Determination of intrinsic equilibrium constants at an alumina/electrolyte interface

ŽAKLINA N. TODOROVIĆ[#] and SLOBODAN K. MILONJIĆ[*#]

Chemical Dynamics Laboratory, The Vinča Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Serbia & Montenegro (e-mail: smiloni@vin.bg.ac.yu)

Abstract: Intrinsic ionization and complexation constants at an alumina/electrolyte interface were studied by the site binding model, while the sorption of alkali cations from aqueous solutions was interpreted by the triple-layer model. The surface properties of alumina were investigated by the potentiometric acid-base titration method. The point of zero charge (pH_{pzc}) of alumina obtained by this method was found to be 7.2. The obtained mean values of the intrinsic protonation and ionization constants of the surface hydroxyl groups and the intrinsic surface complexation constant, in different electrolytes, are $pK^{int}_{a1} = 4.4$, $pK^{int}_{a2} = 9.6$ and $pK^{int}_{M^+} = 9.5$, respectively.

Keywords: alumina, surface properties, point of zero charge, intrinsic ionization and complexation contants.

INTRODUCTION

Alumina is a widely used oxide and one of the most important inorganic materials. It has been applied as an adsorbent and catalyst as well as a ceramic material.

Many theories have been developed and experiments performed to explain the chemical behavior of oxide/water interfaces, but the site binding model, first presented by Yates *et al.*[1], then extended by Davis *et al.*[2–4] and James *et al.*,[5,6] is the one that explains, in the best way, the processes occurring at a solid-liquid interface.

In this work, important surface properties of alumina, including the intrinsic surface protonation and ionization constants of the surface hydroxyl groups as well as the intrinsic surface complexation constants, were determined.

Theoretical

The site binding model, chosen in this work, was developed by Davis *et al.*[2–4] According to the model, association-dissociation processes and counterion adsorption at an alumina/electrolyte interface can be described by the following stoichiometric equations:

*   Corresponding author.
\#   Serbian Chemical Society active member.

$$>AlOH_2^+ \xleftarrow{\quad K_{a1}^{\text{int}}\quad} >AlOH + H_s^+ \tag{1}$$

$$>AlOH_2^+ + A_s^- \xleftarrow{\quad K_{A^-}^{\text{int}}\quad} >AlOH_2^+ A^- \tag{2}$$

$$>AlOH_2^+ A^- \xleftarrow{\quad {}^*K_{A^-}^{\text{int}}\quad} >AlOH + OH_s^+ + A_s^- \tag{3}$$

for the pH range below the point of zero charge ($pH < pH_{pzc}$), and

$$>AlOH \xleftarrow{\quad K_{a2}^{\text{int}}\quad} >AlO^- + H_s^+ \tag{4}$$

$$>AlO^- + M_s^+ \xleftarrow{\quad K_{M^+}^{\text{int}}\quad} >AlO^- M^+ \tag{5}$$

$$>AlOH + M_s^+ \xleftarrow{\quad {}^\bullet K_{M^+}^{\text{int}}\quad} >AlO^- M^+ + H_s^+ \tag{6}$$

for the pH range above pH_{pzc}. Here, $>AlOH_2^+$, $>AlOH$ and $>AlO^-$ denote positive, neutral and negative surface species, respectively. M^+ and A^- are monovalent electrolyte ions, while $>AlOH_2^+ A^-$ and $>AlO^-M^+$ represent surface complexes. The subscript "int" denotes the intrinsic character of equilibrium constants and "s" refers to the solid phase surface.

