

A further simplification of the revised physical adsorption (RPA) model

X. Hao, W.A. Spieker, and J.R. Regalbuto*

Department of Chemical Engineering, University of Illinois at Chicago, 810 S. Clinton, Chicago, IL 60607, USA

Received 27 June 2002; accepted 9 June 2003

Abstract

We present a further simplification of the essentially parameter-free revised physical adsorption model (K. Agashe, J.R. Regalbuto, *J. Colloid Interface Sci.* 185 (1997) 174) in this paper. It has been discovered that a physical adsorption model describing the uptake of various metal complexes from aqueous solutions onto oxide surfaces can most accurately simulate experimental data when the model contains only a coulombic energy term, and not a solvation energy term. The results of the simulation for cobalt/silica, chloroplatinic acid (CPA)/alumina, and tetraammonium platinate (TAP)/alumina and silica are presented here. A reasonable justification for the omission of this term is that solvation effects are negligible when adsorbing metal complexes retain one or more hydration sheaths.

© 2003 Elsevier Inc. All rights reserved.

Keywords: Physical adsorption theory; Noble metal catalyst impregnation; Coulombic and solvation effects

1. Introduction

Various mechanisms and associated models have been employed in the past three decades to describe the adsorption of catalyst precursor metal complexes from aqueous solutions onto the surfaces of oxide support materials. In 1978 Brunelle presented the first evidence to the catalysis community that noble metal adsorption onto support oxides was electrostatic in nature [1]. Oxides adsorb anionic complexes at pHs below the pH of their point of zero charge (PZC), where the surface is protonated and positively charged, and cationic complexes above their PZC, where the surface is deprotonated and negatively charged [1].

Several years earlier, James and Healy had published one of the earliest quantitative frameworks of a physical mechanism in the colloid science literature [2]. They calculated a free energy of adsorption from a priori coulombic and solvation terms, and due to an admitted overestimation of the solvation energy, an adjustable “chemical” energy term [2]. The large relative magnitude of the adjustable term in this model may explain why the model was not widely adopted. For example, in the original publication, to fit the adsorption of Co^{2+} complexes over SiO_2 , coulombic and solvation free energies were calculated at high pH to be -19 and

$+11$ kJ/mol, respectively, while the “chemical” term required was -27 kJ/mol. The chemical interaction term can be made so overwhelmingly large that adsorption of cations over positively charged surfaces can be fit with the James and Healy model [3].

Our fundamental studies of catalyst impregnation have centered on the adsorption of noble metal coordination complexes such as hexachloroplatinate, $[\text{PtCl}_6]^{2-}$, or tetraammonium platinate (TAP), $[(\text{NH}_3)_4\text{Pt}]^{2+}$, onto common catalyst supports such as alumina and silica. We took the original model of James and Healy as a base. In a first work [3] we revised this model in two ways. First, we employed the more rigorously derived solvation free energy term of Levine [4]. This resulted in solvation energy terms about one order of magnitude less than the term of James and Healy, for identical parameters [3]. With only this change the model greatly overpredicted the amount of metal uptake, and the strength of the coulombic interaction had to be reduced. To this end, we substituted a more realistic [5] non-Nernstian description of the surface charge for the simplistic calculation of surface potential by the Nernst equation. This had the desired effect of lowering the surface potential, and many data sets of cations adsorbing over a negatively charged silica surface were simulated either with no adjustable “chemical” term, or with greatly diminished values of this term [3]. We named this model the revised physical adsorption (RPA) model, to contrast it with other mechanisms proposed for metal adsorption that are based on assumed chemical interactions.

* Corresponding author.

E-mail address: jrr@uic.edu (J.R. Regalbuto).

In the course of our modeling of anionic platinum complexes adsorbing over alumina [6–8], we have discovered that the solvation free energy term can, and in some instances must, be omitted altogether. We have retraced our steps and found that the simplified model also works best for our earlier simulations. Thus it appears, for a wide range of systems that qualitatively exhibit electrostatic behavior, a quantitative model that accounts only for a coulombic interaction is sufficient to describe metal uptake.

