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A photocatalytic reaction kinetics model based on electrical double layer theory(Ⅰ)①

——Surface complexation model at TiO_2/water interface

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[Abstract] The kinetics of photocatalysis can be usually described by Langmiur-Hinshelwood adsorption expression. The adsorption can be greatly influenced by the surface properties of photocatalyst. Triple layer model (TLM) was chosen to describe the surface adsorption of TiO_2 based on electrical double layer (EDL) theory at the TiO_2/water interface. And through the potentiometric titration the parameters of TLM were determined by the extrapolation method and Fiteql3.1 software. The results show that surface complexation dominates the surface charge and the numerical calculation fits the experiment data satisfactorily.

[Key words] TiO_2; photocatalysis; model; adsorption
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1 INTRODUCTION

The photocatalytic process is an emergency as a promising technology for oxidation of organic contaminants in environmental control[1]. However, the rate of photocatalytic reaction is one major factor to limit its practical applications. Most experimental results[2] show that the kinetics of photocatalysis can be expressed by Langmiur-Heinshelwood adsorption equation. But the farther study on the relationship between adsorption and photocatalytic reaction is little reported. Because the heterogeneous photocatalytic reaction takes place at the surface of the catalyst[3], it is worth studying the factors that affect the organic adsorption on the surface of photocatalyst, such as properties of catalyst, pH, ionic strength.

Surface complexation model (SCM) proposed by Stumm is well accepted to describe the adsorption and surface reaction at interface. It includes tow kinds of model, non electrical model (NEM) and electrical double layer (EDL)[4]. In EDL, according to the physical description of the electrostatics of the interface provided by classic theories of Gouy, Chapman, Stern, et al, it can be recalled constant capacity model (CCM), Stern model, triple layer model (TLM), Multi-site Complexation (MUSIC)[5] model, etc, in which TLM is widely used.

In conventional photocatalytic process, titanium dioxide (TiO_2) was used as the catalyst. In this paper, the surface adsorption of TiO_2 are described by triple layer model (TLM) based on electrical double layer (EDL) theory at the TiO_2/water interface. And through the potentiometric titration the parameters of TLM can be determined by the extrapolation method and Fiteql3.1 software.

2 EXPERIMENTAL

2.1 Materials

All reagents used in this study were analytical grade and were used without farther purification. TiO_2 was purchased from Japan Titan Kogyokk Co. The BET surface area was 61 m^2/g. By X-ray diffraction analysis no other crystal besides anatase was detected.

2.2 Method

All titration experiments were carried out in the experimental setup which can be found elsewhere[6]. Purified nitrogen was used to create a CO_2-free atmosphere in the titration beaker. The TiO_2 suspension with dry NaCl and NaOH added was stirred. The titration procedure was performed by adding HCl solution. Measurements were performed under non-stirred conditions. The system was taken to be as equilibrium when the drift was less than 0.02 mV/

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min. Detailed and accurate HCl and NaOH dosage were obtained.

3 SURFACE COMPLEXATION MODEL AND DETERMINATION OF PARAMETER

3.1 Surface complexation model

The ionization reaction of surface site on TiO_2 can be written as[6, 7]

$$\equiv SOH_2^+ = \equiv SOH + H^+$$
$$\equiv SOH = \equiv SO^- + H^+$$

and its equilibrium constant can be expressed as

$$K_{a1} = [\equiv SOH_2^+]/[\equiv SOH][H^+]_s \quad (1)$$
$$K_{a2} = [\equiv SO^-][H^+]_s/[\equiv SOH] \quad (2)$$

where $[\equiv SOH_2^+]$ and $[\equiv SOH]$ and $[\equiv SO^-]$ are the concentrations of protonated, unprotonated and deprotonated surface site, respectively.

