The TiO₂/Electrolyte Solution Interface

II. Calculations by Means of the Site Binding Model

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Starting from experimental $\sigma_0$ and $\xi$ potential values of TiO₂ in KCl and KNO₃ solution, calculations were performed in order to check whether a self-consistent description of the data in terms of the site binding model can be obtained. Two adjustable parameters were used: the Stern layer capacitance and the equilibrium constant for the association of surface hydroxyl groups with hydrogen ions (MOH + H⁺ $\leftrightarrow$ MOH₂⁺). In the calculations, assumptions concerning activity coefficients of charged groups near the surface have to be introduced. If the quotients of surface activity coefficients of complexes and free surface hydroxyl groups ($\gamma_{MOH^2/\gamma_{MOH}}$ and $\gamma_{MOH^+/\gamma_{MOH}}$) are thought to be independent of the charge in the adsorption plane, the association and dissociation constant of surface hydroxyl groups turn out to be pH-dependent. This is ascribed to the influence of local deviation from the average values of the potential at a certain distance from the surface. Neglect of this effect leads to internal inconsistencies of the model. © 1986 Academic Press, Inc.

INTRODUCTION

In a previous paper (1), data were presented on the colloid chemical properties of dispersions of TiO₂ in various aqueous solutions. The data comprised surface charge, $\xi$ potential and stability toward coagulation. The main result of this investigation was, that for pure TiO₂ the colloid chemical properties mentioned are not influenced by changes in solid-state properties (donor concentration).

The insensitivity towards changes in donor concentration (effected by pretreatment in O₂ or in H₂) entails independence of differences in surface conductivity. At the highest donor concentration obtained, the surface conductivity apparently is still too low to influence adsorption equilibria; thus TiO₂ can be regarded, as far as surface charge and ion adsorption is concerned, as an insulator. The TiO₂/aqueous solution interface, therefore is suitable to test models for such interfaces, in which the influence of changes in solid state parameters is disregarded.

Oxide/electrolyte solution interfaces are frequently described by the site binding model (2–8) based on the following hypotheses:

1. The origin of surface charges can be described by association/dissociation equilibria of surface hydroxyl groups MOH:

$$\text{MOH}_2^+ \leftrightarrow \text{MOH} + \text{H}_3^+ \quad [1]$$

$$\text{MOH} \leftrightarrow \text{MO}^- + \text{H}_3^+ \quad [2]$$

The suffix “s” denotes surface.

2. Ions behind the electrokinetic slipping plane are all bound to charged sites of opposite sign; thus, in KCl solutions:

$$\text{MOH} + \text{K}_s^+ \leftrightarrow \text{MO}^-\text{K}_s^+ + \text{H}_3^+ \quad [3]$$

$$\text{MOH}_2^+\text{Cl}_s^- \leftrightarrow \text{MOH} + \text{H}_3^+ + \text{Cl}_s^- \quad [4]$$

3. The “free ion concentrations near the surface” ([H₃⁺], [Kₙ⁺], [Clₙ⁻]) are related to bulk concentrations by

$$\gamma_{H_3^+}[H_3^+] = \gamma_{H_3^+}[H_3^+]\exp\left(-\frac{eV_0}{kT}\right) \quad [5]$$
\[ \gamma_{K^+}[K^+] = \gamma_{K^0}[K^0^+] \exp \left( -\frac{e\psi_0}{kT} \right) \]  

\[ \gamma_{Cl^-}[Cl^-] = \gamma_{Cl_0}[Cl_0^-] \exp \left( \frac{e\psi_0}{kT} \right) \]

in which \( \psi_0, \psi_\beta, \) and \( \psi_\beta' \) are the potentials of the solid phase and at distances \( \beta \) and \( \beta' \) from the phase boundary. \( \beta \) and \( \beta' \) are distances of closest approach of \( K^+ \) and \( Cl^- \), respectively, to the solid phase. The suffix “b” denotes “bulk”; \( \gamma \)'s are activity coefficients.