2. Theory

To this point, the RPA model has been employed for noble metal systems with the assumption of a single, representative adsorbing complex [6–9], even though parent complexes such as hexachloroplatinate, $[\text{PtCl}_6]^{2-}$, are known to hydrolyze to chlorohydroxo species in solution such as $[\text{PtCl}_5(\text{OH})]^{2-}$ and $[\text{PtCl}_4(\text{OH})_2]^{2-}$. The adsorption behavior of these different species has been directly compared, and this assumption has been justified [9]. Thus, the model will be derived below for a single species, but is easily extended to multiple species adsorption.

To obtain the total adsorption density at any given pH, total metal concentration, and ionic strength, the adsorption densities are computed from a Langmuir isotherm,

$$\left(\frac{\Gamma}{\Gamma_{\max}}\right) = \frac{KC}{1 + KC}, \quad (1)$$

in which the maximum extent of adsorption (mol/area) is calculated as a steric close-packed layer of adsorbates retaining one hydration sheath,

$$\Gamma_{\max} = \left[\frac{1}{N_0\pi(r_{\text{ion}} + 2r_w)^2} \right].$$

The maximum adsorption density for $[\text{PtCl}_6]^{2-}$, which has a radius of 2.95 Å, is 1.6 $\mu\text{mol}/\text{m}^2$ and is now supported by a good deal of experimental evidence [7,8,10].

The adsorption equilibrium constant, K , is calculated from only the coulombic energy,

$$K = \exp\left(\frac{-\Delta G_{\text{ads}}}{RT}\right) = \exp\left(\frac{-\Delta G_{\text{coul}}}{RT}\right),$$

which in turn is given as a function of the potential at the plane of adsorption,

$$\Delta G_{\text{coul}} = zF\psi_x.$$

In this equation, z is the charge of the adsorbed species, F is the Faraday constant, and ψ_x is the potential, calculated by assuming a simple electric double layer in which all species adsorb in one plane,

$$\psi_x = \left[\frac{2RT}{ZF} \right] \ln\left(\frac{(Y+1) + (Y-1)e^{-\kappa x}}{(Y+1) - (Y-1)e^{-\kappa x}}\right),$$

where

$$x = (r_{\text{ion}} + 2r_w)$$

and

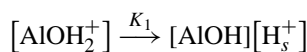
$$Y = \exp\left(\frac{ZF\psi_0}{2RT}\right),$$

where $Z = 1$ (for 1:1 background electrolyte), ψ_0 is the surface potential, and R is the universal gas constant (8.314 J/mol K). The Debye–Hückel reciprocal double-layer length κ is a function of ionic strength I ,

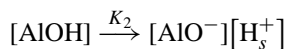
$$\kappa = 3.31 \times 10^9 \sqrt{I} \text{ (m}^{-1}\text{)}, \quad I = \frac{1}{2} \sum_i z_i^2 C_i,$$

where z_i is the charge of the ions and C_i is the concentration of the species.

The surface potential ψ_0 here is treated differently from James and Healy's model, in which it was computed by the Nernst equation [2]. This has been demonstrated to be inadequate for nonelectrode materials such as clays and inorganic oxides [11]. We have instead employed a one-site, two-pK non-Nernstian model of the surface, commonly invoked in the colloid science literature for amphoteric oxides such as Al_2O_3 [5,11]. The protonation and deprotonation of surface hydroxyl groups is formulated in terms of the surface proton concentration at



and



or

$$K_1 = \frac{[\text{AlOH}][\text{H}_s^+]}{[\text{AlOH}_2^+]}$$

and

$$K_2 = \frac{[\text{AlO}^-][\text{H}_s^+]}{[\text{AlOH}]}$$

The surface charge is

$$\sigma_0 \text{ (c/cm}^2\text{)} = eN_s \frac{([\text{AlOH}_2^+] - [\text{AlO}^-])}{([\text{AlOH}] + [\text{AlOH}_2^+] + [\text{AlO}^-])}, \quad (2)$$

where e is the charge of the electron and N_s is oxide surface site density (site/cm²). In terms of the bulk proton concentration $[\text{H}^+] = [\text{H}_s^+] \exp(-e\psi_0/2kT)$, in which k is the Boltzmann constant and T is the absolute temperature. Equation (2) becomes

$$\sigma_0 = eN_s \frac{([\text{H}^+]/K_1)e^{-e\psi_0/2kT} - (K_2/[\text{H}^+])e^{e\psi_0/2kT}}{1 + ([\text{H}^+]/K_1)e^{-e\psi_0/2kT} + (K_2/[\text{H}^+])e^{e\psi_0/2kT}}. \quad (3)$$

