

Intrinsic Surface Reaction Constant in 1-pK Model of Mg-Fe Hydrotalcite-like Compounds

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The relationship among intrinsic surface reaction constant (K) in 1-pK model, point of zero net charge (PZNC) and structural charge density (σ_{st}) for amphoteric solid with structural charges was established in order to investigate the effect of σ_{st} on pK. The theoretical analysis based on 1-pK model indicates that the independent PZNC of electrolyte concentration (c) exists for amphoteric solid with structural charges. A common intersection point (CIP) should appear on the acid-base titration curves at different c , and the pH at the CIP is pH_{PZNC} . The pK can be expressed as $\text{pK} = -\text{pH}_{\text{PZNC}} + \log[(1 + 2\alpha_{\text{PZNC}})/(1 - 2\alpha_{\text{PZNC}})]$, where $\alpha_{\text{PZNC}} = \sigma_{st}/eN_{\text{A}}N_{\text{s}}$, in which e is the elementary charge, N_{A} the Avogadro's constant and N_{s} the total density of surface sites. For solids without structural charges, $\text{pK} = -\text{pH}_{\text{PZNC}}$. The pK values of hydrotalcite-like compounds (HTlc) with general formula of $[\text{Mg}_{1-x}\text{Fe}_x(\text{OH})_2](\text{Cl}, \text{OH})_x$ were evaluated. With increasing x , the pK increases, which can be explained based on the affinity of metal cations for H^+ or OH^- and the electrostatic interaction between charging surface and H^+ or OH^- .

Keywords surface complexation, electric double layer, points of zero charge, acid-base chemistry, structurally charged material

Introduction

The interface electrochemical properties of some amphoteric solid particles have been paid a great deal of attention because they are of theoretical importance and play a significant role in many industrial processes. Two surface charging models, 1-pK model¹ and 2-pK model,^{2,3} have been proposed to describe the charging behavior of solid-water interface. In those models, intrinsic surface reaction constants are important parameters, so many studies⁴⁻⁶ were focused on the determination of the intrinsic constants of solids without structural charges. However, up to now the work on the determination of the intrinsic constants of solid with structural charges, such as clays with structural negative charges and hydrotalcite-like compounds (HTlc) with structural positive charges, has not been reported previously by other researchers.

HTlc have the general formula $\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2]^{x+}[\text{A}_{x/n}^{n-}]^{x-} \cdot m\text{H}_2\text{O}$,^{7,8} where M(II) is divalent metal cation, M(III) is trivalent metal cation, A^{n-} is the charge compensating anion, m is the number of mole of co-intercalated water per formula weight of the compound and x is the number of mole of M(III) per formula weight of the compound. The HTlc contain brucite (magnesium hydroxide)-like layers where some divalent metal cations are substituted by trivalent metal cations

to form positively structural charged layers. The structural positive charges in the layers are compensated by the hydrated interlayer anions.^{7,8} In our previous papers,^{9,10} the determined results of one intrinsic ionization constant (K_{a2}^{int}) in 2-pK model for Zn-Mg-Al and Mg-Fe-Al hydrotalcite-like compounds (HTlc) were reported. It was found that the charging behavior of some oxide-water interfaces can be described with 1-pK model as well with 2-pK model.¹¹ However, the 1-pK model has an advantage that the adjustable parameters of the 1-pK model are less than those of the 2-pK model, so it is gradually paid a great deal of attention. This paper evaluates the intrinsic constant (K) in 1-pK model for Mg-Fe HTlc from the acid-base titration experimental data.¹²

Theory

For amphoteric solid particles with structural charges (denoted by σ_{st}) and adsorbed proton charges (denoted by σ_{H}), the total net charge density (denoted by σ_0) is

$$\sigma_0 = \sigma_{st} + \sigma_{\text{H}} \quad (1)$$

At point of zero net charge (PZNC), $\sigma_0 = 0$; at point of zero net proton charge (PZNPC), $\sigma_{\text{H}} = 0$.¹³ The σ_{H} can be determined by acid-base (or potentiometric) titration

