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Determination of Surface Ionization and Complexation Constants at Colloidal Aluminum Oxide/Electrolyte Interface

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ABSTRACT

The sorption of various inorganic anions (nitrate, chloride, bromide, and iodide) at a colloidal aluminum oxide/water interface was investigated by the potentiometric titration method. The triple-layer model was applied to interpret the experimental data obtained. The intrinsic protonation constant of hydroxyl groups ($\mathrm{p}K_{a1}^{\mathrm{int}}$) was determined and is given as a mean value of 4.9. The intrinsic surface complexation constants ($\mathrm{p}^*K_{\mathrm{A}^-}^{\mathrm{int}}$) for nitrate, chloride, bromide, and iodide were determined and are presented as 5.6, 5.4, 5.5, and 5.5, respectively. The values obtained indicate that the sorption of all the anions examined has mainly a nonspecific character.

INTRODUCTION

During the last 20 years or so, many theories have been developed in order to explain ion adsorption at a hydrous metal oxide/electrolyte solution interface. They are also valid for a colloid oxide/water interface, since the two interfaces are chemically equal, and a selection of these is presented in References 1–5. However, the site-binding model, first presented by Yates et al. (6), then extended by Davis et al. (7–9) and James et al. (10, 11), has generally been considered as the one which, while giving the most realistic picture of the processes in the solid–liquid interface, interprets the experimental results obtained in the majority of cases in the best way.

Adsorption at a hydrous alumina/electrolyte interface has been an object of interest and study in much research (12–18), but very few studies have dealt with adsorption on colloidal alumina (19) rather than determining adsorption isotherms. Such an investigatory treatment would be similar to that of another important industrial product, colloidal silica.

The aim of this work is to determine important surface properties of colloidal alumina, including two of paramount importance: the intrinsic acidity constant of surface alumina hydroxyls and the intrinsic surface complexation constants of monovalent inorganic anions with these groups.

THEORETICAL

According to the chosen site-binding model, as presented by Davis et al. (7–9), the processes of deprotonization and protonization of amphoteric surface hydroxyl groups of colloidal alumina, $>\mathrm{AlOH}$, and counterion adsorption at them can be written in the following stoichiometric equation forms:

$$>\mathrm{AlOH}_2^+ \xrightleftharpoons{K_{a1}^{\mathrm{int}}} >\mathrm{AlOH} + \mathrm{H}_s^+ \tag{1}$$

$$>\mathrm{AlOH}_2^+ + \mathrm{A}_s^- \xrightleftharpoons{K_{\mathrm{A}^-}^{\mathrm{int}}} >\mathrm{AlOH}_2^+\text{—}\mathrm{A}^- \tag{2}$$

$$>\mathrm{AlOH}_2^+\text{—}\mathrm{A}^- \xrightleftharpoons{{}^*K_{\mathrm{A}^-}^{\mathrm{int}}} >\mathrm{AlOH} + \mathrm{H}_s^+ + \mathrm{A}_s^- \tag{3}$$

(in the pH range below the point of zero charge, $\mathrm{pH_{pzc}}$), and:

$$>\mathrm{AlOH} \xrightleftharpoons{K_{a2}^{\mathrm{int}}} >\mathrm{AlO}^- + \mathrm{H}_s^+ \tag{4}$$

$$>\mathrm{AlO}^- + \mathrm{M}_s^+ \xrightleftharpoons{K_{\mathrm{M}^+}^{\mathrm{int}}} >\mathrm{AlO}^-\text{—}\mathrm{M}^+ \tag{5}$$

$$>\mathrm{AlOH} + \mathrm{M}_s^+ \xrightleftharpoons{{}^*K_{\mathrm{M}^+}^{\mathrm{int}}} >\mathrm{AlO}^-\text{—}\mathrm{M}^+ + \mathrm{H}_s^+ \tag{6}$$

(in the pH range above $\mathrm{pH_{pzc}}$). In the equations presented above,

$>AlOH_2^+$, $>AlOH$, and $>AlO^-$ denote positive, neutral, and negative surface sites, respectively; $>AlOH_2^+—A^-$ and $>AlO^-—M^+$ represent the surface complexes; while superscript "int" denotes the intrinsic character of equilibrium constants and subscript "s" refers to the solid phase surface.