If the pH is specified, there are two unknowns in Eq. (3), σ_0 and ψ_0 , so an additional equation is needed; it is the Gouy–Chapman diffuse-layer charge–potential relationship,

$$\sigma_0 = (8 \times 10^{-5} \varepsilon \varepsilon_0 RIT)^{1/2} \sinh(e\psi_0/2kT), \quad (4)$$

where ε is the dielectric constant of the bulk aqueous medium (78.54) at room temperature, ε_0 is the dielectric

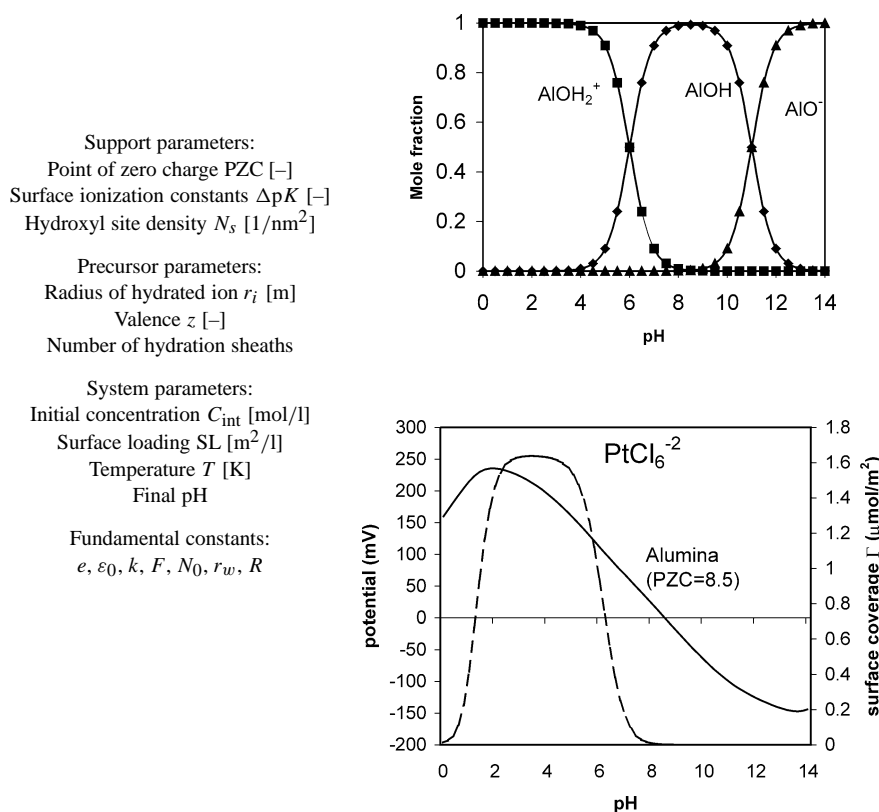


Fig. 1. Summary of the parameters and typical results from the simplified RPA model: 200 ppm Pt, 500 m^2/l , γ -alumina (PZC = 8.5, $\Delta pK = 5$, $N_s = 8 \text{ OH}/\text{nm}^2$).

constant of the free space ($8.854188 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$), and I (mol/l) is the total ionic strength of the electrolytes in the solution.

If only an initial pH is available, an estimate of the final (equilibrium) pH can be made by adding to the $\sigma_0 - [\text{H}^+]^+$ and $\sigma_0 - \Psi_0$ equations above (Eqs. (3) and (4)), a proton balance between the surface and bulk liquid [12],

$$\sigma_0 = \frac{F}{ws} \left[([\text{H}^+]_0 - [\text{OH}^-]_0) + (10^{-(14-\text{pH})} - 10^{-\text{pH}}) \frac{c^0}{y} \right], \quad (5)$$

where $[\text{H}^+]_0$, $[\text{OH}^-]_0$ are the initial concentrations of protons and hydroxyls, w is the mass concentration of oxide (g/l), s is the specific surface area of the oxide (cm^2/g), y is the activity coefficient from the extended Debye–Hückel equation, and c^0 is the standard concentration (1 mol/l).