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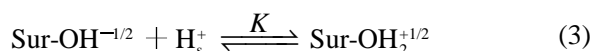
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and is defined by

$$\sigma_H = F(\Gamma_H - \Gamma_{OH})/S \quad (2)$$

where Γ_H and Γ_{OH} are the adsorption amounts of H^+ and OH^- , respectively, during titration, S is the specific surface area of solid particles, F is the Faraday constant. Because at PZNC ($\sigma_0=0$), $\sigma_H = -\sigma_{st}$, the σ_H at PZNC is independent of the inert electrolyte concentration (c).

The 1-pK model is based on the following surface chemical reaction for an amphoteric surface



where the Sur represents the surface of solid, the subscript s denotes the surface phase, and the intrinsic constant, K , is given by

$$K = \frac{[\text{Sur-OH}_2^{+1/2}]}{[\text{Sur-OH}^{-1/2}][H^+]} \exp(e\Psi_0/\kappa T) \quad (4)$$

where the square brackets denote the activity of species, Ψ_0 is the surface potential, e is the elementary charge, κ is the Boltzmann constant, and T is the absolute temperature. The surface species, $\text{Sur-OH}^{-1/2}$ and $\text{Sur-OH}_2^{+1/2}$, are assumed to have activity coefficients equal to unity.

The total density of surface sites, N_s , can be expressed as

$$N_s = [\text{Sur-OH}^{-1/2}] + [\text{Sur-OH}_2^{+1/2}] \quad (5)$$

The following equation can be obtained

$$\sigma_H = e N_A ([\text{Sur-OH}_2^{+1/2}] - [\text{Sur-OH}^{-1/2}])/2 \quad (6)$$

where N_A is the Avogadro's constant.

Because at PZNPC, $[\text{Sur-OH}_2^{+1/2}] = [\text{Sur-OH}^{-1/2}] = N_s/2$, the following equations can be obtained

$$[\text{Sur-OH}_2^{+1/2}] = N_s/2 + \sigma_H/eN_A \quad (7a)$$

$$[\text{Sur-OH}^{-1/2}] = N_s/2 - \sigma_H/eN_A \quad (7b)$$

A parameter, net proton charge fraction α , is introduced by the definition

$$\alpha = \sigma_H/eN_A N_s \quad (8)$$

According to Eqs. (7a, b) and (8), Eq. (4) may be rewritten as

$$K = \frac{1+2\alpha}{(1-2\alpha)[H^+]} \exp(e\Psi_0/\kappa T) \quad (9)$$

At PZNC ($\sigma_0=0$, $\sigma_H = -\sigma_{st}$), $\Psi_0=0$, and

$$[\text{Sur-OH}_2^{+1/2}] = N_s/2 - \sigma_{st}/eN_A$$

$$[\text{Sur-OH}^{-1/2}] = N_s/2 + \sigma_{st}/eN_A$$

Eq. (9) may be rewritten as

$$K = \frac{N_s/2 - \sigma_{st}/eN_A}{(N_s/2 + \sigma_{st}/eN_A)[H^+]_{\text{PZNC}}} = \frac{1-2\alpha_{\text{PZNC}}}{(1+2\alpha_{\text{PZNC}})[H^+]_{\text{PZNC}}} \quad (10)$$

where $[H^+]_{\text{PZNC}}$ is the concentration of H^+ at PZNC, α_{PZNC} is the α value at PZNC.

$$\alpha_{\text{PZNC}} \equiv \sigma_{st}/eN_A N_s \quad (11)$$

Eq. (10) may be rewritten in a negative logarithmic form as

$$pK = -pH_{\text{PZNC}} + \log[(1+2\alpha_{\text{PZNC}})/(1-2\alpha_{\text{PZNC}})] \quad (12)$$

For solid without structural charges, $\sigma_{st}=0$, thus $pK = -pH_{\text{PZNC}}$. It can be seen from Eq. (12) that pH_{PZNC} is independent of c in the absence of specific adsorption.