The intrinsic surface ionization constants, pK^{int}_{a1} and pK^{int}_{a2}, defined by Eq. (1) and Eq. (4), respectively, can be calculated from:

$$pK_{a1}^{\text{int}} = pH + \log\frac{\alpha_+}{1-\alpha_+} + \frac{e\psi_0}{2.3kT} \tag{7}$$

$$pK_{a2}^{\text{int}} = pH - \log\frac{\alpha_-}{1-\alpha_-} + \frac{e\psi_0}{2.3kT} \tag{8}$$

The intrinsic surface complexation constants, ${}^*K^{\text{int}}_{A^-}$, and ${}^*K^{\text{int}}_{M^+}$ for reactions (3) and (6), can be calculated from:

$$p{}^*K_{A^-}^{\text{int}} = pH - \log\frac{\alpha_+}{1-\alpha_+} - \log[A^-] + \frac{e(\psi_0 - \psi_\beta)}{2.3kT} \tag{9}$$

$$p{}^*K_{M^-}^{\text{int}} = pH - \log\frac{\alpha_-}{1-\alpha_-} - \log[M^+] + \frac{e(\psi_0 - \psi_\beta)}{2.3kT} \tag{10}$$

where α_+ and α_- denotes the fraction of charged sites, which can be calculated as a ratio of the surface charge densities, σ_0, and the total number of surface groups, N_s ($\alpha_+ = \sigma_0/N_s$ for a positive, and $\alpha_- = -\sigma_0/N_s$ for a negative surface). In our case, it was assumed that the alumina surface was fully hydroxylated, which gives N_s a

value of 8 OH nm^{-2} or 128 $\mu C\ cm^{-2}$ in charge units.[7] ψ_0 represents the mean potential of the surface charge plane, which depends on the potential-determining ion reactions (Eqs. (1) and (4)), ψ_β represents the mean potential of the plane of specifically sorbed cations, k is the Boltzman constant, and T is the temperature.

The numerical values of the constants in equations (7–10) may be estimated by zero charge extrapolation or using the double extrapolation method proposed by James *et al.*[5,6]

EXPERIMENTAL

Materials

In this work, a commercial sample of alumina (aluminium oxide for Chromatography) product of VEB Laborchemie Apolda (Germany) was used. The alumina had a boehmite crystal structure as shown by X-ray analysis performed using a Siemens Kristalloflex 4 with a Geiger-Müller counter. The specific surface area of the alumina, measured by the BET method, was 110 m^2/g. All chemicals (NaCl, KCl, LiCl, $NaNO_3$ and NaI), obtained from various commercial sources, were of a.r. quality and used as received.

Methods

The surface charge densities of the alumina in aqueous solutions were determined by the potentiometric titration method developed by Bolt,[8] Parks and de Bruyn.[9] Two titrations were carried out: one in the presence of alumina (1.0 g Al_2O_3, in 200 cm^3 aqueous electrolyte solution of various concentrations from 0.001 to 1 mol dm^{-3}), and the other with the same electrolyte but in the absence of alumina (blank). A solution of either HCl or NaOH (both 0.1 mol dm^{-3}) was used as the titrant in the pH range from 3 to 10. A volume of titrant, 0.005–0.5 ml, depending on the soluton pH and the electrolyte concentration, was added every 5 min and the pH values were recorded.

The temperature was kept constant (25 ± 0.5 °C) by thermostating with water through the jacket surrounding the titration cell. N_2 gas was bubbled through the electrolyte before and during the titrations to prevent CO_2 absorption from the air. The solutions were stirred with a magnetic stirrer.

RESULTS AND DISCUSSION

The surface charge density (σ_0 in $\mu C\ cm^{-2}$) was calculated from the following equation:

$$\sigma_0 = \frac{\Delta v M F 100}{SAV} \tag{11}$$

where Δv (cm^3) is the difference between the titrant volumes used for the suspension and the blank at given pH values, M is the molarity of the titrant, F is the Faraday constant (96500 C), S ($m^2\ g^{-1}$) is the specific surface area of alumina, A (g dm^{-3}) is the amount of alumina used for the titration, and V (cm^3) is the volume of electrolyte used for the titration.