Equations (3)–(5) can be solved simultaneously and independent of the adsorption equations, to arrive at equilibrium values of σ_0 , Ψ_0 , and $[\text{H}^+]^+$. An article devoted completely to this portion of the model, in which the dramatic pH buffering effect of oxides was demonstrated, has been published previously [12] and a simple accurate method to measure oxide PZC was presented.

Finally, the equilibrium liquid-phase concentration of each species is found from a mole balance on each species, $C = C_{\text{init}} - C_{\text{adsorbed}}$, where the amount adsorbed, C_{adsorbed} ,

is calculated as

$$C_{\text{adsorbed}} = (SL)\Gamma = \frac{m_{\text{ox}} S_{\text{ox}} \Gamma}{V_L} = \frac{m_{\text{ox}} S_{\text{ox}} \Gamma_{\text{max}} \left(\frac{KC}{1 + KC} \right)}. \quad (6)$$

A summary of the model parameters and a typical set of results are shown in Fig. 1. The support is described by its PZC, hydroxyl density, and surface ionization constants (which are centered on the PZC and are represented as) ΔpK . The precursor is described by its radius, its valence, and the number of hydration sheaths it retains upon adsorption. While anionic chloroplatinates retain one sheath, cationic amine complexes of Pt and Pd appear to retain two [10]. The extensive system parameters are metal concentration, surface loading, temperature (almost always assumed to be 25 °C), and equilibrium pH.

In Fig. 1 the adsorption of a 200-ppm solution of $[\text{PtCl}_6]^{2-}$ is simulated as a function of pH over 500 m^2/l of an alumina surface, characterized by a PZC of 8.5 and a ΔpK of 5, with $N_s = 8 \text{ OH}/\text{nm}^2$. The mole fractions of protonated, neutral, and deprotonated hydroxyl groups generated from these parameters are shown in the upper plot. In the lower graph, the surface potential and surface coverage are plotted versus pH. At the PZC, the surface potential and surface coverage are both zero, and no uptake is predicted above the PZC, where the surface potential is negative. Be-

low the PZC, adsorption of the anion increases in response to increasing positive surface potential. At the lowest pH, however, high ionic strength causes both the potential and the adsorption equilibrium constant to fall, the latter quite dramatically. We have offered this physical “double layer compression” effect as an alternate to the common assumption of chemical adsorption theories that the retardation is caused by the strong and competition adsorption of chloride, and we have supported it with direct measurement of chloride uptake [7].

It should be noted that the model parameters either are physical constants or can be measured independent of adsorption. The adsorption model contains essentially no adjustable parameters. In this work the model has been “fit” to data by the wholesale elimination of the solvation term, and this has been done retroactively to all other data sets we ever simulated using the RPA model.

3. Results and discussion

One of the Pt/alumina data sets that led us to investigate the RPA model’s sensitivity to the solvation energy term is shown in Fig. 2. It is the data of Santacessaria et al. [13] and was originally reported as uptake versus CPA concentration (Fig. 2a). The CPA concentration is coupled to the pH; as the CPA concentration increases, the initial pH decreases. We have estimated the equilibrium pH for each data point by computing the initial pH from the CPA concentration and then applying the proton balance (Eqs. (2)–(4)) [6,8]. In Fig. 2b, then, uptake is plotted as a function of equilibrium pH.

The model parameters are the same as those used above (PZC = 8.5, $\Delta pK = 5.0$, $N_s = 8 \text{ OH/nm}^2$). Simulations with and without the solvation energy term are shown in the figure as the solid and dashed lines, respectively. With the solvation energy term, predicted uptake falls far below the observed uptake as the CPA concentration increases/pH decreases. Without this term, agreement is quite reasonable.

The omission of this term might be justified from the aqueous-like local environment retained by the adsorbed complexes. A common assumption in adsorption models, dating back to that of James and Healy, is that metal complexes can adsorb with one or more of their hydration sheaths intact [2]. It was mentioned in the theory section that anionic Pt and Pd complexes adsorb with one hydration sheath has been rather well established; with cationic Pt and Pd complexes, the number of retained hydration sheaths appears to be 2 [10]. It is reasonable to assume that water is bound only weakly to a metal beyond the first or second hydration layer (for anions and cations respectively) such that the energy required for its removal can be neglected.