The concentrations of protons at some location in the electrical double layer is related to the bulk solution concentration by the Boltzmann distribution, e. g. ,

$$[H^+]_s = [H^+]\exp[-F\psi_0/(RT)]$$

where ψ_0 is the mean potential in the plane of surface change (σ_0), F is Faraday constant (96 484.5 C/mol), $[H^+]$ is the concentration of protons in the bulk solution, R is the universal gas constant, T is the absolute temperature. And hence

$$K_{a1} = [\equiv SOH_2^+]/[\equiv SOH][H^+] \cdot \exp[-F\psi_0/(RT)] \quad (3)$$
$$K_{a2} = [\equiv SO^-][H^+]/[\equiv SOH] \cdot \exp[-F\psi_0/(RT)] \quad (4)$$

Similarly, to account for specific adsorption of electrolyte (NaCl) ions, its equilibrium equation can be written as

$$\equiv SOH_2^+ + Cl^- = \equiv SOH_2^+ \equiv Cl^-$$
$$\equiv SO^- + Na^+ = \equiv SO^- \equiv Na^+$$

and its equilibrium constant can be expressed as

$$K_{Cl^-} = [\equiv SOH_2^+ \equiv Cl^-]/[\equiv SOH][H^+] \cdot [Cl^-]\exp[F(\psi_0 - \psi_\beta)/(RT)] \quad (5)$$
$$K_{Na^+} = [\equiv SO^- \equiv Na^+][H^+]/[\equiv SOH] \cdot [Na^+]\exp[-F(\psi_0 - \psi_\beta)/(RT)] \quad (6)$$

where $[\equiv SOH_2^+ \equiv Cl^-]$ and $[\equiv SO^- \equiv Na^+]$ are the concentrations of protonated surface site bound to countercation and deprotonated surface site bound to counteranion, respectively, $[Cl^-]$ and $[Na^+]$ are the concentrations of anion and cation in bulk solutions, respectively. The surface site concentration is given by

$$N_s = [\equiv SO^-] + [\equiv SOH_2^+] + [\equiv SOH] + [\equiv SO^- \equiv Na^+] + [\equiv SOH_2^+ \equiv Cl^-] \quad (7)$$

For TiO_2, N_s was fixed at 20.8 $\mu mol/m^2$ that is the value recommended by Yates et al based on crystallographic consideration and tritium exchange and mass loss experiment[8].

3.2 Relationship between charge and potential

For TLM[7], electroneutrality requires that

$$\sigma_0 + \sigma_\beta + \sigma_d = 0 \quad (8)$$

and

$$\sigma_0 = ([\equiv SOH_2^+] - [\equiv SO^- \equiv Na^+] + [\equiv SOH_2^+ \equiv Cl^-] - [\equiv SO^-]) \cdot F/(\rho A) \quad (9)$$

$$\sigma_\beta = ([\equiv SO^- \equiv Na^+] - [\equiv SOH_2^+ \equiv Cl^-]) \cdot F/(\rho A) \quad (10)$$

Constant capacitances are assumed in the surface regions between the planes and the charge potential relationship as follows:

$$\sigma_0 = C_1(\psi_0 - \psi_\beta) \quad (11)$$
$$\sigma_d = C_2(\psi_d - \psi_\beta) \quad (12)$$

From Gouy-Chapman diffuse layer theory, the charge in the diffuse layer is

$$\sigma_d = -(8\varepsilon\varepsilon_0 RTI)^{1/2}\sinh[F\psi_d/(2RT)] \quad (13)$$

where σ_0, σ_β and σ_d are the charge at the plane 0, β and d, respectively; C_1 and C_2 are capacity values in inner and outer plane, respectively; ε and ε_0 are the bulk dielectric constant of medium (water) and permittivity of vacuum, respectively; I is ionic strength.

3.3 Determination of equilibrium constant and parameter

Equilibrium constant can be determined by the method of extrapolation or numerical fit. Fiteql family are the widely used software[9, 10], but its model-dependent fitting parameters are too many for the result to be unique. By the method of extrapolation, the other parameter, such as C_1, C_2, can not be determined. In this paper, the complexation constants were determined by the extrapolation first, then the other parameters were done by Fiteql3.1.

3.3.1 Extrapolation

Surface charge density is a function of pH and is defined by

$$\sigma_0 = (C_a - C_b - 10^{-pH} + 10^{-14+pH}) \cdot F/(\rho A) \quad (14)$$

where C_a and C_b are the concentrations of acid or base after addition.

