S_{mes} and volume V_{mes} of mesopores were also calculated using the theory of capillary evaporation by the improved program package described in detail elsewhere (Gun'ko, 1992). The all studied systems contained micropores.

Table 1. Structural AS parameter (Gun'ko et al., 2004)

Sample	AS1	AS3	AS8	AS23	AS30
S_{BET} [m^2/g]	207	188	308	353	239
V_p [cm^3/g]	0.42	0.39	0.66	0.8	0.57
R_p [nm]	3.7	3.8	3.8	4	4.8
S_K [m^2/g]	158	146	241	283	-
S_{mes} [m^2/g]	90	82	135	158	-
V_{mes} [cm^3/g]	0.18	0.16	0.26	0.28	-

where:
S_{BET} - the specific surface area;
V_p - the pore volume
R_{p}.- pore radius
S_K - specific surface area was calculated using the Kiselev equation
S_{mes} - surface area was calculated using the theory of capillary
V_{mes} – volume of mesopores

Particle size distribution and electrophoresis study were carried out using a Zetasizer 300 (Malvern Instruments) apparatus based on photo correlation spectroscopy (PCS). The dispersions of silica-alumina oxide (100 ppm of solid)) prior electrokinetic and particle size measurements were ultrasonicated for 3 min using an ultrasonic disperser (Sonicator Misonix Inc.). The results of particle size measurements are presented in Table 2. The zeta potential of the Al_2O_3-SiO_2 dispersions was determined by electrophoresis with Zetasizer 3000. The pH values, measured by a precision digital pH meter were adjusted by addition of 0.1 mol/dm^3 $HClO_4$ or NaOH solution.

Table 2. The particle size and factors of polydispersity

Sample	AS1	AS3	AS8	AS23	AS30
Mean particle size, nm	255	259	235	253	244
Factors polydispersity	0.18	0.22	0.17	0.2	0.06

As it can be seen from Table 2 that the values of particle size and polidispersity of samples containing different amount of alumina are similar, so the same formula for zeta potential calculation from electrophoretic mobility had been used.

Surface charge measurements were performed in suspensions having such solid contents to ensure the same surface area to electrolyte volume ratio, to keep identical conditions of the experiments in a thermostated Teflon vessel at 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 REF 451 and calomel pHG201-8 electrodes with Radiometer assembly. Surface charge density was calculated from the difference of the amounts of acid or base added to obtain the same pH value of the suspension as the background electrolyte.

RESULTS AND DISCUSSION

Table 3 presents the values of pH_{PZC} and pH_{IEP} for the studied Al_2O_3-SiO_2 oxides/electrolyte solution interface.

Table 3. Values of pH_{PZC} and pH_{IEP} for the Al_2O_3-SiO_2/$NaClO_4$ solution system

	AS1	AS3	AS8	AS23	AS30
pH_{PZC}	4	4	4	4.4	4.6
pH_{IEP}	<3	<3	<3	<3	<3

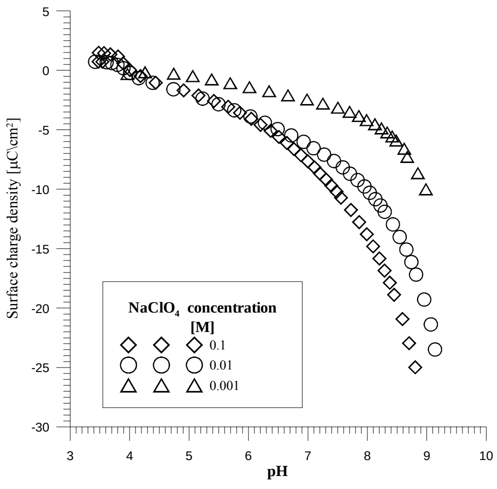

Fig. 1. Surface charge density at the AS1/$NaClO_4$ solution interface as a function of pH

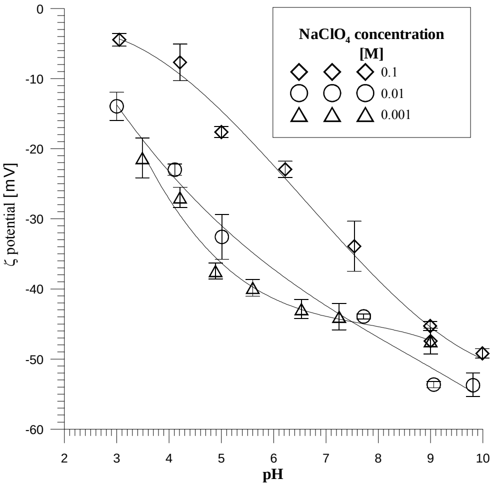

Fig. 2. The ζ potential of AS1/$NaClO_4$ solution interface function of pH

Figs 1, 3 and 5 present the surface charge density as a function of pH for three concentrations of $NaClO_4$ solutions for AS1, AS3 and AS23 samples, respectively. The change of pH_{PZC} with the percentage of Al_2O_3 in the Al_2O_3-SiO_2 sample depends of the acid-base properties of the surface hydroxyl groups (that are determined by atoms that surround the oxygen). At low Al_2O_3 concentration, the SiO_2 layer probably covers the oxide surface.