The impact of the abbreviated calculation on other sets of data is illustrated in the remaining figures. We earlier found that a wide variety of phases and surface areas of aluminas, which possessed a common PZC, all behaved roughly the

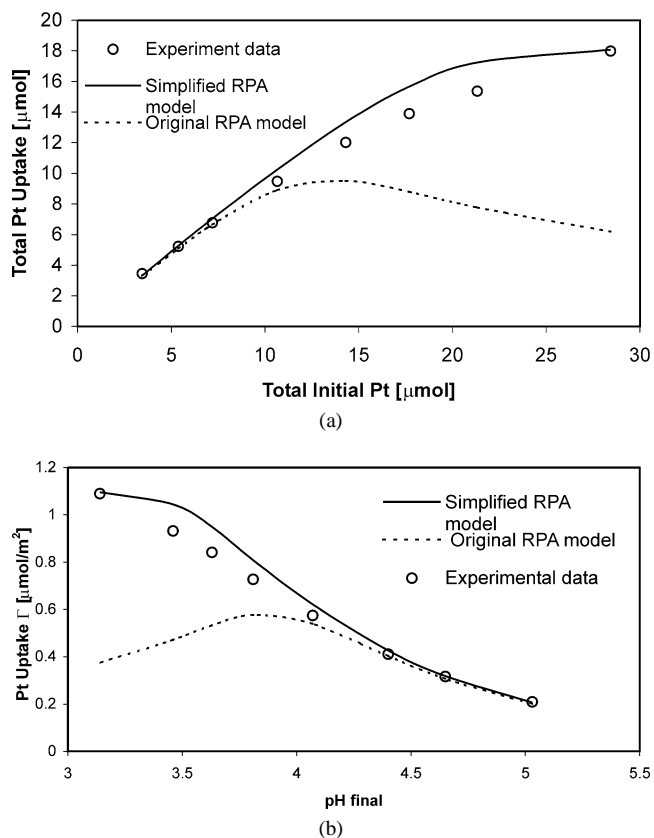


Fig. 2. Simulations of uptake of CPA versus (a) concentration and (b) final pH, data from Santacessaria et al. [13]: 0.7–40 mmol/l Pt, 33000 m²/l, γ -alumina (PZC = 8.5, $\Delta pK = 5$, $N_s = 8 \text{ OH/nm}^2$).

same in regard to CPA adsorption [7]. In this case a single, low Pt concentration was employed, 200 ppm or about 10^{-3} molar, with the same “surface loading” (area of oxide per volume of solution, m²/l) of each type of alumina. All materials could be reasonably modeled with one curve, using the average PZC of 8.5. Figure 3 shows these data together with the abbreviated and unabbreviated adsorption energy calculation. At this low Pt concentration, the uptake displays very little sensitivity to the solvation energy term.

In addition to studying the adsorption of anionic Pt over a positively charged alumina surface (on the acidic side of alumina’s PZC), we have investigated the complementary cases of cationic Pt adsorption on the basic side of alumina’s and amorphous silica’s PZC, the latter of which is in the range 3.5–4.5 [14]. Experimental details of these experiments are given in Ref. [14]. Shown in Fig. 4 is the uptake of 200 ppm of tetraammonium platinate over 1000 m²/l of silica (Fig. 4a) and alumina (Fig. 4b) which have been simulated with and without the solvation energy terms. The PZC, ΔpK , and N_s for alumina (8.5, 5, and 8 OH/nm²) have been kept the same as in the previous two figures, while for silica, the alumina parameters have been substituted for those of silica (measured independently as 4.2, 5.2, and 5, respectively [15]). Under these conditions the solvation energy exhibits relatively little effect on the predicted uptake over silica (Fig. 4a)