For a positively charged surface,

$$\sigma_0 = ([\equiv SOH_2^+] + [\equiv SOH_2^+ \equiv Cl^-])F/(\rho A) \quad (15)$$

For a negatively charged surface,

$$\sigma_0 = -([\equiv SO^-] + [\equiv SO^- \equiv Na^+])F/(\rho A) \quad (16)$$

According to the calculation procedure by Stumm and Schinlder, the surface charge is assumed to result from only simple amphoteric acid-base reaction of surface. The surface complexation is ignored.

However, there are errors in the approximation of the above procedure if the complexation is significant. Sprycha[11] proved in theory that when $\Delta pK_a>2$, in the range of all pH, either $[-SOH_2^+]$ or $[-SO^-]$ is much less than $[-SOH]$. Yates et al proved the ΔpK_a of TiO_2 make an appointment of 3[11]. So the intrinsic acidity constant cannot be determined by the procedure above. In fact, surface complexation dominated the surface charge. The complexation can be done by the extrapolation method below.

For a positively charged surface,

$\sigma_0=[-SOH_2^+-Cl^-]F/(\rho A)$,

$[-SOH]=N_s-[-SOH_2^+-Cl^-]$

For a negatively charged surface,

$\sigma_0=-[-SO^--Na^+]F/(\rho A)$,

$[-SOH]=N_s-[-SO^--Na^+]$

Let $\alpha=\sigma_0/N_s$,

and for a positively charged surface, let

$$pQ_{Na^+}=pH-\lg[\alpha_-/(1-\alpha_-)]+\lg[Na^+] \quad (17)$$

then

$$pK_{Na^+}=pQ_{Na^+}+F(\psi_0-\psi_\beta)/2.303RT \quad (18)$$

For a negatively charged surface, let

$$pQ_{Cl^-}=pH+\lg[(\alpha_+/(1-\alpha_+)]-\lg[Cl^-] \quad (19)$$

then

$$pK_{Cl^-}=pQ_{Cl^-}+F(\psi_0-\psi_\beta)/2.303RT \quad (20)$$

When $pH=pH_{pzc}$, $\sigma_0=0$, $\psi_0=\psi_\beta=0$, the last terms in Eqns. (18) and (20) are vanished, $pK_{Na^+}=pQ_{Na^+}$, $pK_{Cl^-}=pQ_{Cl^-}$. The point of intersection of pQ vs pH curves with the vertical line $pH=pH_{pzc}$ fixes the pK_{Na^+} and pK_{Cl^-} value.

3.3.2 Fiteql3.1

Fiteql3.1 is a business software, by which the surface equilibrium can be solved. According to the material and mass law, the equation matrix, in which the species are expressed by components of reaction products, can be solved by the iterative method of Newton-Raphson[5, 9, 10]. Tables 1 and 2 are the Stoichiometry matrix **A** and **B** in the Fiteql3.1 software.

4 RESULTS AND ANALYSIS

4.1 Potential titration of TiO_2

The surface charge is formed on the metal oxide as a result of ionization and complexation reactions of surface hydroxyl groups. Electric charge vs pH value

Table 1 Species, lg*K*, and stoichiometry matrix ***A***

Name	lg*K*	XOH	PSI(0)	PSI(b)	PSI(d)	H[+]	I/f	Cl[−]	Na[+]	*K*+	*K*−
XOH_2[+]	0.000	1.000	1.000	0.000	0.000	1.000	1.000	0.000	0.000	1.000	0.000
XOH	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
XO[−]	0.000	1.000	−1.000	0.000	0.000	−1.000	−1.000	0.000	0.000	0.000	1.000
XOH_2Cl	3.100	1.000	1.000	−1.000	0.000	1.000	2.000	1.000	0.000	1.000	0.000
XONa	3.100	1.000	−1.000	1.000	0.000	−1.000	0.000	0.000	0.000	1.000	0.000
Na[+]	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	1.000
Cl[−]	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000
H[+]	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000
OH[−]	−13.8	0.000	0.000	0.000	0.000	−1.000	2.000	0.000	0.000	0.000	0.000