The surface charge densities as a function of NaCl electrolyte concentration and pH, calculated from Eq. (11) are presented in Fig. 1. The curves obtained with different ionic strengths intersect at pH 7.2, which represents the point of zero charge of the alumina (pH_{pzc}). The obtained pH_{pzc} value is in good agreement with
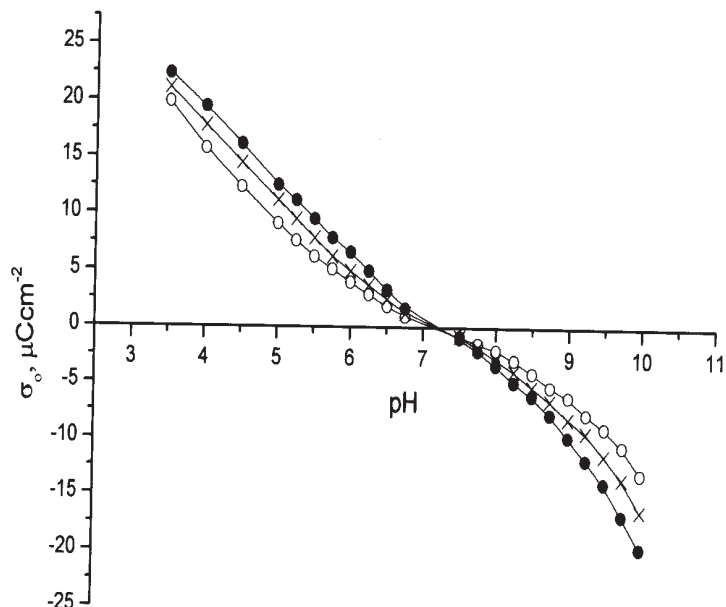
Fig. 1. Surface charge densities of alumina in aqueous NaCl solutions as a function of pH, for different ionic strengths (0.01, 0.05, 0.25 mol dm^{-3}).

those (6.8 and 7.2) for γ-alumina (Merck) determined by the batch equilibration and mass titration method, respectively.[10] According to this paper, the pH$_{pzc}$ of an alumina sample depends on the alumina/solution ratio. Increasing the alumina/solution ratio leads to an increase in pH$_{pzc}$ to a constant value. Also, the obtained pH$_{pzc}$ values for γ- and α-alumina powders are very similar, indicating a rather insignificant influence of the crystal structure. It has also been shown recently[11] that the pH$_{pzc}$ of AlOOH nanoparticles determined from the inflection point of the curve (oxidaton rate constant of iodide by persulphate on AlOOH nanoparticles *vs*. pH) appears at pH 7.1 which is in good agreement with the value (pH 7.2) obtained from stability measurements performed on a similar sol.[12] Sidorova *et al*.[13] obtained approximately the same pH$_{pzc}$ value (≈7.3) for γ-Al$_2$O$_3$ ("for chromatography") in NaCl solutions, using the potentiomeric titration method. Recently, Goyne *et al*.[14] reported that the pH$_{pzc}$ of Al$_2$O$_3$ minerals of varying porosity lie in the range from 6.5 to 6.9.

The positive surface charge density increases with increasing ionic strength and acidity at pH < pH$_{pzc}$ while the negative σ$_0$ increases with incresing ionic strength and alkalinity of the solution at pH > pH$_{pzc}$.

Data on the surface charge densities of alumina as a function of electrolyte concentration and pH were calculated using Eq. (11) and are presented in Table I.

The pK^{int}_{a1} value can be obtained from the dependence pQ_{a1} = pH + log ($α_+$/(1–$α_+$)) *versus* the degree of surface ionization, $α_+$ extrapolating pQ_{al} to the

zero α_+ value, surface charge $\sigma_0 = 0$ and surface potential $\psi_0 = 0$ (absence of specific sorption). Similarly, the pK^{int}_{a2} value can be obtained from the dependence $pQ_{a2} = pH - \log(\alpha/(1-\alpha))$ *versus* the degree of surface ionization, α_-, extrapolating pQ_{a2} to the zero α_- value and surface potential $\psi_0 = 0$.

