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Interaction of Metal Ions with Hydrous Oxide Surfaces

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In this paper, the results on the adsorption of cation on hydrous SiO_2, Al_2O_3 and MnO_2 surfaces are presented. Robust (kinetically inert) complexes, *e. g.* $[Co(NH_3)_6]^{3+}$, contrary to metal ions, *e. g.* $Pb \cdot aq^{2+}$, are not able to displace the alkalimetric titration curves of hydrous oxides. In the case of robust complexes the pH-dependence of adsorption is only the function of the surface charge (and its pH-dependence). The interpretation of metal ion adsorption in terms of different models is also given.

In solution of monomeric metal species, hydrolysis need not be invoked to account for the pH-dependence of adsorption to hydrous oxide surfaces; this dependence can be explained with the basicity of the MeO^- group and the affinity of this group to the metal ion. Polymeric or colloidal metal species are usually adsorbed strongly to surfaces; in this case the surface substrate, as long as the surface charge is opposite to the charge of the adsorbing species, has little influence upon the adsorption.

Reactions of metal ions with oxides in water systems are of importance in colloid chemistry, in natural water systems[1-3] and in geochemical processes. Various theories have been advanced to describe and interpret the adsorption of metal ions at hydrous oxide interfaces[4-8]:

(1) The Gouy-Chapman-Stern-Graham Model which accounts for specific and electrostatic adsorption[8-10];

(2) The adsorption-hydrolysis model which postulates that the adsorption of hydrolyzable metal ions is directly related to the presence of hydrolyzed species[11,12];

(3) The ion-solvent interaction model which considers coulombic, solvation and specific chemical energy interactions as the ion approaches the interface and which implies that a lowering of the ionic charge of the metal species (*e. g.* by hydrolysis) decreases the ion-solvent interaction which represents a barrier to close approach of multiply-charged ions to the surface[13];

(4) The ion exchange model according to which cations upon adsorption on the hydrous oxide surface groups $\equiv$Me—OH replace protons[14-17]; and

(5) The surface complex formation model in which the hydrous oxide surface groups $\equiv$Me—OH, or $=\mathrm{Me}<^{\mathrm{OH}}_{\mathrm{HO}}$ are treated, similar to amphoteric functional group in polyelectrolytes, as complex forming species[7,18-21].

In this article we interpret metal ion adsorption in terms of this latter model. Specifically we try to illustrate that hydrolysis need not be invoked to account for the pH-dependence of the metal ion sorption to the hydrous oxide surface, because this dependence can be explained by the pH-dependence of the activity of the surface ligand (the Me—O$^-$ group, where Me stands for a metal or a metalloid) and the affinity of this ligand for the metal ion. By comparing the adsorption behavior of aquo metal ions with those of robust (kinetically inert) cation complexes, *e. g.* $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5Cl]^{2+}$ which do not dissociate and do not hydrolyze, we can show that chemical interaction energies characterize primarily the interaction of aquo metal ions while electrostatic interaction energies above all govern the adsorption of small robust cation complexes.

A preliminary approach to the interfacial coordination chemistry of hydrous oxides has been published earlier[7,21]. This paper presents a brief review with some modifications. The acid-base or amphoteric properties of the hydrous oxide surface can be characterized with the help of alkalimetric or acidimetric titration curves in analogy with solube monoprotic or polyprotic acids. In Figure 1 the acid-base behavior of a dissolved monoprotic acid (such as H_4SiO_4) is compared schematically with that of a polymeric acid (*e. g.* polysilicic acid), and a cross-linked polyacid (*e. g.* amorphous SiO_2).

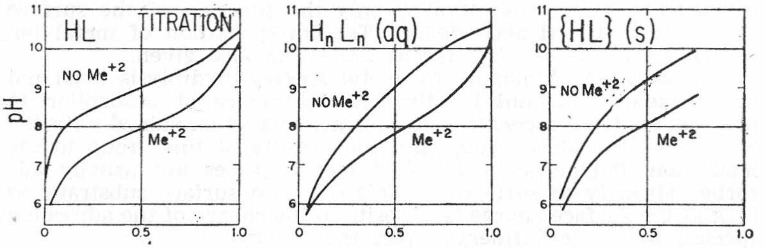


Figure 1. Schematic representation of the acid-base and complex formation behavior of monoprotic (e. g. H_4SiO_4), polyelectrolytic acid (*e. g.* polysilicic acid) and cross-linked polyacid (*e. g.* amorphous SiO_2).

I. Amphoteric Properties of the ≡Me—OH Group and the pH of Zero Charge

The surfaces of metal or metalloid hydrous oxides are generally covered with OH groups; the pH-dependent charge of an oxide results from proton transfers at the surface:

$$\equiv MeOH_2^+ \rightleftarrows \equiv MeOH + H^+; \quad K^s_{a_1} = \{\equiv MeOH\}\,[H^+]/\{\equiv MeOH_2^+\} \qquad (1)$$

$$\equiv MeOH \rightleftarrows \equiv MeO^- + H^+; \quad K^s_{a_2} = \{\equiv MeO^-\}\,[H^+]/\{\equiv MeOH\} \qquad (2)$$

where [ ] and { } indicate concentrations of species in the aqueous phase (moles dm^{-3}) and concentrations of surface species (moles kg^{-3}), respectively. That portion of the charge due to specific interaction with H$^+$ and OH$^-$ ions, corresponds to the difference of protonated and deprotonated ≡MeOH groups and is available from the titration curve (see for example the curve for γ—Al_2O_3, Figures 2 and 6b) on the basis of the proton condition (or charge balance)

$$(C_B - C_A + [H^+] - [OH^-])/a = \{\equiv MeO^-\} - \{\equiv MeOH_2^+\} = -Q \qquad (3)$$