Table 2 Species, lg*K*, and stoichiometry matrix ***B***

Name	XOH	PSI(0)	PSI(b)	PSI(d)	H[+]	I/f	Cl[−]	Na[+]
XOH	1.000	1.000	0.000	0.000	1.000	0.000	0.000	0.000
XO[−]	1.000	−1.000	0.000	0.000	−1.000	0.000	0.000	0.000
XOH_2Cl	1.000	1.000	−1.000	0.000	1.000	0.000	1.000	0.000
XONa	1.000	−1.000	1.000	0.000	−1.000	0.000	0.000	1.000
Na[+]	0.000	0.000	0.000	0.000	0.000	0.500	0.000	1.000
Cl[−]	0.000	0.000	0.000	0.000	0.000	0.500	1.000	0.000
H[+]	0.000	0.000	0.000	0.000	1.000	0.500	0.000	0.000
OH[−]	0.000	0.000	0.000	0.000	-1.000	0.500	0.000	0.000

dependence is one of the most important characteristics of the surface properties of the metal oxide suspension solutions. The position of pH_{pzc} depends on the alkali-acid character of surface hydroxyl groups[12]. The values of pH_{pzc}, presented in many papers, are often very divergent, they range from 5.2 to 7 for TiO_2 of the anatase structure[13].

The surface charge, expressed as surface excessive H, versus pH dependence for TiO_2 suspension, whose concentrations are 0.000 89, 0.000 15, 0.1 and 0.000 69 mol/L, respectively, is depicted in Fig. 1. As can be seen, the obtained pH_{pzc} value is about 6.6.

Based on the dependence of surface charge density on pH, the surface equilibrium constants and other parameters were calculated as follows.

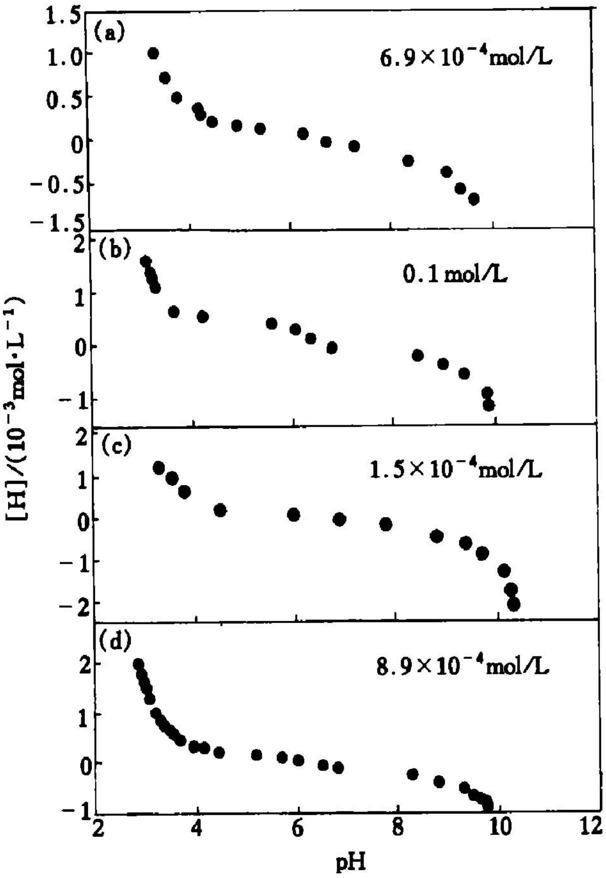


Fig. 1 Surface excessive H vs pH curves in system at different concentration of electrolyte

4.2 Determination of pK_{Na^+}, pK_{Cl^-} by extrapolation

According to Eqns. (18) and (20), $pK_{Na^+} = 5.24$ and $pK_{Cl^-} = 8.2$ can be determined by linearity extrapolation of pQ_{Na^+} or pQ_{Cl^-} vs α at $\alpha = 0$ as shown in Fig. 2(a) and (b).

4.3 Determination of pK_{a1} and pK_{a2}

The results of pK_{a1} and pK_{a2} at different electrolyte system can be obtained by Fiteql3.1 software as shown in Table 3. The average values of pK_{a1} and pK_{a2} are 5.20 and 7.96, respectively. The point of zero charge of TiO_2 can be calculated as

$$pH_{pzc} = (pK_{a1} + pK_{a2})/2 = 6.58$$

The point of zero charge for rutile is $pH_{pzc} = 5.4$, and that for commercial product P25 (rutile/anatase = 30/70) is 6.25. Our calculation for TiO_2 (anatase), $pH_{pzc} = 6.58$, is approximated to that reported by Ref. [13].