The intrinsic surface ionization constant, K_{a1}^{int}, defined by Eq. (1), was calculated using the following expression:

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

while the intrinsic surface complexation constant, $*K_{A^-}^{int}$, was calculated using the equation

$$p*K_{A^-}^{int} = pH + \log \frac{\alpha_+}{1 - \alpha_+} - \log[A^-] + \frac{e(\psi_0 - \psi_\beta)}{2.3kT} \tag{8}$$

where α_+ denotes the fraction of charged sites, ψ_0 represents the mean potential of the surface charge plane which depends on the potential-determining ion reaction (Eqs. 1 and 4), ψ_β represents the mean potential of the plane of specifically sorbed anions, and k is the Boltzman constant. The fraction of charged sites can be calculated as a ratio of the surface charge densities, σ_0, and the total number of surface groups, N_s:

$$\alpha_+ = \sigma_0/N_s \tag{9}$$

In our case, we assumed the alumina surface to be fully hydroxylated, which gives N_s a value of 8 OH nm^{-2}, or 128 $\mu C \cdot cm^{-2}$ in charge units (20). The surface charge densities can be calculated using the well-known equation

$$\sigma_0 = F(\Gamma_{H^+} - \Gamma_{OH^-}) \tag{10}$$

where F is the Faraday constant and Γ_{H^+} and Γ_{OH^-} are the sorption densities of H^+ and OH^-, respectively.

If the numerical values of the expression $pQ_{a1} = pH + \log[\alpha_+/(1 - \alpha_+)]$ are plotted versus the corresponding values of the fraction of charged sites, α_+, then one can obtain the numerical value of pK_{a1}^{int} by extrapolating pQ_{a1} to the zero α_+ value, which also means $\sigma_0 = 0$ and $\psi_0 = 0$, i.e., there is no specific anion sorption. If these conditions are satisfied, $pQ_{a1} = pK_{a1}^{int}$.

The values of $p*K_{A^-}^{int}$ can be obtained in a similar way. If graphically plotted values of $p*Q_{A^-} = pH + \log[\alpha_+/(1 - \alpha_+)] - \log[A^-]$ as a function of α_+ are extrapolated to $\alpha_+ = 0$, i.e., $\sigma_0 = 0$ and $\psi_0 = \psi_\beta$, then $*K_{A^-}^{int} = p*Q_{A^-}$.

EXPERIMENTAL

The colloidal alumina used in this study was prepared from an aluminum chloride solution by the hydrothermal peptization method, in a manner similar to that described elsewhere (21). The sol obtained had a pH value of 3.12, which means that the colloid particles were positively charged. The specific surface area of the solid phase, determined by a modified BET method (22), was found to be 203 m^2/g, and the solid phase content, determined gravimetrically, was 3.21% (w/w).

The solid phase had the boehmite crystal structure as shown by Röntgen analysis performed using a Siemens Kristalloflex 4 with a Geiger-Müller counter (Fig. 1). The colloid particles had a spherical form with a rather narrow size distribution as determined by the transmission electronic microscope method (Fig. 2).

KCl, KBr, KI, and KNO_3, obtained from various commercial sources, were of A.R. quality and used "as received."

The amounts of sorbed ions were determined by the potentiometric titration technique, which actually consisted of two titrations: one with colloidal alumina (1 g solid phase in 200 cm^3 solution) in the presence of a given electrolyte at a concentration of 0.001–1.0 $mol{\cdot}dm^{-3}$, and the other with the same electrolyte but without alumina (blank). Titrations were carried out by a Beckman ϕ70, with a glass and a saturated calomel electrode, with an electrolytic bridge containing the same electrolyte (and same concentration) as the system in order to avoid the suspension effect (23). The titrations, carried out in a PVC vessel, were started at a