(4) The equilibrium constants describing the equilibria [3] and [4] can be determined by linear extrapolation of \( pQ_{K^+}^* \) and \( pQ_{Cl^-}^* \) as functions of \( \alpha_0 \), toward \( \alpha_0 = 0 \). Here the following definitions are employed:

\[ pQ_{K^+}^* = pH + \log \gamma_{K^0}[K^0^+] - \log \frac{[MO^{-}K^+]}{[MOH]} \]  

\[ pQ_{Cl^-}^* = pH - \log \gamma_{Cl_0}[Cl_0^-] - \log \frac{[MOH]}{[MOH_2Cl^-]} \]  

\[ \alpha_0 = \frac{([MO^{-}K^+] - [MOH_2Cl^-])}{N_s} \]

with \( N_s \) = the total number of sites per unit surface area.

Recently, Johnson (9) formulated the site-binding model with the surface site density and the standard free energies of adsorption of the ions concerned as parameters. Onoda and Casey (10) stressed the influence of transfer of oxygen ions from the solid to the liquid phase, involving nonstoichiometry in the solid. In the present paper, this possibility is not taken into account because at the TiO\(_2\)/electrolyte solution colloid chemical phenomena are not influenced by the nonstoichiometry of the solid to a noticeable degree (1).

Among the assumptions of the site-binding model in particular those about the existence of single valued potentials \( \psi_0, \psi_\beta, \) and \( \psi_\beta' \), appear to us questionable, at least for interfaces with an insulating solid phase. It is true that the theory can be formulated in a way, in which these potentials are average potentials at the phase boundary and at distances \( \beta \) or \( \beta' \) from it; the local deviations from those average values are then accounted for by the surface activity coefficients (11). However, it should be realized that these surface activity coefficients, by the close mutual proximity of ionic charges near the interface, will deviate substantially from unity; much more so than bulk activity coefficients in a solution which is in equilibrium with the interface concerned.

Thus, all assumptions concerning the behavior of activity coefficients, which are introduced during the calculations, must be regarded with caution.

Although the site binding model has frequently been applied in recent years, it is not the only theory which aims at describing surface charge generation at oxide/electrolyte solution interfaces.

Among the alternatives, we mention the porous gel model by Lyklema (12–14) and the stimulated adsorption model (15–17). In the former, a hydrolyzed surface gel is considered to be in equilibrium with the electrolyte solution; this region is supposed to be permeable to all ions in the electrolyte solution. The stimulated adsorption model, on the other hand, stresses the importance of local deviations from the average values of the potential; through such a deviation, cations are adsorbed and promote in turn the adsorption of anions.

In the present paper we describe the method of calculation by the site binding model in some detail, because the assumptions involved are not always given due consideration.

**METHODS**

The experimental method employed has been described in the preceding paper (1). The data employed in the calculations refer to \( \sigma_0 \) and \( \xi \) values for TiO\(_2\) DP 25 in both KCl and KNO\(_3\) solutions; phenomena near the interface TiO\(_2\) M808/electrolyte solution are considered to be too much influenced by chemisorbed impurities to be amenable for a simplified model of this interface.

From the \( \xi \) potential, the net charge behind the electrokinetic slipping plane (\( \sigma_\xi \)) was cal-
culated by the relation between \( \sigma_r \) and \( \zeta \) for flat interfaces (18) (it will be recalled that \( \zeta \) potentials had been calculated from electrophoretic mobilities by the formula for \( k \alpha \gg 1 \), on the basis of the argument that in electrophoresis the movements of flocs rather than of primary particles is followed (1)). For comparison's sake, we calculated \( \sigma_r \) also by the approximate relation (19)

\[
\sigma_r = 4\pi\varepsilon_0\varepsilon_r \frac{kT}{\varepsilon} \frac{ka^2}{\zeta}
\]

with \( a \) = the primary particle radius as calculated from the BET surface area for spherical particles. When relation [11] was used, the \( \zeta \) potential was employed as calculated by the Wiersema–Loeb–Overbeek method (19). The results obtained by these calculations are qualitatively similar to those obtained by using the \( \sigma_r \) vs \( \zeta \) relation for flat interfaces; although in quantitative respect differences exist. For more details, see Ref. (20).