The intrinsic stability constant, $K_{Na^+}^{int}$ and $K_{Cl^-}^{int}$ can be calculated as

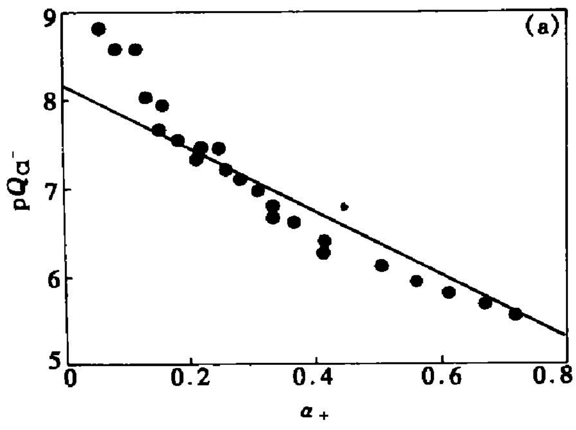
$$\lg K_{Na^+}^{int} = pK_{a2} - pK_{Na^+},\quad \lg K_{Cl^-}^{int} = pK_{Cl^-} - pK_{a1}$$

so, $\lg K_{Na^+}^{int} = 2.72$ and $\lg K_{Cl^-}^{int} = 3.0$, which is approximated to the calculation by Sprycha[11], $\lg K_{Na^+}^{int} = \lg K_{Cl^-}^{int} = 3.1$.

4.4 Determination of parameters C_1 and C_2

For the triple-layer model, the outer layer capacitance (C_2) is assumed to be 0.2 since this is a reasonable value for compact layer capacitance and provide good agreement with electro-kinetic data[8]. The inner layer capacitance(C_1) is an adjustable parameter in our model. The capacitance value is relative to dielectric constant of the Stern layer(ε) and the distance of charge separation (d) between both electrostatic planes of the Stern layer,

$$C = \varepsilon\varepsilon_0/d$$



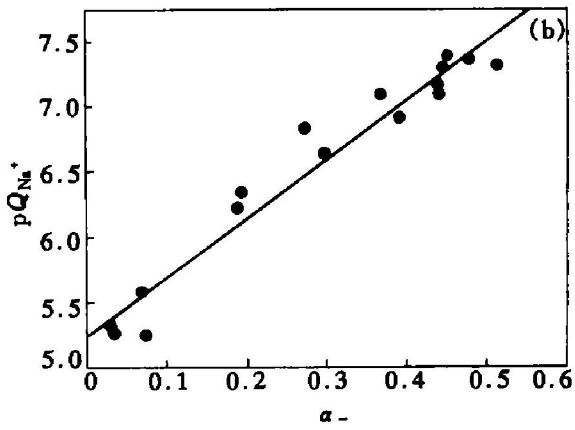


Fig. 2 Linearity regression of pQ_{Cl^-} vs α_+ (a) and pQ_{Na^+} vs α_- (b)

Table 3 pK_{a1} and pK_{a2} calculated by Fiteql3. 1

Electrolyte concentration/ ($mol \cdot L^{-1}$)	pK_{a1}	pK_{a2}
0. 000 89	5. 206	7. 865
0. 1	5. 216	7. 855
0. 000 69	5. 178	8. 087
0. 000 15	5. 194	8. 038
Average	5. 20	7. 96

The value of ε is not known, but its maximum possible value can be taken as ε_b, the bulk dielectric constant of water. So, given $\varepsilon_b = 78.45$, freedom space penetration coefficient $\varepsilon_0 = 8.854 \times 10^{-12}$, the ionic radii of Na^+ and Cl^- are 1.02×10^{-10} m and 0.99×10^{-10} m at 25 ℃, respectively. C_1 maximum value can be estimated to be 6. 81 and 6. 87, respectively. This help to partially constrain the fitted capacitance. $C_1 = 4.8$ is obtained through minimization the error value between calculation and experimental data as shown in Fig. 3.