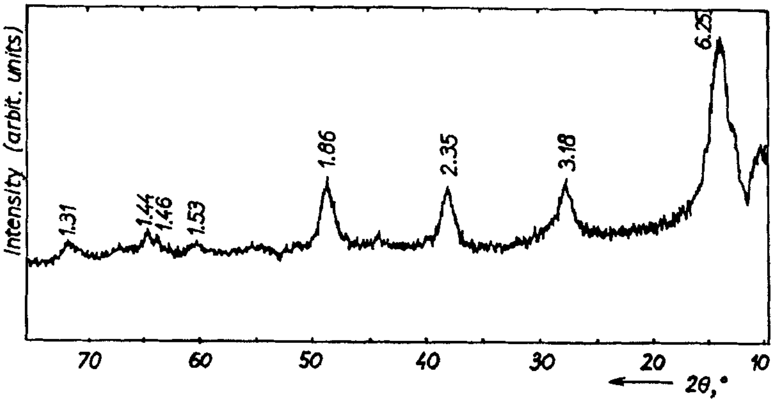

FIG. 1 X-ray diffraction patterns of the solid phase of the colloidal alumina (numbers above peaks indicate distance, 10^{-10} m, between the crystal planes).

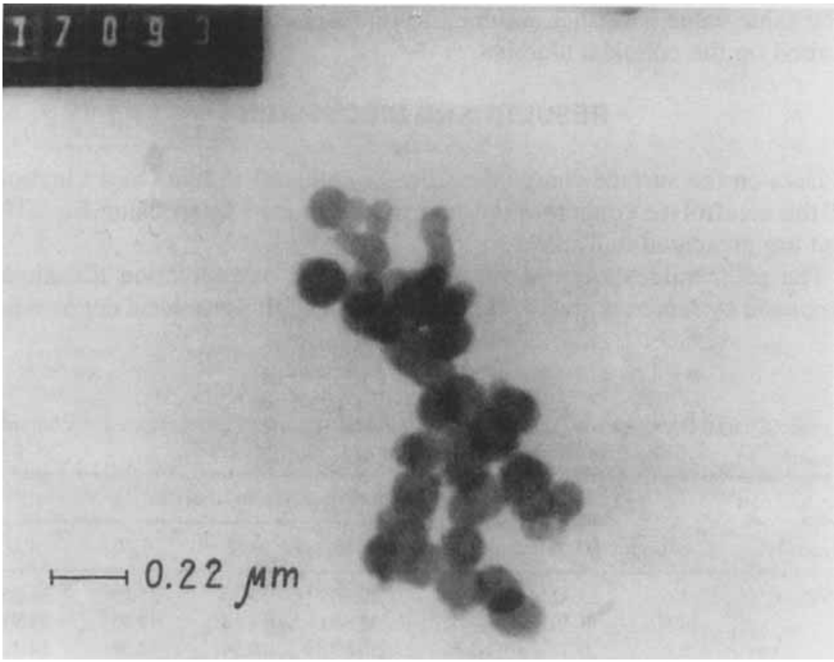

FIG. 2 A photograph obtained by the transmission electronic microscope method representing a spherical form of colloid particles.

pH value of 7.5, which is a somewhat higher value than the pH_{pzc} value determined previously as a part of stability investigations of our system ($pH_{pzc} = 6.8$). The pH value of ~7.5 (adjusted by adding the KOH solution) assured electroneutrality or a slightly negative charge for the colloid particles.

The titration acids were HNO_3, $c = 0.1012$ mol·dm^{-3}, and HCl, $c = 0.1000$ mol·dm^{-3}, of A.R. quality (HCl was used only in investigations of Cl^- sorption). A titrant dose, 0.5 to 2.0 cm^3 depending on the solution pH and the electrolyte concentration, was added every 3 to 5 minutes. The temperature was maintained at 293 ± 3 K, and purified nitrogen gas was bubbled through the electrolyte before and during the titration. The suspension as well as the blank were stirred with a magnetic stirrer.

The difference in the acid quantities used to reach the same pH value in both systems (test suspension and the blank) equals the difference in concentrations of potential-determining ions (H^+ and OH^-), and is considered to represent the gain of H^+ ions on the colloid alumina surface.

The same value is further assumed to represent the amount of A^- anion sorbed on the colloidal alumina.

RESULTS AND DISCUSSION

Data on the surface charge densities of colloidal alumina as a function of the electrolyte concentration and pH were calculated using Eq. (10) and are presented in Table 1.

