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Effect of Salicylic Acid upon Trace-Metal Sorption (Cd^{II}, Zn^{II}, Co^{II}, and Mn^{II}) onto Alumina, Silica, and Kaolinite as a Function of pH

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The sorption of four trace metals (Cd^{II}, Zn^{II}, Co^{II}, and Mn^{II}) onto alumina, silica, and kaolinite, in the presence or absence of salicylic acid (as well as the salicylic acid sorption), was investigated in batch experiments in the pH range from 4 to 9. The sorption was interpreted in terms of surface complexation using the diffuse layer model (DLM). Equilibrium parameters were optimized using the FITEQL program. The salicylic acid was only significantly sorbed onto the alumina and the sorption was modeled using the anionic monodentate surface complex. In the absence of salicylic acid, the sorption of the trace metals presented different pH edge behaviors, depending on the substrate. Using the cationic monodentate surface complex, the model fitted the experimental data well. In the presence of salicylic acid, at a given pH and depending on the substrate, the sorption of metals was (i) increased, suggesting the occurrence of ternary complexes; (ii) reduced (sometimes totally inhibited), due to the complexation with dissolved salicylic acid; or (iii) very weakly changed, in terms of net effect compared to free-organic-ligand systems. Modeling of the trace-metal sorption in the presence of salicylic acid was performed using ternary surface complexes. In the acidic pH range, this allowed the experimental data to be simulated, but in the alkaline pH range, the model failed to simulate the decrease in sorption. Probable causes of the discrepancies between the experimental data and modeling results are discussed.

Introduction

In natural aquatic systems, the behavior of trace metals is controlled by their competitive complexation with surface functional groups of the particulate phase and ligands of the dissolved phase. There is abundant evidence that, besides mineral and organic particles, the presence of dissolved organic matter, especially humic substances, is an important factor in the fate of trace metals (*1−5*). To better understand trace-metal complexation in natural systems, it appears relevant to investigate, in well-controlled laboratory experiments, the behavior of trace metals in the presence of model particles and organic ligands both representative of natural systems. Therefore, we investigated the sorption of four trace metals (Zn^{II}, Cd^{II}, Co^{II}, and Mn^{II}), introduced in ionic radiotracer form, onto alumina, silica, and kaolinite selected to simulate natural particles in the presence or absence of salicylic acid. This aromatic ligand was chosen to simulate the reactivity of natural humic substances, since it possesses both carboxylic and phenolic groups which are the most common reactive functional groups of natural organic matter.

Many studies have been devoted to the sorption of metals onto (hydr)oxides, especially iron (hydr)oxides (*6−11* and other references in *9*), aluminum (hydr)oxides (*12−17*), silicon (hydr)oxides (*18−22*), and kaolinite (*23, 24*). In these studies, most of the time, the ratio ($r_{S/M}$) between the concentration of surface sites and that of metals was low (less than 50). In our experiments, this ratio is higher than 10^3 (see below), hence closest to that found in natural systems.

The sorption of organic ligands onto mineral particles has also been extensively studied. Available data mostly cover natural organic compounds (*23, 25−34*) and other data concern simple organic ligands (*6, 10, 35−41*). Salicylic acid was found to sorb significantly onto alumina (*35, 37*) and goethite (*6*) with a continuous decrease of sorption with increasing pH. A ligand exchange model, where the carboxylic group of salicylic acid replaces the surface hydroxyl group, was proposed as a sorption mechanism (*35*) which was confirmed by infrared spectroscopy (*40*).

The sorption of metals onto mineral particles in the presence of organic ligands concerned mainly EDTA, because of the strong complex-forming properties of this ligand. The effects of EDTA have been studied either on (hydr)oxides as model solids for natural particles (*42−45*) or on isolated natural particles (*46−48*). Trace-metal sorption in systems containing isolated fractions of natural organic matter was also investigated, either on clay minerals (*23, 49*) or on (hydr)oxides (*50−53*). Fewer studies dealt with trace-metal sorption in systems containing simple organic ligands chosen to simulate the complex-forming properties of natural humic substances. Most of them were concerned with aromatic ligands bearing amine groups (*6, 10−11, 20, 54*) and a few with aromatic ligands bearing only carboxylic and phenolic groups (*6, 11*). In all the above-mentioned experimental studies, depending on the pH as well as on the chemical solid-surface properties, trace-metal sorption in the presence of organic ligands was found to increase, due to ternary surface complex formation, or to decrease, due to complex formation in solution.

Most of the chemical reactions at the solid/water interface can be satisfactorily described by the surface complexation theory which was developed by Schindler and Stumm and their co-workers (*12, 19, 55−57*). Several models based on the surface complexation theory are available (*58*) and the most commonly used is the diffuse layer model.