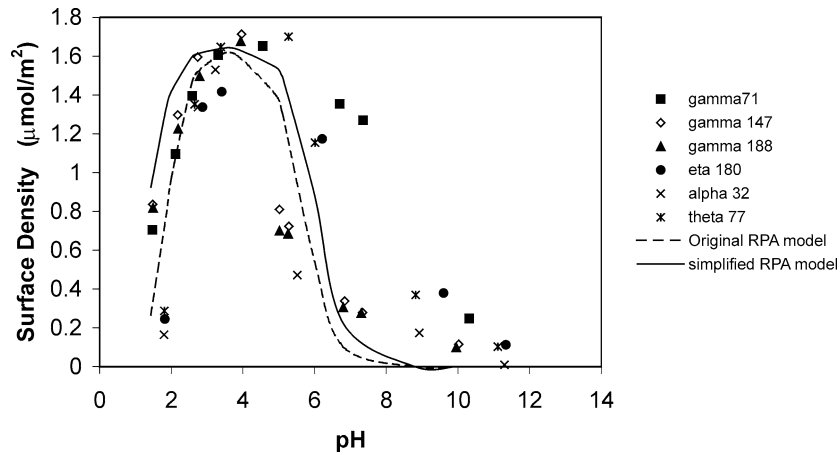


Fig. 3. Anionic Pt (CPA) uptake by various aluminas versus pH (data taken from [7]): 200 ppm Pt, 500 m²/l, alumina (PZC = 8.5, $\Delta pK = 5$, $N_s = 8 \text{ OH/nm}^2$).

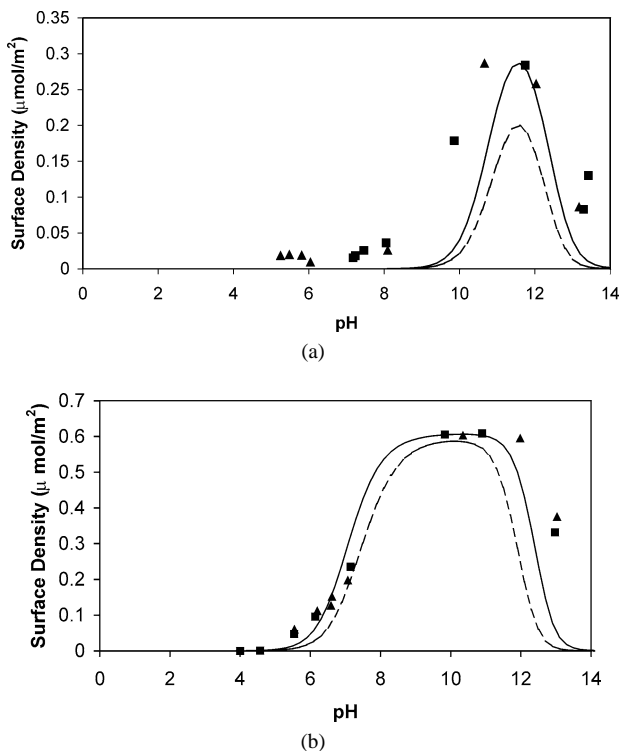


Fig. 4. RPA simulations of cationic Pt (TAP) uptake by (a) γ -alumina (PZC = 8.5, $\Delta pK = 5$, $N_s = 8 \text{ OH/nm}^2$) and (b) amorphous silica (PZC = 4.2, $\Delta pK = 5.2$, $N_s = 5 \text{ OH/nm}^2$) versus pH. Data from Ref. [14].

and about a 30% difference at the uptake maximum over alumina (Fig. 4b) that more accurately fits the data.

A final comparison is made for $\text{Co}^{2+}/\text{SiO}_2$, a simulation for which was originally presented in the first RPA model paper [3]. At that time the PZC of amorphous silica was believed to equal that of quartz, about 2. Since then, by various simple and accurate methods such as mass titration and the measurement of equilibrium pH at high oxide loading, the PZC of amorphous silica has been determined to be in the neighborhood of 4 [14–16]. In Fig. 5, the adsorption of Co^{2+} onto silica is simulated with three models. The first (dotted line) is with James and Healy's original model, us-