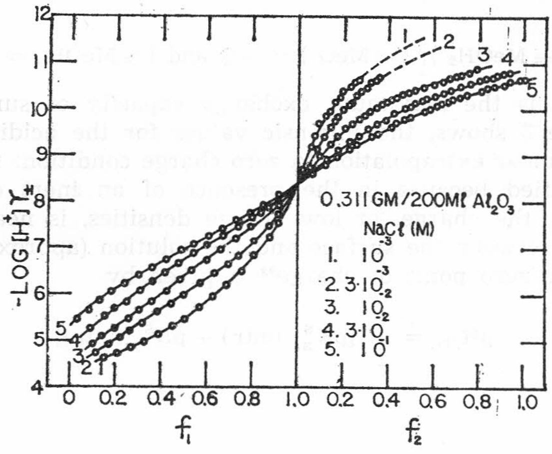


Figure 2. Alkalimetric titration curves for γ-Al_2O_3 suspension at various ionic strengths (f = equivalent fraction of titrant added). pH_{ZPC} is determined from the point at which the pH of the suspension is independent of electrolyte concentration[21].

the corresponding surface charge σ_o is given by

$$\sigma_o = QFs^{-1} \qquad (4)$$

where Q and σ_o are, respectively, the charge in mol kg^{-1} and the surface charge in coulombs cm^{-2}; C_B and C_A are concentrations (in mol dm^{-3}) of a strong base and strong acid added; a and s are, respectively, the quantity of oxide used (kg dm^{-3}) and the specific surface area (cm^2 kg^{-1}); and F is the Farady constant [coulombs mol^{-1}]. The corresponding proton condition where $\sigma_o = 0$, *i. e.* where the charge caused by H^+ or OH^- is zero, is called the zero point of charge, or pH_{ZPC}. The acidity constants in eqs. (1, 2) are microscopic equilibrium constants, because each loss of a proton reduces the charge on the solid poly-acid and thus affects the acidity of the neighbor groups[22]. The free energy of deprotonation consists of the dissociation as measured by an intrinsic acidity constant, $K_a{}^8$ (intr.) and the removal of the proton from the site of the dissociation into the bulk of the solution as expressed by the Boltzman factor; thus

$$K^s_{a_i} = K^s_{a_i} \text{ (intr.) } \exp (F\psi_s/RT) \qquad (5)$$

where ψ_s is the effective potential difference between the surface site and the bulk solution. $K_a{}^s$ (intr.) is the acidity constant of an acid group in a hypothetically completely chargeless surrounding. There is no direct way to obtain ψ_s theoretically or experimentally. It is possible, however, to determine the microscopic constants experimentally and to extrapolate these constants to zero surface charge in order to obtain intrinsic constants. At pH values below and above the pH of the zero point of charge, pH_{ZPC}, respectively the following approximations are justified:

$pH < pH_{ZPC}$:

$$\{\equiv MeOH_2{}^+\} > \{\equiv MeO^-\};\ \{\equiv MeOH_2{}^+\} = Q \text{ and } \{\equiv MeOH\} = [\equiv MeO_T] - Q \qquad (6)$$

$pH > pH_{ZPC}$:

$$\{\equiv MeO^-\} > \{\equiv MeOH_2^+\};\ \{\equiv MeO^-\} = -Q \text{ and } \{\equiv MeOH\} = [\equiv MeO_T] + Q \quad (7)$$

where $[\equiv MeO_T]$ is the maximum exchange capacity of surface groups. As shown in Figure 3 shows, the intrinsic values for the acidity constants can be obtained by linear extrapolation to zero charge condition; this linear extrapolation is justified because in the presence of an inert electrolyte (ionic strength $I = 0.1$), the charge, at low charge densities, is nearly proportional to the potential between the surface and the solution (approximately constant capacitance). The zero point of charge[23] is given by

$$pH_{ZPC} = \frac{1}{2}\,[pK^s_{a_1}\ (\text{intr.}) + pK^s_{a_2}\ (\text{intr.})] \quad (8)$$