The pK_{a1}^{int} values were obtained by a double extrapolation technique proposed by James et al. (10, 11). An example of this graphical determina-

TABLE 1

Surface Charge Densities, σ_0 ($\mu C \cdot cm^{-2}$), of Colloidal Alumina Particles as a Function of the Electrolyte Concentration and pH, T = 293 K

		Electrolyte concentration ($mol \cdot dm^{-3}$)					
Electrolyte	pH	0.001	0.01	0.10	0.25	0.50	1.0
KNO_3	4.0	23.42	26.56	30.04	31.24	35.09	36.05
	4.5	11.40	14.06	17.19	18.63	19.95	20.91
	5.0	6.97	8.35	10.09	10.94	12.98	14.18
	5.5	4.21	5.53	6.25	6.85	9.61	9.97
	6.0	2.35	3.55	4.09	4.57	6.97	7.33
	6.5	1.50	2.35	2.88	3.36	4.69	4.93
	7.0	0.84	1.26	1.80	1.92	2.40	2.64
KCl	4.0	15.20	17.46	20.07	19.77	22.32	24.94
	4.5	9.86	11.16	13.36	14.96	15.56	17.58
	5.0	7.24	8.08	10.27	10.75	11.04	12.53
	5.5	5.22	5.94	7.96	8.31	8.67	9.98
	6.0	3.44	4.16	5.94	6.18	6.65	7.54
	6.5	2.02	2.85	4.10	4.39	4.75	5.05
	7.0	0.89	1.42	2.14	2.38	2.49	2.55
KBr	4.0	34.61	36.53	38.70	43.50	44.22	45.91
	4.5	12.26	14.42	18.03	21.51	22.47	23.31
	5.0	8.70	9.73	11.30	13.22	14.06	14.66
	5.5	6.25	6.73	8.17	9.37	10.34	11.18
	6.0	4.33	4.81	5.65	7.09	7.57	8.41
	6.5	2.76	2.88	3.73	4.81	5.05	5.53
	7.0	1.20	1.44	1.92	2.52	2.64	2.76
KI	4.0	32.93	34.25	35.81	38.58	47.35	54.08
	4.5	11.54	13.46	15.98	18.27	20.67	22.59
	5.0	6.13	7.21	9.25	11.06	11.78	13.10
	5.5	3.60	4.69	6.49	8.17	8.41	9.85
	6.0	1.92	3.12	4.33	5.89	6.25	7.33
	6.5	1.44	2.04	2.88	3.85	4.21	5.29
	7.0	0.72	0.96	1.44	2.04	2.40	2.76

tion method is given in Fig. 3 for the system AlOOH/KCl solution. According to James et al., two routes can be used for extrapolation, which should lead to a single $K_{\mathrm{a1}}^{\mathrm{int}}$ value. First, a curve through experimental points for each electrolyte concentration (presented as open circles in Fig. 3) is extrapolated to intersect the vertical line having the value $10\alpha_+ + c_{\mathrm{Cl}^-}^{1/2} = c_{\mathrm{Cl}^-}^{1/2}$. At the intersect points, both σ_0 and α_+ must have zero values. The next step is to draw a smooth curve through all points having zero values for α_+ for each electrolyte concentration (represented by filled circles in Fig. 3). The curve obtained in this way is now extrapolated to the zero abscissa value, at which the c_{Cl^-} value must be zero since α_+ is equal to zero for each point. The intercept value is, finally, $\mathrm{p}K_{\mathrm{a1}}^{\mathrm{int}}$, since it corresponds to $\alpha_+ = 0$, $\sigma_0 = 0$, and $c_{\mathrm{Cl}^-} = 0$. The second route for extrapolation begins with a selection of several arbitrary α_+ values for the same