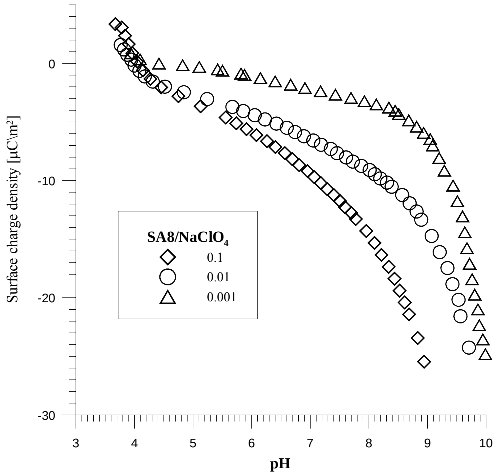

Fig. 3. Surface charge density at the AS3/NaClO$_4$ solution interface as a function of pH

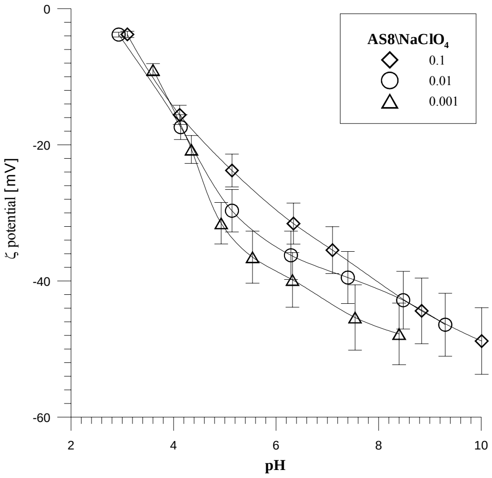

Fig. 4. The ζ potential of AS3/NaClO$_4$ interface solution function of pH

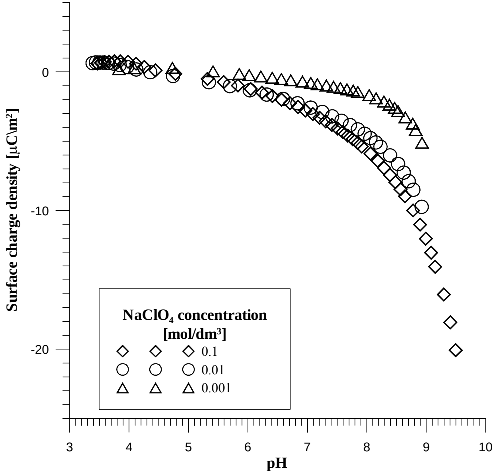

Fig. 5. Surface charge density at the AS23/NaClO$_4$ solution interface as a function of pH

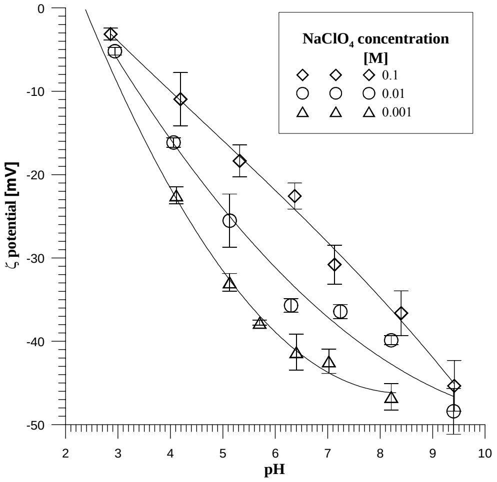

Fig. 6. The ζ potential of AS23/NaClO$_4$ interface solution function of pH

After exceeding certain aluminum oxide concentration in surrounding of oxygen of surface hydroxyl groups, the Al(III) atoms may appear. That means that the substrate ratio and method of sample preparation influences the subsurface region composition and it may differ from the bulk composition of particle. The surface hydroxyl groups on such oxides may have acidic character (as $\equiv \mathrm{SiOH}$) or totally different basic character (as $= \mathrm{AlOH}$). There may occur also groups of higher coordination level eg. $= (\mathrm{AlO})_3\mathrm{OH}$ or mixed as $\equiv \mathrm{SiO(H)Al} \equiv$ which also have more acidic. According to Sempels and Rouxhet (1976) the last one group has about ¼ weaker acidic character than $\equiv \mathrm{SiOH}$.