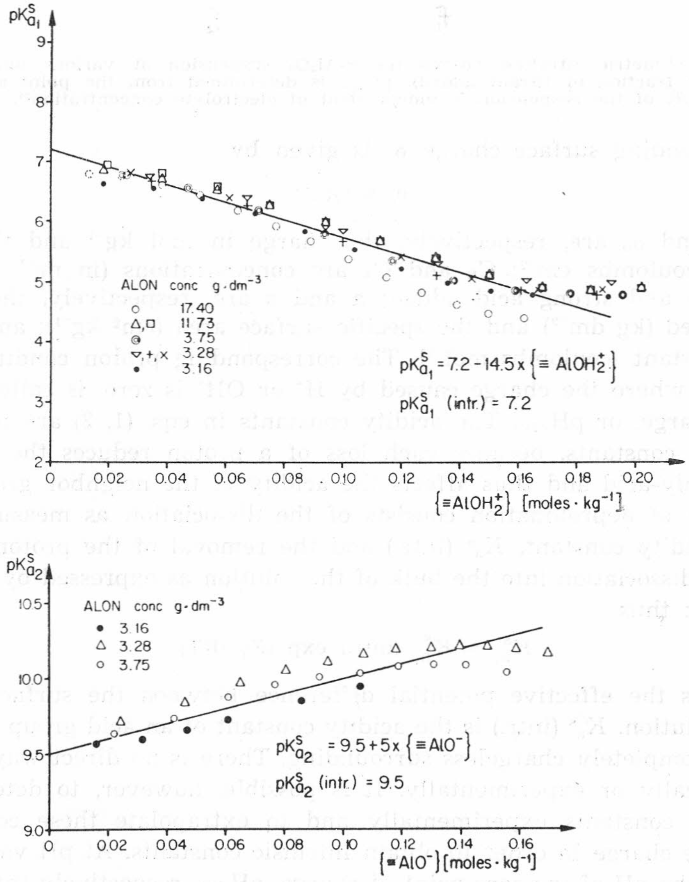


Figure 3. Acidity constants of the surface groups $\equiv AlOH_2^+ \rightleftarrows AlOH + H^+$; $K^s_{a_1}$ and $\equiv AlOH \rightleftarrows AlO^- + H^+$; $K^s_{a_2}$. The microscopic acidity constants are a function of the surface charge, *i. e.* of $\{\equiv AlOH_2^+\}$ and $\{\equiv AlO^-\}$ in the acid and alkaline region, respectively. Extrapolation to zero charge conditions gives intrinsic acidity constants.

TABLE I

Acidity Constants of Surface OH-Groups (25 °C)

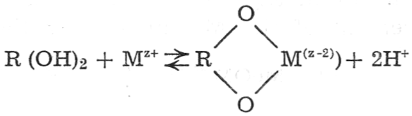
Group	Solid phase	Electrolyte	$pK^{s}_{a_1}$ (intr.)	$pK^{s}_{a_2}$ (intr.)	Ref.
SiOH	amorph. SiO_2	0.1M $NaClO_4$ 0.5M $NaClO_4$ 1 M $NaClO_4$	— — —	6.8 7.2 7.2	24 24 24
MnOH	δ-MnO_2	0.1M $NaClO_4$	—	6.8	7
TiOH	Anatase	3 M $NaClO_4$	4.98	7.8	19
AlOH	γ-Al_2O_3	0.1M $NaClO_4$	7.2	9.5	25

Table I lists intrinsic constants for some hydrous oxides. The pH_{ZPC} obtained in this way should agree with the common intersection point of the titration curves obtained with different concentrations of an inert salt (Figure 2).

II. Complex Formation in Solution and at Interfaces

The free OH^- ion is a powerful ligand for both hard and soft metal ions[18,26]. Similarly, OH-groups attached to non-metal or metalloid elements readily form metal ion complexes (*e. g.* phosphate, carbonate, carboxylate),

$$ROH + M^{z+} \rightleftarrows ROM^{(z-1)} + H^+, \text{ or} \quad (9)$$



$$R(OH)_2 + M^{z+} \rightleftarrows R{<}\genfrac{}{}{0pt}{}{O}{O}{>}M^{(z-2)} + 2H^+ \quad (10)$$

For example, silicic acid forms complexes with many bi- and trivalent cations[27-30]. Obviously the $\equiv SiOH$ and $=Si{<}\genfrac{}{}{0pt}{}{OH}{OH}$ groups in polysilicic acid and on the surface of amorphous SiO_2 will also form such complexes.

As has been pointed out by James and Healy[13] and others, metal ion adsorption on oxides cannot be accounted for in terms of a simple electric double layer model (Gouy-Chapman theory). Since many metal cations can also be adsorbed to hydrous oxides even against electrostatic repulsion in these cases, the chemical interaction energy must predominate over the coulombic interaction energy. Olson and O'Melia[29,30] have plausibly demonstrated the equality of the binding in soluble silicato iron(III) complexes and of iron(III) complexes on surface silanol groups.

Figure 4 illustrates the binding (adsorption) of Pb^{2+} on hydrous γ-Al_2O_3[25]; although positively charged under these pH conditions, the Al_2O_3-surface removes Pb^{2+} cations from the solution most efficiently. In the pH range considered Pb^{2+} does not hydrolyze to any substantial extent.

The complex forming properties of the oxide can be characterized quantitatively by the following surface coordination reactions

$$\equiv MeOH + M^{z+} \rightleftarrows \equiv MeOM^{(z-1)} + H^+$$

$$*K_1^s = \{\equiv MeOM^{(z-1)}\}[H^+]/\{\equiv MeOH\}[M^{z+}] \quad (11)$$

$$2 \equiv MeOH + M^{z+} \rightleftarrows (\equiv MeO)_2M^{(z-2)} + 2H^+$$

$$*\beta_2^s = \{(\equiv MeO)_2M^{(z-2)}\}[H^+]^2/\{\equiv MeOH\}^2[M^{z+}] \quad (12)$$