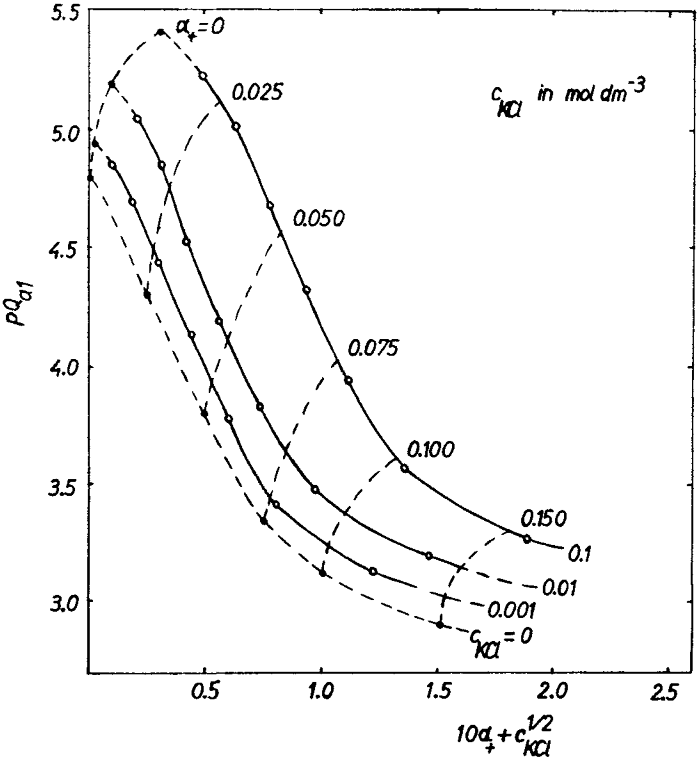

FIG. 3 Variation of $\mathrm{p}Q_{\mathrm{a1}}$ values with fractional surface charge and KCl electrolyte concentration. The solid lines represent experimental data. The dashed lines and the filled circles are extrapolated. $T = 293$ K.

plot (Fig. 3). In our example, the selected values are 0.025, 0.050, 0.075, 0.100, and 0.150. A smooth curve is drawn connecting the points of the same α_+ values for each electrolyte concentration. The curve is then extrapolated to intersect the vertical line corresponding to $10\alpha_+ + c_{Cl^-}^{1/2} = 10\alpha_+$, i.e., $c_{Cl^-} = 0$ (the intersect points are represented by filled circles in Fig. 3). Finally, a smooth curve connecting points with $c_{Cl^-} = 0$ can be constructed and extrapolated to the zero abscissa value. The intercept thus obtained gives the second estimation value of pK_{a1}^{int}.

The two described extrapolation routes give a single pK_{a1}^{int} value (4.80, cf. Fig. 3). The intrinsic acidity constants of surface hydroxyl groups in the presence of the other cited anions were determined in the same way.

The same double extrapolation technique can be applied for determination of the intrinsic surface complexation constants for monovalent inorganic anions on colloidal alumina, with two routes similar to those described above. An example of the technique for $p^*K_{Cl^-}^{int}$ determination is illustrated in Fig. 4. The two extrapolation methods lead to a common value of $p^*K_{Cl^-}^{int} = 5.45$, cf. Fig. 4. The intrinsic surface complexation constants for the other anions under study on colloidal alumina are determined in the way described above, but the diagrams representing the graphical determination of $p^*K_{A^-}^{int}$ values are not presented here for the sake of brevity.

The calculated intrinsic surface ionization constants for hydroxyl groups and intrinsic surface complexation constants for monovalent inorganic anions on colloidal alumina are listed in Table 2, which also contains selected literature data for different Al_2O_3 forms.

TABLE 2

Intrinsic Surface Ionization Constants of Hydroxyl Groups and Intrinsic Surface Complexation Constants for Monovalent Inorganic Anions on Aluminum Oxide, $T = 293$ K

System	pK_{a1}^{int}	$p^*K_{A^-}^{int}$	Reference
Colloidal $AlOOH/KNO_3$	5.0	5.6	This study
Colloidal AlOOH/KCl	4.8	5.4	This study
Colloidal AlOOH/KBr	5.0	5.5	This study
Colloidal AlOOH/KI	4.8	5.5	This study
α-Al_2O_3/0.1 M NaCl	8.50	—	24
α-Al_2O_3/0.01 M NaBr	2.0	5.0	12
α-$Al_2O_3/10^{-3}$–10^{-1} M NaCl	5.1	6.7	25
γ-$Al_2O_3/10^{-3}$–10^{-1} M NaCl	5.2	7.9	11
γ-Al_2O_3/0.1 M NaCl	7.89	—	24
γ-$Al_2O_3/10^{-3}$–10^{-1} M NaCl	4.8	6.8	25