The ζ potential of AS1, AS3 and AS23 samples in the $NaClO_4$ solution as a function of pH is presented in Fig. 2, 4 and 6. As it can be seen from these Figs that the ζ potential decreases with the increase of the pH and increases with electrolyte concentration. For all studied samples only negative values of zeta potential were observed. The pH_{IEP} and pH_{PZC} values for all Al_2O_3-SiO_2/$NaClO_4$ systems are collected in Table 3. A comparison of the pH_{PZC} and pH_{IEP} values is presented in Table 4. The pH_{IEP} values are below pH=3 for all mixed oxide whereas the pH_{PZC} for the mixed oxides of low percentage of alumina are equal to 4 while for higher aluminum oxide concentration the pH_{PZC} shifts to a higher pH value. The difference between pH_{PZC} and pH_{IEP} may arise from different surfaces of oxide accessible in the potentiometric titration and electrophoresis experiments. Since the studied Al_2O_3–SiO_2 oxides have mean pores radius about 4 nm, that is almost equal to the electrical double layer thickness for 0.01 mol/dm^3 $NaClO_4$ solutions, for lower concentration of the electrolyte solutions the double layers from individual walls of pores may overlap. Part of pores may be smaller than 1nm and assuming that the slipping plane is 1.5 nm from the solid surface, such pores maybe blocked during electrophoresis, so the surface properties of this part of the solid will not be active during electrophoresis. A great part of charge may be compensated inside particle pores and only part, created by ionized groups on the oxide surface, is responsible for electrophoretic mobility. The pH_{PZC} and pH_{IEP} values of SiO_2 reported in literature range from 1 to 3 (Jung, 2001; Pickup et al., 1999; Gunawidjaja et al., 2003 and for Al_2O_3 respective values are from 8 to 9 (Parks, 1967). Comparing this to values for the Al_2O_3-SiO_2 system, one can see that the SiO_2surface has decisive influence on the mixed oxide surface properties.

Basing on the potentiometric titration data, the ionization and complexation constants of surface hydroxyl groups were calculated for the electrical interfacial layer on Al_2O_3-SiO_2/$NaClO_4$ using the TLM theory The ionization and complexation constants of the surface hydroxyl groups were calculated using the approaches by Davis et al. (1978), Sprycha (1984), the modified Schwarzenbach method (Schwarzenbach and Ackerman, 1948), and a numerical optimization method basing on the surface charge density versus pH and electrolyte concentration data for the AS1/$NaClO_4$ system. The calculated values are collected in Table 4. One can see a better agreement of the constants with the values calculated by the Davis et al. method than by the Schwarzenbach method and numerical optimization. Small values of pK_{a1} and pK_{Cl} indicate that positive groups are scarce. The contribution of the particular surface groups in the surface charge of AS1 is depicted in Fig.7. As it can be seen, the calculated concentration of surface charge density with data obtained experimentally shows acceptable consistency for both values (Fig.7). The results for one system only has been presented because of similar tendency for others concentration background electrolyte.

Comparing the constants values of hydroxyl groups for system Al_2O_3-SiO_2 with the data from literature for SiO_2/$NaClO_4$ (pK_{a2}=5.7; pK_{Na}=7.24) (Sprycha, 1982) and for

$Al_2O_3/NaClO_4$ (pK_{a1}=4.45, pK_{a2}= 8.45) (Davis et al., 1978), we can see that acid-base character of surface hydroxyl groups bond with Al or Si in mixed Al_2O_3-SiO_2 oxide is different than SiO_2 or Al_2O_3 alone. The surface properties of Al_2O_3-SiO_2 cannot simply be described by addition of surface properties of hydroxyl groups to the pure SiO_2 or Al_2O_3.

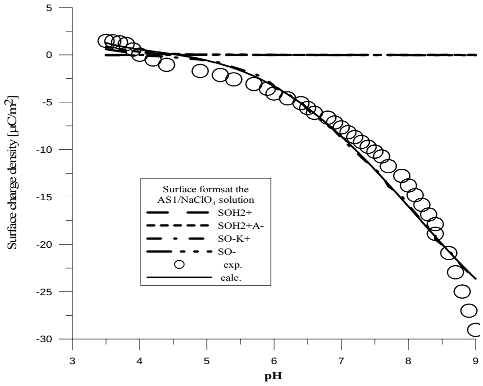

Fig. 7. Model calculation of concentration of surface groups forms at the AS1/0.1 M $NaClO_4$ solution interface

Table 4. The values of surface ionization and complexation constants for AS/ $NaClO_4$ system