4. 5 Numerical simulation analysis

The comparison between numerical calculation and experimental data is shown in Fig. 4 at system in 0. 000 89 mol/ L electrolyte concentration. The agreement is satisfied. The surface species distribution is shown in Fig. 5. In the range of pH, [$\equiv SOH_2^+$] and [$\equiv SO^-$] are much less than [$\equiv SOH$] which is in favor of the theoretical analysis by Sprycha[11].

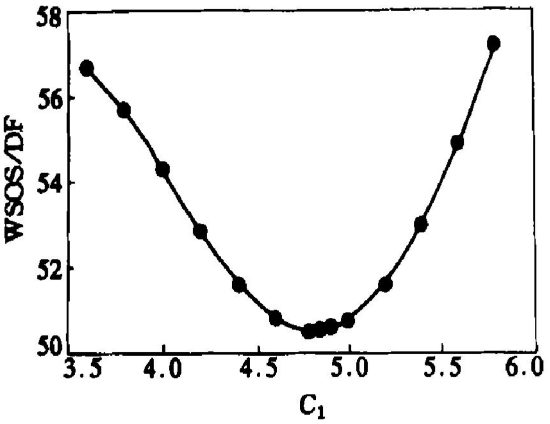


Fig. 3 Error values vs C_1

5 CONCLUSIONS

In this paper, the surface properties of TiO_2 were described by TLM through the potentiometric titration. The complexation constants were determined by the extrapolation first, then the other parameters were done by Fiteql3. 1 software. For the TiO_2, $pH_{pzc} = 6.58$, $pK_{a1} = 5.20$, $pK_{a2} = 7.96$, $pK_{Na^+} = 5.24$, $pK_{Cl^-} = 8.2$, and $C_2 = 0.2$, $C_1 = 4.8$. The numerical calculation fits the experimental

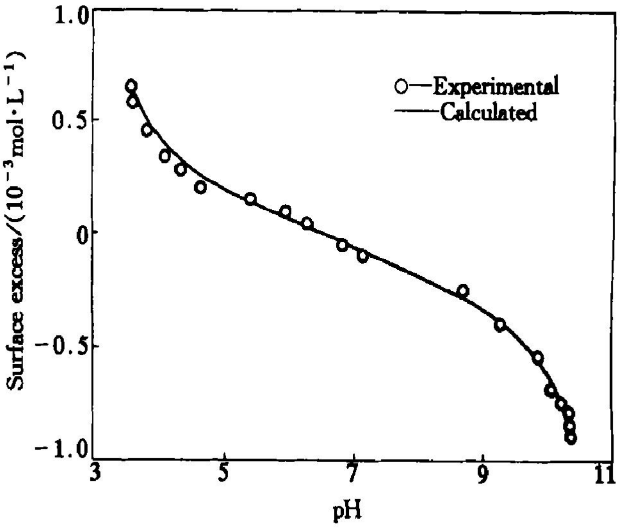


Fig. 4 Comparison between calculated and experimental data at system in 0. 000 89 mol/ L electrolyte concentration

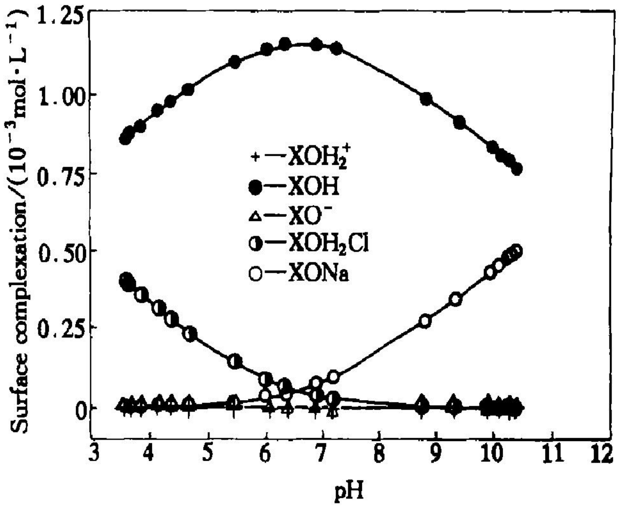


Fig. 5 Distribution of surface species as function of pH

data satisfactorily.

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