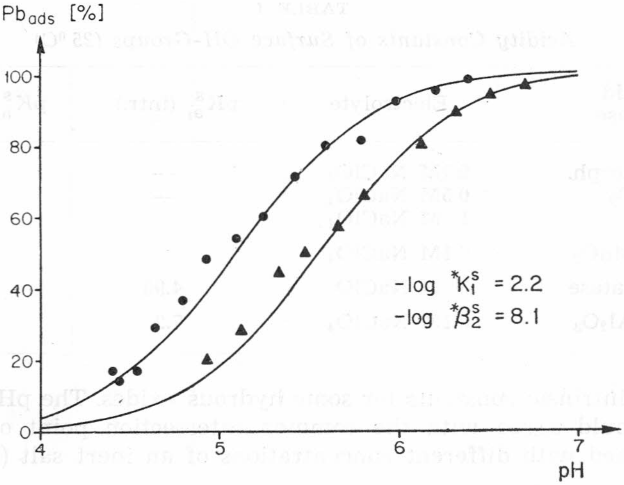


Figure 4. pH-dependence of the adsorption of Pb(II) to γ-Al_2O_3 %. Adsorption (relative to Pb(II) in solution) measured in batch experiments (48 hr equilibration time). The lines are theoretically (*i. e.* calculated with the help of the complex formation constants, $^*K_1{}^s$ and $^*\beta_2{}^s$) determined.

● 11.72 g alon dm^{-3}, $Pb(II)_T = 2.94 \times 10^{-4}$ M;
▲ 3.18 g alon dm^{-3}, $Pb(II)_T = 9.8 \times 10^{-5}$ M.

The concentration terms in Eq. (11 and 12) are accessible experimentally, *e. g.*, by direct measurement of the M^{z+} uptake by the surface:

$$\{M^{z+}{}_{bound}\} = \{\equiv MeOM^{(z-1)}\} + \{(\equiv MeO)_2M^{(z-2)}\} \tag{13}$$

which can be rearranged with Eqs. (11) and (12) to

$$\{M^{z+}{}_{bound}\} = [M^{z+}] \left({}^*K_1{}^s \frac{\{\equiv MeOH\}}{[H^+]} + {}^*\beta_2{}^s \frac{\{\equiv MeOH\}^2}{[H^+]^2}\right) \tag{14}$$

where

$$\{\equiv MeOH\} = \alpha_1 ([\equiv MeO_T] - \{MeOM^{(z-1)}\} - 2\{(\equiv MeO)_2M^{(z-2)}\}) \tag{15}$$

and α_1 α_o and α_2 are the fractions of that portion of surface ligands not bound to M^{z+} which is present, respectively, as $\equiv MeOH$, $\equiv MeOH_2{}^+$ and $\equiv MeO^-$; *e. g.*,

$$\alpha_1 = K_{a1}{}^s/([H^+] + K_{a1}{}^s) \tag{16}$$

This implies that the protolysis equilibria of the surface ligands not bound to M^{z+} are unaffected by the presence of M^{z+} at the surface.

Figure 4 exemplifies that the experimental results can be generalized quantitatively in terms of surface complex formation equilibria; the lines through the experimental points have been calculated with the constants $^*K_1{}^s$ and $^*\beta_2{}^s$ experimentally determined. Figure 5[18] gives the pH-dependence of the surface coordination of Fe(III), Pb(II), Cu(II) and Cd(II) on amorphous SiO_2. Table II lists some of the stability constants for cation interaction with hydrous oxides.

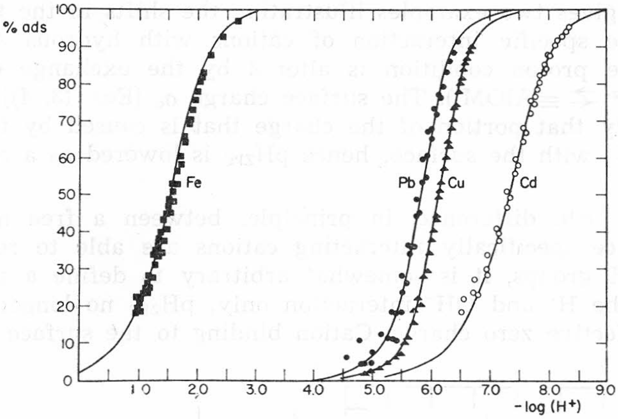


Figure 5. Adsorption of metal ions on amorphous silica as a function of $-\log [H^+]$ from Schindler *et al.*[18]

TABLE II

Stability Constants of Surface Complexes (modified from Schindler[33])

Oxides	Metal	$\log {}^*K_1^s$	$\log {}^*\beta_2^s$	I	Ref.
SiO_2 (amorphous)	Mg^{2+} *	— 8.1	— 16.7	1 M $NaClO_4$	31
	Ca^{2+} *	— 7.3	— 14.7	,,	31
	Fe^{3+}	— 1.8	— 4.2	,,	18
	Cu^{2+}	— 5.5	— 11.2	,,	18
	Cd^{2+}	— 6.1	— 14.2	,,	18
	Pb^{2+}	— 5.1	— 10.7	,,	18
TiO_2 (Rutile)	Cu^{2+} *	— 1.5	— 5.0	,,	32
	Cd^{2+} *	— 3.2	— 10.5	,,	32
	Pb^{2+} *	0.2	— 2.0	,,	32
δ-MnO_2	Ca^{2+} *	— 5.5	—	0.1 M $NaNO_3$	7
γ-Al_2O_3	Ca^{2+} *	— 6.1	—	,,	21
	Mg^{2+} *	— 5.4	—	,,	21
	Ba^{2+} *	— 6.6	—	,,	21
	Pb^{2+}	— 2.2	— 8.1	0.1 M $NaClO_4$	25
	Cu^{2+} *	— 2.1	— 7.0	,,	25

* preliminary results

III. Proton Displacement; Zero Point of Charge and Isoelectric Point

As shown schematically in Figure 1, complex formation (or specific adsorption of metal ions) causes a displacement of the titration curve due to the exchange of H^+ by M^{z+} ions, Eqs. (9, 10), the extent of displacement being related to the extent of coordination.