TABLE I. Surface charge densities, σ_0 (μC cm^{-2}), of alumina as a function of the electrolyte concentration and pH, $T = 298$ K. All σ_0 values are positive for pH < 6.5 and negative for pH > 7.5, for the investigated electrolytes

Electrolyte	pH	Electrolyte concentration/mol dm^{-3}							
		0.001	0.005	0.01	0.05	0.10	0.25	0.50	1.0
LiCl	7.5	0.57	0.66	0.57	0.49	0.41	0.41	0.49	0.49
	8.0	1.80	1.80	1.64	1.72	1.72	2.05	2.46	2.62
	8.5	3.28	3.69	3.28	3.86	4.18	4.92	5.74	6.56
	9.0	5.74	5.74	5.74	6.56	7.38	8.20	9.43	11.5
	9.5	7.87	7.79	8.20	9.84	10.7	12.7	14.8	16.0
	10.0	10.7	10.3	11.5	13.9	14.8	17.2	20.4	22.6
NaCl	3.5	15.7	–	19.9	21.1	21.9	22.4	22.4	22.0
	4.0	12.4	–	15.7	17.8	18.2	19.5	19.5	19.5
	4.5	8.70	–	12.3	14.5	14.9	16.2	16.2	16.2
	5.0	5.80	–	9.11	11.18	12.0	12.5	12.4	12.84
	5.5	3.73	–	6.21	7.87	8.70	9.52	9.11	9.52
	6.0	2.07	–	3.98	4.97	5.38	6.62	5.96	6.21
	6.5	0.91	–	1.82	2.48	2.65	3.31	3.15	2.98
	7.5	1.23	1.39	0.82	0.82	0.82	0.98	0.82	0.82
	8.0	2.87	2.95	2.05	2.87	2.46	3.44	2.87	3.28
	8.5	4.51	4.92	4.10	5.33	4.59	6.15	6.15	6.56
	9.0	7.38	6.97	6.23	8.20	7.38	9.84	9.84	10.7
	9.5	10.7	9.43	9.02	11.5	11.5	13.9	14.4	15.2
	10.0	12.6	13.1	13.1	16.4	16.8	19.7	19.7	21.3
NaNO$_3$	3.5	17.8	–	21.7	–	22.34	23.6	22.4	22.4
	4.0	13.2	–	17.4	–	19.0	20.3	19.5	19.0
	4.5	9.11	–	12.8	–	14.5	17.0	16.2	15.7
	5.0	5.80	–	9.11	–	12.4	13.7	12.8	12.8
	5.5	3.48	–	6.21	–	9.11	9.94	9.94	9.94
	6.0	2.48	–	4.14	–	5.96	7.04	7.04	6.62
	6.5	1.49	–	2.07	–	3.31	3.98	3.81	2.98

TABLE I. Continued

Electrolyte	pH	Electrolyte concentration/mol dm^{-3}							
		0.001	0.005	0.01	0.05	0.10	0.25	0.50	1.0
NaI	3.5	17.4	–	19.9	–	21.5	19.9	22.0	22.8
	4.0	12.8	–	15.7	–	19.0	17.0	18.6	17.8
	4.5	8.70	–	11.6	–	14.9	13.7	15.3	14.9
	5.0	5.80	–	7.87	–	11.2	10.2	12.3	12.4
	5.5	3.73	–	5.38	–	7.95	7.45	9.11	9.94
	6.0	2.15	–	3.73	–	5.80	4.64	6.62	7.45
	6.5	0.99	–	1.99	–	2.98	2.32	3.73	4.14
KCl	7.5	0.82	0.82	0.98	0.41	0.41	0.25	0.41	0.41
	8.0	1.80	2.05	2.46	1.64	1.80	1.64	1.64	1.64
	8.5	3.28	3.69	4.10	3.86	4.10	4.10	4.51	4.59
	9.0	5.08	5.74	6.15	6.23	6.97	7.38	7.79	8.61
	9.5	6.97	7.79	8.20	9.02	9.84	10.7	11.5	13.1
	10.0	9.84	11.1	11.1	12.7	13.9	14.8	15.6	18.9

By analogy, p$^*K^{int}_{M^+}$ can be obtained from the dependence p$^*Q_{M^+}$ = pH – log $(\alpha / (1 - \alpha_-))$ + log [M$^+$] *versus* α_- extrapolating p$^*Q_{M^+}$ to $\sigma_0 = 0$ and $\psi_0 = \psi_\beta$, when p$^*K^{int}_{M^+}$ = p$^*Q_{M^+}$.

Figures 2-4 present the double extrapolation plots for the pK^{int}_{a1}, pK^{int}_{a2} and p$^*K^{int}_{M^+}$ determinations in NaCl electrolyte. Similar dependencies were obtained for the other investigated electrolytes, but for the sake of brevity, these figures are not included in the paper.