From \( \sigma_0 \) and \( \sigma_r \), the charge between the phase boundary and the electrokinetic slipping plane \( (\sigma_\beta) \) was calculated by

\[
\sigma_\beta = \sigma_r - \sigma_0.
\]

The set of equations to be solved consists of

\[
\sigma_0 = e\left( [\text{MOH}^+] + [\text{MOH}^-\text{Cl}^-] \right) - [\text{MO}^-] - [\text{MO}^-\text{K}^+] \]  
[13]

\[
\sigma_\beta = e\left( [\text{MO}^-\text{K}^+] - [\text{MOH}^-\text{Cl}^-] \right) \]  
[14]

\[
N_s = [\text{MOH}] + [\text{MOH}^+] + [\text{MOH}^-\text{Cl}^-] + [\text{MO}^-\text{K}^+] + [\text{MO}^-] \]  
[15]

In Eqs. [13] and [14], \( e \) is the charge of a proton. \([\text{MOH}^+]\), \([\text{MOH}^-\text{Cl}^-]\), etc. are numbers of sites per unit surface area. Thus, \( \sigma_0 \) and \( \sigma_\beta \) are surface charge densities.

The consecutive steps in the solution of these equations were

1. For \( \text{pH} < \text{pH}_{\text{pzc}} \), \( |\sigma_\beta| \approx e[\text{MOH}^-\text{Cl}^-] \) and \([\text{MOH}^+]\gg [\text{MO}^-] \). We can solve then [13]–[15] for the three unknowns \([\text{MOH}^-\text{Cl}^-]\), \([\text{MOH}^+]\), and \([\text{MO}^-\text{K}^+]\), and calculate \( pQ^\text{Cl}^-_\beta \) according to Eq. [9]. This was performed for various values of \( \alpha_\beta \) (see Eq. [10]), and \( pQ^\text{Cl}^-_\beta \) was plotted as a function of \( \alpha_\beta \) (Fig. 1).

Activity coefficients in the bulk solutions were taken from Harned and Owen (21). By extrapolation to \( \alpha_\beta = 0 \) we find

\[
K_{\text{Cl}^-}^\alpha = \frac{[\text{MOH}]\gamma_{\text{H}_2\text{O}}[\text{H}^+]}{[\text{MOH}^-\text{Cl}^-]} \]  
[20]

which differs from \( K_{\text{Cl}^-}^\alpha \) as defined by Eq. [17] because

\[
K_{\text{Cl}^-}^\alpha = \frac{\gamma_{\text{MOH}}}{\gamma_{\text{MOH}^-\text{Cl}^-}} \exp\left(-\frac{e}{kT}(\psi_\beta' - \psi_0)\right)K_{\text{Cl}^-}^\alpha
\]

where \( \gamma_{\text{MOH}}, \gamma_{\text{MOH}^-\text{Cl}^-} \) and \( \psi_\beta' - \psi_0 \) values should be substituted valid at \( \alpha_\beta = 0 \).

Thus, \( K_{\text{Cl}^-}^\alpha \) will be equal to the thermodynamic constant \( K_{\text{Cl}^-}^\alpha \) only on the assumption that \( \gamma_{\text{MOH}}/\gamma_{\text{MOH}^-\text{Cl}^-} \rightarrow 1 \) and \( \psi_\beta' \rightarrow \psi_0 \) for \( \alpha_\beta \rightarrow 0 \). The latter assumption should be kept in mind because it is possible that there is a surface charge on the solid while \([\text{MO}^-\text{K}^+]\) \( = [\text{MOH}^-\text{Cl}^-] \) which gives \( \alpha_\beta = 0 \). This situation will arise whenever the tendencies of the
K\textsuperscript+ and Cl\textsuperscript- ions for chemisorption are not exactly equal.

The slope of the straight line in Fig. 1a is given by

$$\frac{\partial pQ_{\alpha}}{\partial \alpha} = \frac{e}{2.3kTC_\alpha} \frac{\partial \gamma_{\text{MOH}}}{\partial \alpha}$$ \[22\]

with $C_\alpha = \sigma_0(\psi_0 - \psi_d)$, considered to be independent of $\alpha_\beta$. If in addition $\gamma_{\text{MOH}}/\gamma_{\text{MOH}}$ is thought to be independent of $\alpha_\beta$ as well, we can calculate $C_\alpha$ from

$$\frac{\partial pQ_{\alpha}}{\partial \alpha}$$.