Figure 6 gives two examples illustrating the shifts in the titration curve caused by the specific interaction of cations with hydrous Al_2O_3-surfaces. Obviously, the proton condition is altered by the exchange of H^+ by M^{z+} ($\equiv AlOH + M^{z+} \rightleftarrows \equiv AlOM^+$). The surface charge σ_o [Eqs. (3, 4)] measures, by definition, only that portion of the charge that is caused by the interaction of H^+ and OH^- with the surface; hence pH_{ZPC} is lowered as a result of metal ion binding.

There is little difference, in principle, between a free metal ion and a proton. Since specifically interacting cations are able to replace protons from $\equiv MeOH$ groups, it is somewhat arbitrary to define a surface charge in terms of the H^+ and OH^- interaction only; pH_{ZPC} no longer characterizes a point of effective zero charge. Cation binding to the surface must increase

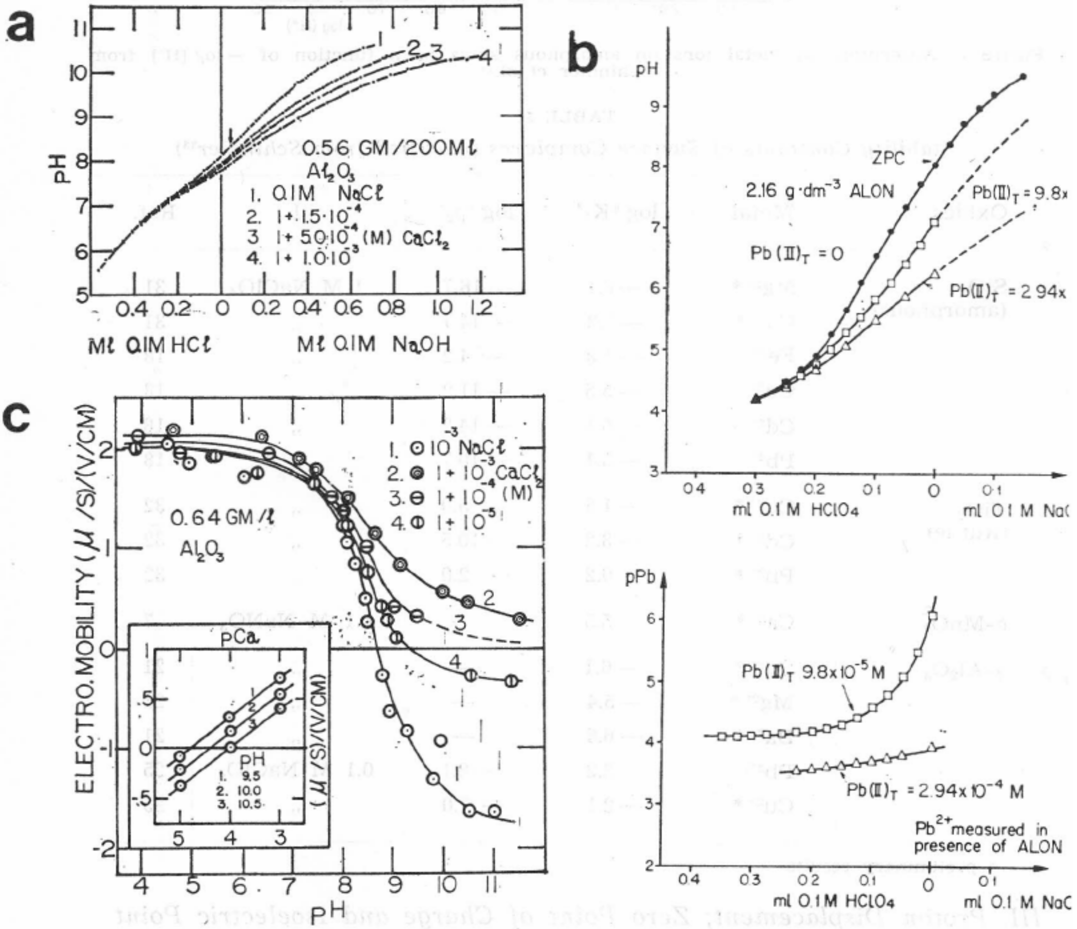


Figure 6. Effect of (a) Ca^{2+} and (b) Pb^{2+} on alkalimetric titration curves of γ-Al_2O_3[21,25] ZPC = pH of zero point of charge.
(c) Electrophoretic mobility of γ-Al_2O_3 in the presence of calcium ions as function of suspension pH. The insert is the plot of mobility as a function of calcium concentrations.
These results illustrate that specifically interacting cations lower pH_{ZPC} but increase pH_{IEP}.