As mentioned above, two routes can be used for extrapolation. According to the first one, for each electrolyte concentraton, a curve through the experimental points (presented as open symbols in Fig. 2) is extrapolated to intersect the vertical line having the value (10 $\alpha_+ + C_{NaCl}^{1/2} = C_{NaCl}^{1/2}$), where $\sigma_0 = 0$ and $\alpha_+ = 0$. Next, a smooth curve is drawn through all $\alpha_+ = 0$ points (filled squares), for each electrolyte concentration. The line is extrapolated to the value $\alpha_+ + C_{NaCl}^{1/2} = 0$, and since α_+ for each point is equal to zero, C_{NaCl} must also be zero. Thus, the intercept point corresponds to $\alpha_+ = 0$, $\sigma_0 = 0$ and $C_{NaCl} = 0$, so giving an estimate of pK^{int}_{a1}. According to the second route (same plot in Fig. 2), several arbitrary values for α_+ (0.01, 0.02, 0.04, 0.06, 0.08,...) are selected. Then, the points of the same α_+ values are connected by a smooth curve, for each electrolyte concentration. The curve is then extrapolated to intersect the vertical line corresponding to 10 $\alpha_+ + C_{NaCl}^{1/2} = 10 \alpha_+$, where $C_{NaCl} = 0$ (filled squares). Finally, a smooth curve connecting all $C_{NaCl} = 0$ points (filled square) is constructed and extrapolated to 10 $\alpha_+ + C_{NaCl}^{1/2} = 0$, where $\sigma_0 = 0$ and $\alpha_+ = 0$. The thus

obtained intercept gives the second estimation value of pK^{int}_{a1}. The two routes of extrapolation lead to a single K^{int}_{a1} value (*i.e.,* $pK^{int}_{a1} = 4.4$, *cf.* Fig. 2).
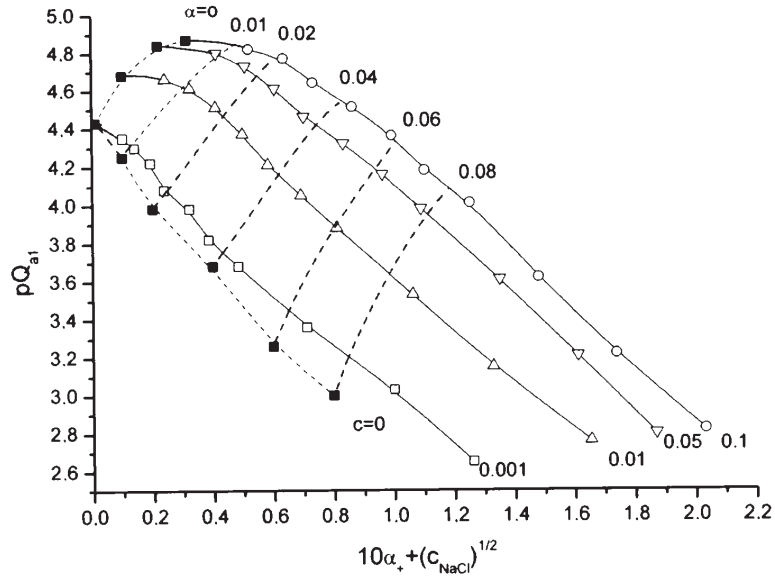