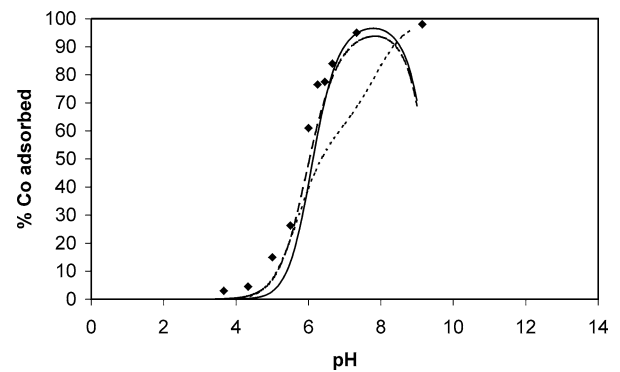


Fig. 5. Simulations of cobalt adsorption ($1.2 \times 10^{-6} \text{ M Co}^{2+}$) onto amorphous silica ($75 \text{ m}^2/\text{l}$, room temp); diamonds—experimental data, dotted line—James and Healy's model with $\Delta G_{\text{chem}} = -27.17 \text{ kJ/mol}$, dashed line—original version of RPA model with PZC = 2.0, $\Delta pK = 5.2$, $N_s = 5 \text{ OH/nm}^2$; solid line—simplified version of RPA model, PZC = 3.8, $\Delta pK = 5.2$.

ing a PZC of 2.0 and the Nernst equation, with coulombic, solvation, and chemical energy terms. The second (dashed line) is the RPA model utilizing a PZC of 2.0, ΔpK of 5.2, and Levine's solvation energy term. In this case and the next no adjustable chemical term was needed. Third, the simplified RPA model (solid line) uses only the coulombic term, with a PZC of 3.8 and ΔpK of 5.2, which are the parameters used in Fig. 4 above. The retardation of adsorption due to high ionic strength at high pH, as seen in Fig. 4, is again predicted here. The last data point, near pH 10, remains high due to the precipitation of cobalt as $\text{Co}(\text{OH})_2$ at this pH [2,3]. The latter, simplest model actually produces the best simulation. James and Healy estimated that cobalt complexes adsorbed with one or two hydration sheaths [2], which is again consistent with our reasoning for negligible solvation effects.

4. Conclusion

It has been discovered that an electrostatic adsorption mechanism describing the uptake of some metal complexes

from aqueous solutions onto the oxide surfaces can most accurately simulate experimental data when the model contains only a coulombic energy term, and not a solvation energy term. A possible explanation is that solvation effects are negligible when adsorbing metal complexes retain one or more hydration sheaths. In future work we will attempt to isolate the effect of solvation energy in order to confirm the present results and further refine the RPA model.

Acknowledgment

The support of the National Science Foundation (Grant CTS-9908181) is gratefully acknowledged.

References

- [1] J.P. Brunelle, *Pure Appl. Chem.* 50 (1978) 1211.
- [2] R.O. James, T.W. Healy, *J. Colloid Interface Sci.* 40 (1972) 65.
- [3] K. Agashe, J.R. Regalbuto, *J. Colloid Interface Sci.* 185 (1997) 174.
- [4] G.R. Weise, R.O. James, T.W. Healy, *Chem. Soc. London Faraday Discuss.* 51 (1971) 302.
- [5] T.W. Healy, L.R. White, *Adv. Colloid Interface Sci.* 9 (1978) 303.
- [6] J.R. Regalbuto, K. Agashe, A. Navada, M. Bricker, Q. Chen, *Stud. Surf. Sci. Catal.* 118 (1998) 147.
- [7] J.R. Regalbuto, A. Navada, S. Shadid, M.L. Bricker, Q. Chen, *J. Catal.* 184 (1999) 335.
- [8] W.A. Spieker, J.R. Regalbuto, *Chem. Eng. Sci.* 56 (2000) 2365.
- [9] W.A. Spieker, J. Liu, J. Kropf, J.T. Miller, J.R. Regalbuto, *Appl. Catal. A Gen.* 243 (2003) 53.
- [10] N. Santhanam, T.A. Conforti, W.A. Spieker, J.R. Regalbuto, *Catal. Today* 21 (1994) 141.
- [11] T.W. Healy, D.E. Yates, L.R. White, D. Chan, *J. Electroanal. Chem.* 80 (1977) 57.
- [12] J. Park, J.R. Regalbuto, *J. Colloid Interface Sci.* 175 (1995) 239.
- [13] E. Santacassaria, S. Carra, I. Adami, *Ind. Eng. Chem. Prod. Res. Dev.* 16 (1977) 41.
- [14] W.A. Spieker, J.R. Regalbuto, *Stud. Surf. Sci. Catal.* 130 (2000) 203.
- [15] M. Schrier, J.R. Regalbuto, in preparation.
- [16] J.S. Noh, J.A. Schwarz, *J. Colloid Interface Sci.* 130 (1989) 157.