the effective charge of the surface; thus, in the presence of a specifically interacting cation, a higher OH^--activity than in the absence of such a specific interaction is necessary to »neutralize« the surface charge. The isoelectric point, pH_{IEP}, *i. e.*, the pH where the effective surface is zero (*i. e.*, the surface is electro-kinetically uncharged), is shifted to higher pH values when cations become specifically »sorbed« to the surface. As has been pointed out by Lyklema[2], ZPC and IEP are identical only in the absence of specific adsorption. Figure 6 shows that the coordination of Ca^{2+} with Al_2O_3 causes a lowering of pH_{ZPC} and a rise of pH_{IEP}. Since specifically interacting cations reduce the negative charge on hydrous oxides, these cations can destabilize hydrous oxide dispersions. As shown earlier[7], a stoichiometric relationship exists (at a constant pH) between the critical coagulation concentration and the concentration of the dispersed phase. Because of the pH-dependence of the extent of specific cation interaction, the critical coagulation concentration decreases, for a given surface area concentration, with increasing pH. This has been observed for SiO_2[34], MnO_2[7], Al_2O_3[21] and for aluminum silicates[35].

The proton displacement, resulting from the specific interaction with cations can be used as a measure of the extent of interaction. In the presence of an interacting metal ion — for illustration we consider a bivalent cation, M^{2+} —, the proton condition of Eq. (3) can be rewritten as

$$(C_B^* - C_A^* + [H^+] - [OH^-]/a = \{\equiv MeO^{*-}\} - \{\equiv MeOH_2^{*+}\} + \{\equiv MeOM^+\} + \\ + 2\{(\equiv MeO)_2M\} \qquad (17)$$

C^* is used to distinguish the concentration in the presence of M^{2+} from those in its absence. At any given pH, the proton displacement, $\Delta C_B = (C_B^* - C_A^*) - (C_B - C_A)$ is given by deducting eqn. (3) from eqn. (17) and by rearranging**)

$$\Delta C_B/a = (2 - \alpha_1 - 2\alpha_2)\ (\{MeOM^+\} + 2\{(\equiv MeO)_2M\} \qquad (18)$$

where, depending on the pH range α_1 or α_2 can be neglected. Figure 7 illustrates that within the range investigated (pH 4—7) ΔC_B is related to Pb(II) bound to Al_2O_3; approximately 1.5 protons are released per Pb(II) ion sorbed[25]. The ligand number, $\bar{n}$, measures the number of ligands (*i. e.*, $\equiv MeO^-$) bound to M^{z+} per M_T^{z+} totally present in the system:

$$\bar{n} = \Delta C_B/(2 - \alpha_1 - 2\alpha_2)\ [M_T^z] \qquad (19)$$

IV. Difference in Adsorptive Behavior between Aquo Metal Cations and Robust Complex Cations

Coordination reactions in a solution or at interfaces are exchange reactions where the metal ions exchange the coordinated water molecule for some preferred ligands; for example, one metal-oxygen bond, $M \ldots OH_2$, is replaced by another metal-oxygen bond, $M \ldots OR$, or $M \ldots OMe\equiv$. Hydrous oxides are considered to have a strongly structured, probably hydrogen bonded and chemisorbed water layer immediately adjacent to their surfaces. A semi-quantitative coordination model for the interaction of a hydrous oxide surface with H^+ and cations has been proposed earlier[7]. In this model, the free energy

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** Considering that $\{MeO^-\} = \alpha_2[\equiv MeO_T]$; $\{\equiv MeOH_2^+\} = \alpha_0[\equiv MeO_T]$ [cf. eqn. (15)]; $\{\equiv MeO^{*+}\} = \alpha_2\ ([\equiv MeO_T] - \{\equiv MeOM^+\} - 2\{(\equiv MeO)_2M\}$; and $\{\equiv MeOH_2^{*+}\} = \alpha_0\ ([\equiv MeO_T] - \{\equiv MeOM^+\} - 2\{(\equiv MeO)_2M\}$; and $\alpha_0 + \alpha_1 + \alpha_2 = 1$.

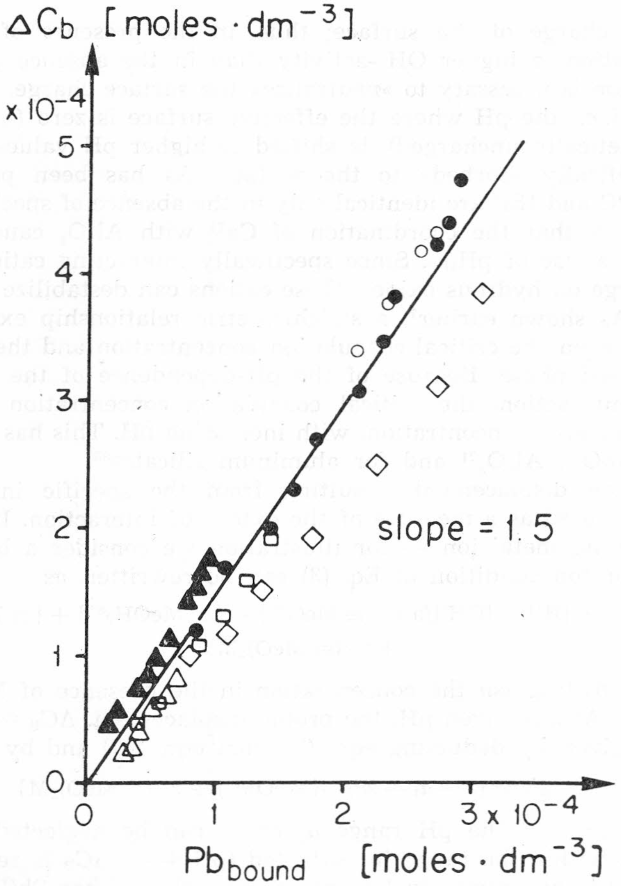

Figure 7. Proton displacement, ΔC_B, caused by the interaction of Pb(II) with the γ-Al_2O_3 surface. Relation between proton displacement and the adsorption of Pb(II). Closed circles and triangles are for 48 hr equilibration time. Open symbols from data of titration curves (short equilibration time).