Fig. 2. Variation in pQ_{a1} values with fractional surface charge and NaCl electrolyte concentration. The open symbols and solid lines are the experimental and the filled squares and dashed lines are the extrapolated values.
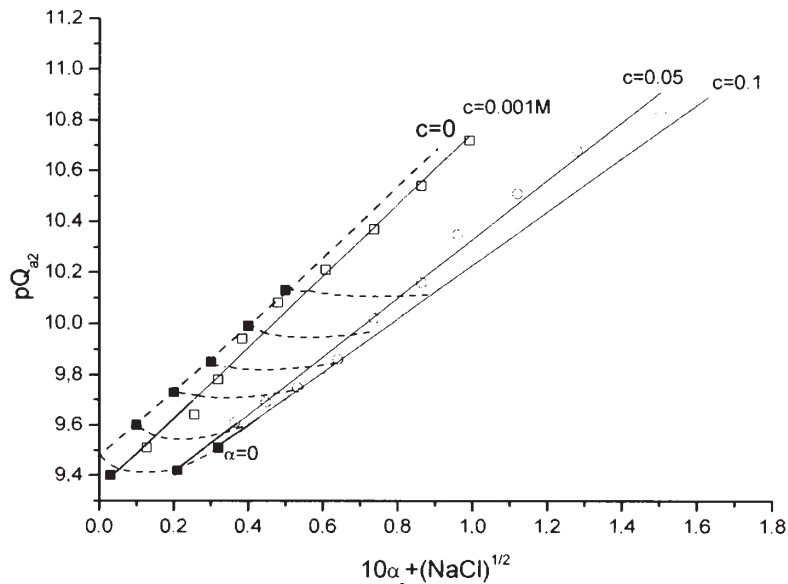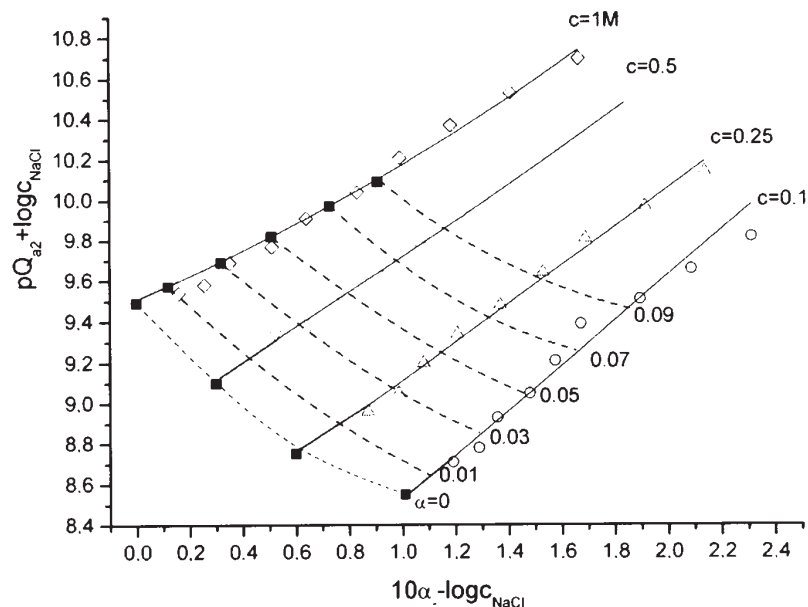

Fig. 3. Variaton in pQ_{a2} values with fractional surface charge and NaCl electrolyte concentration. The open symbols and solid lines are the experimental and the filled squares and dashed lines are the extrapolated values.

Fig. 4. Variation in p*Q_{Na^+} values with fractional surface charge and NaCl electrolyte concentration. The open symbols and solid lines are the experimental and the filled squares and dashed lines are the extrapolated values.

TABLE II. Intrinsic surface protonation and ionization equilibrium constants of the hydroxyl groups and intrinsic surface complexation constants for the monovalent inorganic ions

System	pK^{int}_{a1}	pK^{int}_{a2}	p*$K^{int}_{A^-}$	p*$K^{int}_{M^+}$	Reference
Alumina/NaCl	4.4	9.5	–	9.5	This work
Alumina/KCl	–	9.6	–	9.7	This work
Alumina/LiCl	–	9.7	–	9.4	This work
Alumina/NaI	4.4	–	–	–	This work
Alumina/NaNO$_3$	4.4	–	–	–	This work
γ-Al$_2$O$_3$/NaCl	5.2	–	7.9	–	6
Colloidal AlOOH/KCl	4.8	–	5.4	–	15
Colloidal AlOOH/KBr	5.0	–	5.5	–	15
Colloidal AlOOH/KI	4.8	–	5.5	–	15
Colloidal AlOOH/KNO$_3$	5.0	–	5.6	–	15
Alumina/NaCl	4.5	11.5	6.8	10.6	16
α-Alumina/NaCl	5.1	11	6.7	9.7	17
γ-Alumina/KNO$_3$	4.8	10	6.8	9.9	17

The other two constants, pK^{int}_{a2} and $p^*K^{int}_{Na+}$, were determined in the same way as described above (Figs. 3 and 4). The numerical values of the intrinsic constants, obtained in the same way but with different electrolytes, are presented in Table II, which also contains, for the sake of comparison, selected literature data for different Al_2O_3 forms.