Similarly, for $\text{pH} \gg \text{pH}_{\text{pzc}}$, $|\alpha_\beta| \approx e \times [\text{MO}^-K^+]$, and $[\text{MO}^-] \gg [\text{MOH}_2^-]$. We solve Eqs. [13]–[15] now for the unknown $[\text{MOH}]$, $[\text{MO}^-]$ and $[\text{MO}^-K^+]$; on calculating $pQ_k$ according to Eq. [8] for various values of $\alpha_\beta$, we obtain Fig. 1 (right side). On extrapolating to $\alpha_\beta = 0$ we obtain

$$K_{K^+} = \frac{[\text{MO}^-K^+][\text{H}_2^+\beta][\text{H}^+]^\beta}{[\text{MOH}][\text{K}^+]^\beta} \gamma_{\text{MOH}}$$ \[23\]

differing from $K_{K^+}$ because

$$K_{K^+}^\alpha = \frac{\gamma_{\text{MOH}}K^+}{\gamma_{\text{MOH}}} \exp\left(\frac{e}{kT}(\psi_{\beta} - \psi_{\beta})\right)K_{K^+}$$ \[24\]

Again we can calculate from the slope of the straight line in Fig. 1b the parameter $C_\alpha = \sigma_0/\psi_{\beta}$ on the assumption that $C_\alpha$ and $\gamma_{\text{MOH}}/\gamma_{\text{MO}^-K^+}$ are independent of $\alpha_\beta$. Similar data for KNO\textsubscript{3} solutions are plotted in Fig. 2.

(3) With the values of $C_+$ and $C_-$ thus obtained, and substituting $K_{K^+}$ for $K_{K^+}$ and $K_{C^-}$ for $K_{C^-}$, we solved the equations mentioned analytically following the method outlined by Dousma (22) and Bousse (23). As adjustable parameters we used the differential Stern capacitance

$$C_{\text{Stern}} = d\sigma_0/d(\psi_0 - \psi_d)$$ \[25\]

with $\psi_d = \xi$ and $K_{s1}$ as given by Eq. [18].

Note that we have only two adjustable parameters since

$$(pK_{s1} + pK_{s2}) = 2*\text{pH}_{\text{pzc}}$$ \[26\]

from Eqs. [18] and [19].

The adjustable parameters were chosen such as to obtain a fit to the experimental $\sigma_0$ and $\xi$ values.

RESULTS

Table I contains the values for the adjustable parameters giving the best fit to our data, together with other parameters ($N_s$, $C_+$, $C_-$, $K_{K^+}$, $K_{C^-}$). Figures 3–5 show the final fit of the $\sigma_0$ and $\xi$ data for KNO\textsubscript{3} solutions; similar results were obtained for KCl solutions.

From this table it can be seen that the model necessary for fitting the experiments comprises the following features:

(1) The planes where anions and cations are adsorbed do not coincide.

(2) Different $pK_{s1}$ values are necessary for $\text{pH} < \text{pH}_{\text{pzc}}$ and for $\text{pH} > \text{pH}_{\text{pzc}}$. In other words: the $K_{s1}$ values necessary to obtain a reasonable fit to both surface charge and $\xi$ potential data, are a function of the sign of the surface charge and of the concentration of supporting electrolyte.

(3) The Stern capacitance is a function of the concentration of supporting electrolyte. The value of the Stern capacitance, however, is not critical; a rather broad range of values could be used.

(4) Agreement between model calculations and experimental data is particularly good at high electrolyte concentration.
TABLE I