involved in an ion exchange reaction at the surface site can be estimated by considering the coulombic work and that involved in the change in hydration resulting from the exchange (or adsorption) process. In the Gibbs free energy change of this reaction $\Delta G = \Delta H - T\Delta S$, the electrostatic interaction is predominantly entropy stabilized ($T\Delta S > 0$) while the change in hydration is dominated by enthalpy stabilization ($\Delta H < 0$)[26]. The metal ion binding at the hydrous oxide surface is not necessarily accompanied by the dehydration or by a full displacement of a H_2O molecule at the $\equiv MeO^-$ surface (inner sphere complexes); the change in hydration can be a rearrangement of H_2O molecules during the adsorption process. A part of the hydration sheath of the cation may be substituted by the surface environment of the oxide lattice[36]. Naturally the formation of the surface complex may also benefit from (non-electrostatic) ligand field stabilization effects. The free energy change of the reaction has been shown[7] to be dependent on the field strength of the oxide (inversely proportional to the hypothetical equivalent radius of the surface anion

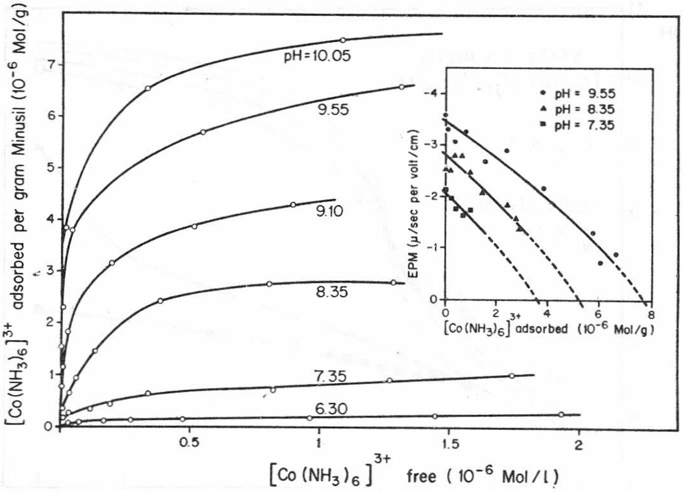

Figure 8. Isotherms for the adsorption of $[Co(NH_3)_6]^{3+}$ on SiO_2 (Minusil). Unlike $Me^{z+} \cdot aq$ ions, robust complexes like $[Co(NH_3)_6]^{3+}$ are not specifically adsorbed on SiO_2.

($\equiv MeO^-$) and upon the change in hydration of the adsorbed and released cations (M^{z+} and H^+).

We have compared the adsorption behavior at the hydrous oxide surfaces of aquo metal ions with that of small robust cation complexes such as $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_5Cl]^{2+}$; these species are kinetically inert cations which do not dissociate (or hydrolyze) and which cannot form covalent bonds. Figure 8 shows isotherms for the adsorption of $[Co(NH_3)_6]^{3+}$ on SiO_2 (minusil). Calculations on the electrostatic interaction energy[37] reveal that the pH-dependence of the adsorption of $[Co(NH_3)_6]^{3+}$ is almost exclusively a function of the surface charge density, *i. e.*, $\{\equiv SiO^-\}$, and its pH-dependence. There appears to be no specific adsorption*) (adsorption other than to coulombic interaction). Hence these complex cations cannot cause charge reversal. Dalang[37] has shown that such robust complexes can be used conveniently to determine the maximum exchange capacity of $\equiv MeOH$ groups.

The remarkable difference in the adsorption behavior between an aquo metal cation and a robust cation is displayed in Figure 9; acidimetric and alkalimetric titration curves of γ—Al_2O_3 in the presence of either robust cations or Pb^{2+} are plotted. That the cobalt complexes are not specifically adsorbed follows from the common intersection point for titration curves carried out in the presence of various complex concentrations. Pb^{2+}, although less charged than $[Co(NH_3)_6]^{3+}$, exerts a pronounced displacement of the titration curve. Obviously a nonelectrostatic effect, most likely a partial replacement in the hydration sheath of the cation, dominates the interaction with Pb^{2+}. Apparently Pb^{2+} ions can penetrate efficiently the structured water layers adjacent to the Al_2O_3 surface to form a »chemical« bond between the $\equiv AlO^-$

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* Robust complexes with large ligands such as phenanthrolin or dipyridyl etc. are specifically adsorbed because the large ligand molecules contribute significantly by their van der Waals cohesive energy to the interaction energy.