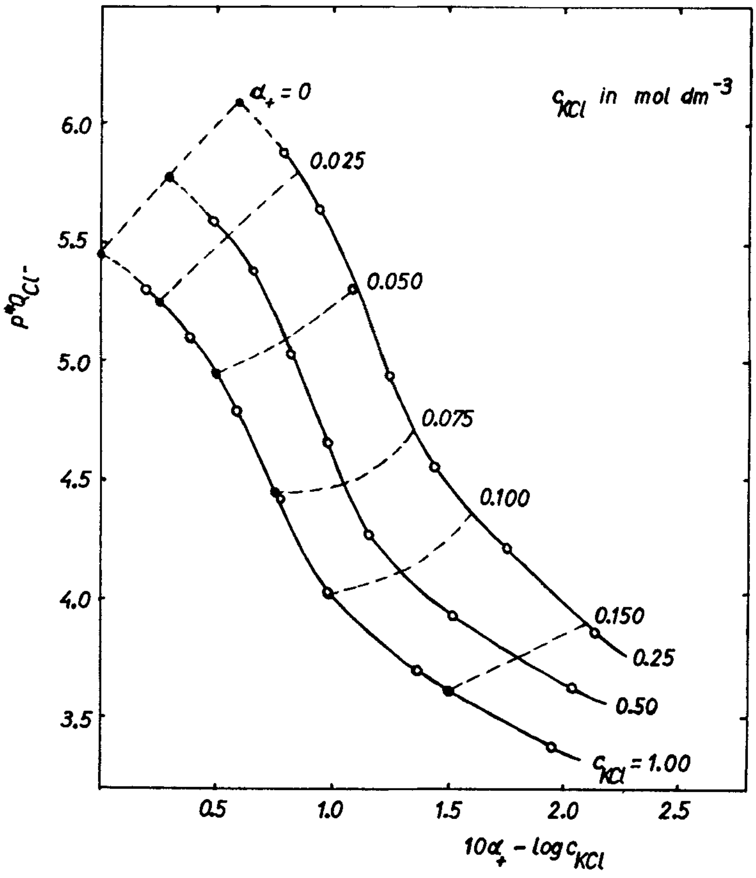

FIG. 4 Variation of $p^*Q_{Cl^-}$ values with fractional surface charge and KCl electrolyte concentration. The solid lines represent experimental data. The dashed lines and the filled circles are extrapolated. $T = 293$ K.

It can be seen from Table 2 that the differences between all experimentally determined $pK_{\mathrm{al}}^{\mathrm{int}}$ values are negligible. Hence, it can be concluded that the mean $pK_{\mathrm{al}}^{\mathrm{int}}$ value for colloidal alumina is 4.9 ± 0.1.

A survey of experimentally determined $pK_{\mathrm{al}}^{\mathrm{int}}$ values for colloidal alumina and those for hydrated crystal modifications of Al_2O_3 (Table 2) shows excellent agreement between the results for colloidal alumina and those presented in Refs. 11 and 25. The noticeably higher values reported by Huang (24) have to be accepted with reservation since they result from a nonadequately-based model ignoring a possibility of ion binding to the surface. The value for pK_{a1}^{int} (12) also differs from the value for colloidal alumina, but it was obtained numerically on the basis of electrophoretic measurement data, and the pH_{iep} of the system was ~4, which greatly differs from our corresponding value indicating different surface properties.

The values for the intrinsic surface complexation constant, $p^*K_{A^-}^{\mathrm{int}}$, for colloidal alumina presented in Table 2 are also practically equal, since there are no significant differences between them. The mean value is 5.5.