Constants	Method		
	AS1		
	Davis *at al.*	Modified Schwarzenbach’s	Numerical Optimalization
pK_{a1}	1.01	3.63	1.37
pK_{a2}	9.7	6.62	10.99
pK_{Cl}	2.04	5.67	2.07
pK_{Na}	6.7	0	5.96
AS3			
pK_{a1}	2.5	5.74	1.96
pK_{a2}	8.28	8.62	13
pK_{Cl}	-0.29	0	0.004
pK_{Na}	6.96	6.62	6.76
	AS8		
pK_{a1}	1.5	2.11	1.82
pK_{a2}	5.71	6.32	6.74
pK_{Cl}	1.9	3.22	3.53
pK_{Na}	6.04	5.15	4.85
	AS23		
pK_{a1}	1.34	1.56	2.4
pK_{a2}	7.14	7.72	7.51
pK_{Cl}	2.1	2.71	2.13
pK_{Na}	7.1	7.44	7.3
	AS30		
pK_{a1}	5.77	5.23	1.8
pK_{a2}	7.79	8.11	10
pK_{Cl}	0.4	0	1.59
pK_{Na}	7.4	6.85	6.68

One can see a good agreement of the constants with the values calculated by various methods. For example AS1 - Davis et al. method and numerical optimization except pKa_2, for AS3system - Davis et al., then Schwarzenbach's method (without pK_{a1}) and numerical optimization. For AS8 system - Davis et al. method (without pK_{Cl}, pK_{Na}), than Schwarzenbach's method and numerical optimization, and for mixed oxide AS23 and AS30 - Davis et al., then Schwarzenbach's method and numerical optimization (without pK_{a1}, pK_{Na}). Small values of pK_{a1}, pK_{Cl} for all mixed oxide, suggest low number of the concentration of positively charged groups on the surface. Comparing surface hydroxyl groups reaction constants obtained for Al_2O_3-SiO_2 systems with literature data for SiO_2/$NaClO_4$ (pK_{a2}=5.7; pK_{Na}=7.24) (Kosmulski, 1997) and for Al_2O_3/$NaClO_4$ (pK_{a1}=4.45, pK_{a2}= 8.45) (Brady, 1994), one can see that the acid-base character of the surface hydroxyl groups bonded to Al or Si atoms in mixed Al_2O_3-SiO_2 oxides differs from the one for SiO_2 or Al_2O_3, without pK_{a2} for AS3 (Davis et al. and Schwarzenbach's method), pK_{a2} for AS8 (Devis et al. method), pK_{Na} for AS23 (Davis et al. then Schwarzenbach's method and numerical optimization). According to above it is rather impossible to describe properties of SiO_2 and Al_2O_3 by simple surface properties summation in the case of the Al_2O_3-SiO_2/$NaClO_4$ interface.

CONCLUSION

The aim of this paper was to characterize the electrical double layer structure at the Al_2O_3-SiO_2 /$NaClO_4$ interface. The properties of the interface of the mixed oxide/electrolyte solution in a wide range of concentration, mechanism of surface charge creation, and structure of the edl were described. Complex investigations of the mixed oxides/electrolyte interface properties have been carried out for wide concentrations range taking into account the influence of ionic strength on the surface charge generation mechanism and edl composition. The experimental data acquired were used to describe quantitative the electrical double layer with use of proper models.

1. On basis of the dependences of surface charge density as a function of pH and electrolyte concentration the values of surface ionization and complexation constants for system Al_2O_3-SiO_2/$NaClO_4$ were calculated. The contributions of the particular surface groups in the surface charge of Al_2O_3-SiO_2 were calculated. Calculated concentration of surface charge density shows acceptable consistency with the data obtained experimentally.
2. Parks' theories related to foreseeing the IEP(s) of oxide and Parks' theories modification (Yoon theories and MUSIC) are unable to determine exactly the pH_{PZC} value of mixed oxide because the acid–base surface hydroxyl groups properties are depended on concentration and surface structure.
3. The mixed Al_2O_3-SiO_2 oxides with various Al_2O_3 concentrations showed differences between pH_{PZC} and pH_{IEP} value not correlated with oxide composition.

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Badania właściwości powierzchniowych tlenków mieszanych są ważne z praktycznego i teoretycznego powodu, ponieważ są szeroko rozpowszechnione w glebach i nowoczesnych technologiach np. jako katalizatory. Struktura podwójnej warstwy elektrycznej na granicy faz Al_2O_3-SiO_2/$NaClO_{4,}$ z różną zawartością objętościową tritlenku glinu w badanych układach została zinterpretowana przy użyciu odpowiedniego modelu pwe. Określono gęstość ładunku powierzchniowego i wartość potencjału dzeta w zależności od pH dla następujących stężeń elektrolitu 0.1, 0.01 i 0.001 mol/dm^3 $NaClO_4$.Obliczono stałe jonizacji i kompleksowania metodą optymalizacji numerycznej dla poszczególnych układów oraz porównano wartości gęstości ładunku powierzchniowego wyznaczonego metodą miareczkowania potencjometrycznego do wyznaczonego teoretycznie.