Results and discussion

Because both σ_H and pH at PZNC are independent of c , the curves of σ_H - pH at different c obtained by the acid-base titration should have a common intersection point (CIP) for solid with structural charges, similar to solid without structural charges. The pH at CIP is pH_{PZNC} . This analytic conclusion was proved by experimental observations of HTlc with structural positive charges.^{9,10,12}

Table 1 shows the chemical composition, the number of structural charge per HTlc molecule (x), the N_s and the σ_{st} calculated from crystal structure,^{9,10} the pH_{PZNC} determined by the acid-base titration¹² and the pK of Mg-Fe HTlc samples calculated using Eq. (12). With increasing x (or σ_{st} or the content of trivalent metal cation of HTlc), pK increases. This is because the affinity of the HTlc samples for H^+ decreases with increasing x . The affinity of HTlc for H^+ is determined by two factors: metal element itself composing HTlc and its structural charge. The K_{sp} of $Mg(OH)_2$ and $Fe(OH)_3$ are 1.8×10^{-11} and 4×10^{-38} , respectively. The pH_{PZNC} of $Mg(OH)_2$, α - $FeOOH$ and γ - $FeOOH$ are about 12.31, 6.7 and 7.4,¹⁴ respectively. The K_{sp} and the pH_{PZNC} of those metal hydroxides indicate that the affinity of Mg^{2+} for OH^- is lower than that of Fe^{3+} , on the contrary, the affinity of Mg^{2+} for H^+ should be higher than that of Fe^{3+} . Thus, with increasing x (*i.e.*, with decreasing the content of Mg^{2+}) the affinity of HTlc for H^+ will decrease. On the other hand, according to the electrostatic interaction principle, the presence of positive charges on

Table 1 *K* of Mg-Fe HTlc samples

No.	Chemical composition	<i>x</i>	$N_s/(\text{sites nm}^{-2})$	$\sigma_{st}/(\text{C} \cdot \text{m}^{-2})$	pH _{PZNC}	p <i>K</i>
1	[Mg _{0.79} Fe _{0.21} (OH) ₂]Cl _{0.08} (OH) _{0.13}	0.21	12.02	0.20	10.90	-10.71
2	[Mg _{0.70} Fe _{0.30} (OH) ₂]Cl _{0.06} (OH) _{0.24}	0.30	11.79	0.28	10.78	-10.51
3	[Mg _{0.68} Fe _{0.32} (OH) ₂]Cl _{0.05} (OH) _{0.27}	0.32	11.70	0.30	10.58	-10.29
4	[Mg _{0.64} Fe _{0.36} (OH) ₂]Cl _{0.03} (OH) _{0.33}	0.36	11.47	0.33	10.30	-9.97

HTlc will lower the affinity of HTlc for H⁺, thus the affinity of HTlc for H⁺ will decrease with increasing *x* (or σ_{st}). So on the basis of both the affinity of metal cations for H⁺ and the electrostatic interaction between charging surface and H⁺, the increase of *x* will lower the affinity of HTlc for H⁺, in turn rise the p*K*.

Conclusion

For amphoteric solid with structural charges and in the absence of specific adsorption, the independent PZNC on *c* also exists just as amphoteric solid without structural charges. A common intersection point (CIP) should appear on the acid-base titration curves at different *c* and the pH at the CIP is pH_{PZNC}.

The p*K* of 1-p*K* model can be expressed as a function of pH_{PZNC} and σ_{st} . For solids with structural charges, p*K* ≠ -pH_{PZNC}; only for solids without structural charges, p*K* = -pH_{PZNC}.

For the HTlc samples with the general chemical formula [Mg_{1-x}Fe_x(OH)₂](Cl,OH)_{*x*}, the p*K* increases with increasing *x*, which can be contributed to the affinity of metal cations for H⁺ or OH⁻ and the electrostatic interaction between charging surface and H⁺ or OH⁻.

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