Knowing the values for the intrinsic surface ionization constants (K_{a1}^{int}) and the intrinsic surface complexation constants ($^*K_{A^-}^{\mathrm{int}}$), one can calculate the equilibrium constant for Reaction (2) according to $\log K_{A^-}^{\mathrm{int}} = p^*K_{A^-}^{\mathrm{int}} - pK_{a1}^{\mathrm{int}}$ (20). The $K_{A^-}^{\mathrm{int}}$ values obtained can be further used for calculation of the specific chemical sorption energy of the anions examined for Reaction (2) according to $\Phi_{A^-} = -RT \ln(K_{A^-}^{\mathrm{int}}/55.5)$. The values for $^*K_{A^-}^{\mathrm{int}}$ can be used to calculate the free energy of sorption (for Reaction 3): $\Delta G_{A^-} = -RT \ln[(55.5)^2 {}^*K_{A^-}^{\mathrm{int}}]$ (20). The values of the three cited properties for colloidal alumina are presented in Table 3 together with the corresponding literature values for hydrous Al_2O_3 forms and two other inorganic oxides (for comparison).

According to the $^*K_{A^-}^{\mathrm{int}}$ and Φ_{A^-} data presented in Table 3, one can conclude that the surface complexation or the specific sorption of bromide and chloride anions is much weaker for colloidal alumina than for hydrated crystal forms of Al_2O_3 or other oxides.

If the differences among the Φ_{A^-} values were significant, they could be explained by the corresponding differences among the degrees of anion hydration. Namely, Cl^- is the most weakly sorbed anion of all the anions

TABLE 3

Specific Chemical Sorption Energy and Free Energy of Sorption for Monovalent Inorganic Anions on Aluminum Oxide Forms and Two Other Inorganic Oxides, $T = 293$ K.

Systems	log $K_{A^-}^{\mathrm{int}}$	Φ_{A^-} ($kJ \cdot mol^{-1}$)	ΔG_{A^-} ($kJ \cdot mol^{-1}$)	Reference
Colloidal $AlOOH/KNO_3$	0.66	6.1	11.6	This study
Colloidal $AlOOH/KCl$	0.55	6.7	11.0	This study
Colloidal $AlOOH/KBr$	0.58	6.5	11.2	This study
Colloidal $AlOOH/KI$	0.60	6.4	11.3	This study
α-$Al_2O_3/NaBr$	3.0	−7.05	8.48	12
γ-$Al_2O_3/NaCl$	2.2	−2.56	25.2	7
$ZrO_2/NaCl$	2.35	−3.41	9.1	26
$TiO_2/NaCl$	3.1	−7.75	15.5	27

studied and has the greatest degree of hydration, a fact that is quantitatively expressed by the enthalpy of hydration (28). This is a logical consequence of a decrease in the effective electrical charge caused by solvated water molecules. On the other hand, the specific sorption energy is greater for anions with a lower degree of hydration, i.e., with lower values for the enthalpy of hydration (Br^-, I^-) (28). The lower the enthalpy of hydration, the larger the sorption energy (this is the case with the iodide anion in the series of anions of halogen elements). Nitrate is an exception—relatively, the largest value for the specific sorption energy for this anion could be expected by its specific chemical structure with its greater number of potential centers for interaction with surface groups.

However, the differences among the $p^*K_{A^-}^{int}$ values are negligible since all the values lie within experimental error which has an order of 0.1, and consequently, all derived properties have practically the same value. This fact leads to the conclusion that the sorption of all the anions examined is mainly nonspecific, i.e., the bonds between the surface centers and the anions are almost exclusively of an electrostatic nature. By comparing the values for the free energy of sorption for the anions under study on colloidal alumina with the corresponding values for other systems (Table 3), it can be concluded that they do not differ greatly, i.e., the surface ionic complexes have approximately equal (relatively low) stabilities. This fact also supports our conclusion regarding the nonspecific character of sorption on colloidal alumina for all the anions examined.

The specific character of ion sorption on a solid surface for a given metal oxide should also be expected for anions which form complexes in water with the corresponding metal cations. Since there is no evidence of complexes between nitrate and the Al^{3+} ion in acidic water media at 25°C, and because chloride, bromide, and iodide complex with the aluminum cation only at elevated temperatures (200°C and more) (29, 30), one should not consequently anticipate the specific character of sorption of the cited anions on colloidal alumina.

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