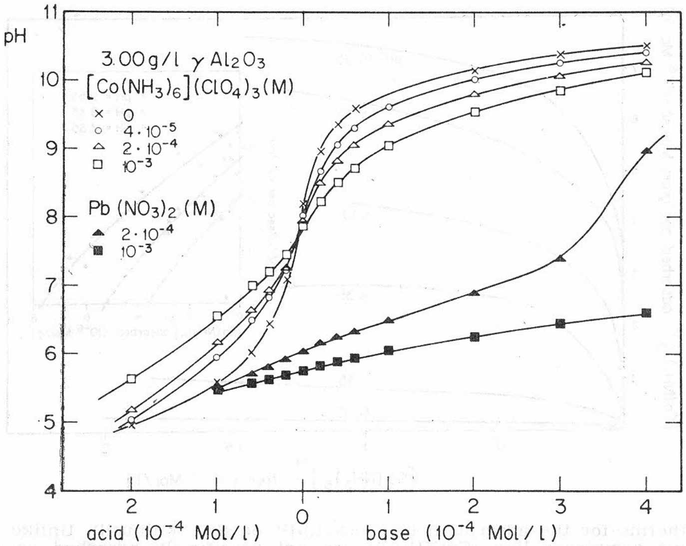

Figure 9. Comparison of the interaction of $[Co(NH_3)_6]^{3+}$ and Pb^{2+} with γ-Al_2O_3. While $[Co(NH_3)_6]^{3+}$ is not specifically adsorbed (common intersection of alkalimetric titration curves for various concentrations of the complex), Pb^{2+} ions displace markedly the titration curves.

groups and the metal ion**). The Co(III) central ion $[Co(NH_3)_6]^{3+}$, on the other hand, remains shielded by the NH_3 ligands; thus, it is more likely that $[Co(NH_3)_6]^{3+}$ will form an outer sphere type of an adduct with $\equiv AlO^-$.

V. Hydrolysis and Adsorption

Matijević *et al.*[11,12] and many other investigators, including ourselves have postulated that the adsorption of hydrolyzable metal ions is directly related to the presence of hydrolyzed species. James and Healy[13] have also emphasized that the hydrolyzed metal ion, because of its lower ionic charge and the concommittant lowering of the ion-solvent interaction in the adsorption process, is (are) the active species to be adsorbed preferably to oxide surfaces.

It is important to distinguish between mononuclear and polynuclear metal ion hydrolysis species. Many investigations on the adsorption of hydrolyzable metal ions have been carried out under solution conditions where, often unknowingly, polynuclear, multimeric, polymeric or even colloidal metal species prevailed. Because of the higher molecular weight and less hydrophilic nature, these polynuclear metal species are usually adsorbed strongly to surfaces; in this case the surface substrate (polystyrene, Ag/AgBr, or oxide surfaces) has little influence upon the adsorption.

It is less likely, however, that mononuclear metal ion hydrolysis species become adsorbed at solid-solution interfaces. In terms of a coordination model, the adsorption of a hydrolyzed species, *e. g.* $MOH^{(z-1)}$, to a hydrous oxide surface would lead to a mixed ligand complex, such as $\equiv MeO \ldots MOH^{(z-2)}$.

** It is tempting to speak of an »inner sphere« complex but we have not established the existence of a direct covalent bond between $\equiv AlO^-$ and Pb^{2+}. Olson and O'Melia[30] provide evidence that the association between Fe^{3+} and $\equiv SiO^-$ is a Fe—O—Si inner sphere, high spin surface complex.

Soluble mixed complexes, such as PbOHCl, have been indentified; however, for statistical reasons such mixed complexes predominate only under very restricted conditions[38].

Other solution variables, in addition to pH, also influence the adsorption process. Cl^-, CO_3^{2-}, or other solution ligands may reduce the free metal ion concentration. Since in these cases the formation of mixed ligand complexes also appears less plausible, the extent of adsorption is usually reduced by competing soluble ligands[39].

As has been explained, hydrolysis need not be invoked to account for the pH-dependence of metal ion adsorption to the hydrous oxide surface. In the coordination model this dependence can be explained by the pH dependence of the activity of the $\equiv MeO^-$ groups and the affinity of this group for the metal ion. One could argue[3] that it is difficult to distinguish unequivocally between a surface complex formation of a hydrolyzable surface with a free metal ion and the adsorption of a surface with a hydrolyzed metal ion. In some of the examples given here, the binding of M^{z+} occurs in a pH region so far below that of hydrolysis and occurs on a positively charged surface, therefore it seems more justified to postulate specific coordinative interaction of $\equiv MeO^-$ groups with unhydrolyzed M^{z+}.

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SAŽETAK

Interakcija metalnih iona sa hidratiziranim površinama oksida

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Ispitivana je adsorpcija kationa alkalnih, zemnoalkalnih i teških metala, kao i kinetički inertnih kompleksnih kationa na hidratiziranim površinama SiO$_2$, Al$_2$O$_3$ i MnO$_2$. Ovisnost pH o adsorpciji, u slučaju kinetičkih inertnih (robustnih) kompleksa, funkcija je površinskog naboja i njegove pH-ovisnosti. U slučaju monomernih metalnih vrsta, hidroliza nije odgovorna za ovisnost pH o adsorpciji na površinama oksida; ovisnost se može objasniti bazičnošću MO skupine i afinitetom te skupine prema metalnim ionima. Polimerne ili koloidne metalne vrste su obično jako adsorbirane na površinama oksida. U tom slučaju površinski supstrat, tako dugo dok je naboj na površini suprotan naboju adsorbirane vrste, pokazuje slab utjecaj na adsorpciju. Adsorpcija metalnih iona interpretirana je pomoću različitih modela.

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