Parameters Used in the Model Calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Remarks</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Remarks</th>
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</thead>
<tbody>
<tr>
<td>( N_1 )</td>
<td>m(^{-2} )</td>
<td>( 1.2 \times 10^{18} )</td>
<td>Ref. (6)</td>
<td>( 1.2 \times 10^{18} )</td>
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<td>( C_+ )</td>
<td>F ( \cdot ) m(^{-2} )</td>
<td>1.4 ± 0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_- )</td>
<td>F ( \cdot ) m(^{-2} )</td>
<td>0.9 ± 0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{K_+} )</td>
<td>—</td>
<td>( (5 \pm 0.2) \times 10^{-8} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{NO_3} ) or ( K_{Cl^-} )</td>
<td>M(^{-2} )</td>
<td>( (2.5 \pm 0.1) \times 10^{-6} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( pK_{a1} )</td>
<td>—</td>
<td>9.1</td>
<td>( 10^{-3} ) M; ( \text{pH} &lt; \text{pH}_{a1} )</td>
<td>10.1</td>
<td>( 10^{-3} ) M; ( \text{pH} &gt; \text{pH}_{a2} )</td>
<td>7.4</td>
<td>( 10^{-2} ) M; ( \text{pH} &lt; \text{pH}_{a2} )</td>
</tr>
<tr>
<td>( C_{\text{stern}} )</td>
<td>F ( \cdot ) m(^{-2} )</td>
<td>0.06</td>
<td>( 10^{-2} ) M; ( 5 \leq \text{pH} \leq 10 )</td>
<td>0.16</td>
<td>( 10^{-2} ) M; ( 5 \leq \text{pH} \leq 10 )</td>
<td>0.06</td>
<td>( 10^{-2} ) M; ( 5 \leq \text{pH} \leq 10 )</td>
</tr>
</tbody>
</table>

DISCUSSION

In the features of the model described in the preceding section, especially the second one is important. It means that \( K_{a1} \) and \( K_{a2} \) are not true thermodynamic constants, but are dependent on concentrations. \( K_{a1} \) differs from the true thermodynamic constants \( K_{a1}^\circ \) by a factor \( \gamma_{MOH}/\gamma_{MOH}\). Thus we must conclude that the activity coefficients are dependent on concentrations in a different way than expressed through the average potential \( \psi_0 \); the same holds for \( \gamma_{MO^-}/\gamma_{MOH} \). In itself this is not surprising because activity coefficients of charged groups are known to strongly depend on the presence of other charged units, while near a charged interface local concentrations of the latter are high.
During the calculations the assumptions had been introduced that $\gamma_{\text{MO}-K^+}/\gamma_{\text{MO}}$ and $\gamma_{\text{MOHCl}^-}/\gamma_{\text{MO}}$ are independent of the ionic environment near the surface. This was introduced both in the calculation of $C_-$ and $C_+$ from the slope of the lines in Figs. 1a and b, respectively, and by the use of $K_{K^+}$ and $K_{Cl^-}$ in calculations for conditions at which $\alpha_p = 0$. Introduction of the independence of $\gamma_{\text{MO}-K^+}/\gamma_{\text{MO}}$ and $\gamma_{\text{MOHCl}^-}/\gamma_{\text{MO}}$ of the ionic environment leads to a conclusion, which is at variance with the same assumption for the analogous case of $\gamma_{\text{MO}}/\gamma_{\text{MOCl}}$ and $\gamma_{\text{MO}}/\gamma_{\text{MO-H}}$.

There is a difference, to be sure, between the cases of $\gamma_{\text{MOHCl}^-}/\gamma_{\text{MO}}$ and $\gamma_{\text{MO}-K^+}/\gamma_{\text{MO}}$ on the one hand, and $\gamma_{\text{MO}}/\gamma_{\text{MOCl}}$ and $\gamma_{\text{MOHCl}^-}/\gamma_{\text{MO}}$ on the other: the former refer to groups which, as a whole, are uncharged while the latter refer to groups which do carry a charge. It should be realized, however, that MOH$_2$Cl$^-$ and MO$^-K^+$ are dipoles rather than uncharged groups: the charges of the Cl$^-$ and the K$^+$ ions are in the model considered to be at some distance from the phase boundary, where other average potentials ($\psi_p$, and $\psi_p$) prevail than at the surface itself ($\psi_0$), and where local deviations from these average potentials certainly will differ from similar deviations at the surface. MOH, on the other hand, should be regarded as an uncharged group.

Thus, it appears that the method to correct for local activity coefficients near the surface, by extrapolating $pQ^*$ to $\alpha_p = 0$, is insufficient to take into account the influence of local deviations from the average potentials.

This conclusion is supported by the work of Johnson (9).

CONCLUSIONS

Calculations with the site binding model, based on the assumptions that local activity coefficients near the surface are independent of the charge at the interface, lead to conclusions which are at variance with these assumptions.

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