As can be seen from Table II, the mean pK^{int}_{a1} value for alumina in all the used electrolytes is 4.4 which is in good agreement with those for other alumina samples obtained by various authors. The mean pK^{int}_{a2} and $p^*K^{int}_{M+}$ values (9.6 ± 0.1 and 9.5 ± 0.2, respectively), for the investigated alumina sample (Table II) are practically equal, since there are no siginificant differences between them. These values are also in good agreement with the literature ones (Table II).

The differences between the mean pK^{int}_{a2} and $p^*K^{int}_{M+}$ values are also negligible, since all the values lie within experimental error. This fact leads to the conclusion that the sorption of all the examined alkali cations is mainly non-specific, *i.e.*, the bonds between the alumina surface and the cations are almost exclusively of an electrostatic nature.

The values for $p^*K^{int}_{M+}$ can be used to calculate the free energy of sorption (for Reaction 6):

$$\Delta G_{M+} = - RT \ln {}^*K^{int}_{M+} \tag{12}$$

where R is the gas constant. The calculated mean ΔG_{M+} value for the investigated alkali cations and alumina sample is 54.2 kJ mol^{-1}. This value is in excellent agreement with the value of the free energy of Na$^+$ sorption on γ-Al_2O_3 (52.4 kJ mol^{-1}), calculated from the corresponding literature $^*K^{int}_{Na+}$ value.[2]

CONCLUSIONS

Surface charge densities of aluminium oxide in various electrolyte solutions (LiCl, NaCl, KCl, NaNO$_3$ and NaI) are reported as a function of pH and ionic strength of electrolytes.

The point of zero charge (pH$_{pzc}$) of the alumina sample was found to be 7.2.

Using surface charge data obtained by the potentiometric titration method, the intrinsic surface protonation and ionization equilibrium constants of the hydroxyl groups, pK^{int}_{a1} and pK^{int}_{a2}, were calculated to be 4.4 and 9.6, respectively. The mean value of the intrinsic surface complexation constants, $p^*K^{int}_{M+}$, of the investigated alkali cations on alumina surface is 9.5, while the corresponding free energy of sorption, ΔG_{M+}, of the investigated cations is 54.2 kJ mol^{-1}.

ИЗВОД

ОДРЕЂИВАЊЕ БИТНИХ РАВНОТЕЖНИХ КОНСТАНТИ НА ГРАНИЧНОЈ ПОВРШИНИ АЛУМИНИЈУМ–ОКСИД/ЕЛЕКТРОЛИТ

ЖАКЛИНА Н. ТОДОРОВИЋ и СЛОБОДАН К. МИЛОЊИЋ

Лабораторија за хемијску динамику, Институт за нуклеарне науке "Винча", п.пр. 522, 11001 Београд

Дате су густине површниског наелектрисања алуминијум-оксида у различитим електролитима (LiCl, NaCl, KCl, $NaNO_3$ и NaI) у функцији pH и јонске јачине електролита. Тачка нултог наелектрисања (pH_{pzc}) употребљенго алуминијум-оксида је при pH 7,2. Користећи податке о површинском наелектрисању, добијене методом потенциометријске титрације, израчунате су битне протонизационе и јонизационе константе површинских група pK^{int}_{a1} и pK^{int}_{a2}, које износе 4,4 и 9,6, респективно. Средња вредност битних константи комплексирања испитиваних алкалних катјона са површином алуминијум-оксида, $p^*K^{int}_{M^+}$, износи 9,5. Одговарајућа вреднсот промене слободне енергије сорпције испитиваних катјона, ΔG_{M^+}, износи 54,2 kJ mol^{-1}.

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