The objectives of this paper are (i) to quantify the competitive complexation of trace metals with the dissolved and sorbed salicylic acid and with the solid-surface functional groups of the selected mineral particles, (ii) to simulate, using the surface complexation modeling, the individual sorption of salicylic acid and trace metals (particle−salicylic acid and particle−metal systems, respectively) and their simultaneous sorption (particle−salicylic acid−metals systems), and (iii) to determine the intrinsic stability constants of the various surface complexes taken into account in the model.

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TABLE 1. Concentrations of Trace Metals (nM)

	carrier[a]	blank[b] min	blank[b] max	M[c]
Mn	0.1			10
Co	0.01			10
Zn	0.02	14	118	50
Cd	0.007	0.4	14	10

[a] Concentrations calculated using the content of carriers (stable form of the element) of the spiking solution (carriers being more abundant than corresponding radioactive elements). [b] Concentrations of the stable form of elements measured in the dissolved phase of typical samples of unspiked suspensions of alumina, silica and kaolinite. Minimum and maximum values depend on the pH and the substrate. [c] *M* refers to the mean concentration used in modeling.

Materials and Methods

Substrates and Reagents. The sorption experiments were conducted using a kaolinite ("China Clay Supreme", English Clay Lovering Pochin & Co. Ltd., UK), an alumina ("powder for polishing", Prolabo), and a silica ("silica gel, TLC high-purity grade without binder", Aldrich). The specific surface area, as determined by the BET method, is 53, 325, and 15 $m^2\ g^{-1}$ for alumina, silica, and kaolinite, respectively. The surface charge was determined by potentiometric acid−base titration. Blank titrations were performed to account for acid or base consumption by processes other than surface acid−base reactions. A more detailed description of (i) solid phase pretreatements, (ii) mineral phase compositions and measurement of the specific surface area, and (iii) acid−base tritation can be found in the Supporting Information. Sodium salicylate salt (99%, Aldrich Chemical Co. Inc.) and the other chemicals ($NaNO_3$, HNO_3, NaOH, purchased from Merck) were of analytical grade. Labeled solutions ($^{65}Zn^{II}$, $^{109}Cd^{II}$, $^{60}Co^{II}$, and $^{54}Mn^{II}$; Amersham) present low carrier concentrations (see Table 1 and below). All solutions were made using Milli-Q water.

Sorption Experiments. All sorption experiments were performed with suspensions of solid in $NaNO_3$ (0.05 M) solution. The temperature was fixed at 20 ± 2 °C and samples were continuously shaken. Suspensions were previously aged (24 h) and the pH adjusted by adding HNO_3 and NaOH. For particle−salicylic acid and particle−metals systems, the adsorbate (salicylic acid, 4×10^{-4} M or trace metals, see below) was added to the suspensions (10 and 1 g L^{-1}, respectively) and samples were equilibrated for a period of 20 h according to the results of a kinetic study (*59*). For particle−salicylic acid−metal systems, the salicylic acid (2×10^{-4} M) was first added to suspensions (1 g L^{-1}) for a reaction time of 20 h, then trace metals were added and samples were equilibrated for a period of 20 h. The measured concentration of trace metals (blank, Table 1) derived from reagents (including water and substrates) was much higher than the concentration derived from the spiking solution (carrier, Table 1). Blank concentrations depended on the substrate as well as on the pH. A mean value (*M*, Table 1) was used when modeling the trace-metal sorption.

The solid phase was separated from the aqueous phase by centrifugation (30 min at 23000*g*). From aliquots of the supernatant, the residual concentration of the salicylic acid and the trace metals was analyzed by spectrophotometry and gamma spectrometry, respectively. Possible loss of adsorbates on the vessel was examined using blanks. No significant loss was found either for salicylic acid or for the trace metals. The amount of sorbed salicylic acid or metals (percentage sorption) was calculated as the difference between the total added concentration and the residual concentration of adsorbate in the dissolved phase. Errors in the percentage sorption of salicylic acid and trace metals were within ±5%. A more detailed description of experimental and analytical methods can be found in the Supporting Information.

Modeling. The solid−liquid interface was described by the diffuse layer model (DLM), which has been extensively used to describe the sorption of organic ligands and metals (e.g., *12−14*, *27*, *44*). Optimization of model parameters (surface site density and surface equilibrium constants) was performed using the nonlinear least squares optimization program FITEQL version 3.1 (*60*). The solution reactions and their equilibrium constants used in model calculations are

TABLE 2. Equations and Constants of Solution Reactions Used in Modeling

reaction[a]	log(K), *I* = 0 M	reaction[a]	log(K), *I* = 0 M
water dissociation[b]		salicylic acid (H_2L) acid−base reactions[b]	
$[OH^-] = [H^+]^{-1}K_W(\gamma_1)^{-2}$	−14.0	$[H_2L] = [H^+]^2[L^{2-}](\gamma_1)^2\gamma_2K$	16.64
		$[HL^{-1}] = [H^+][L^{2-}]\gamma_2K$	13.66

reaction[a]	log(K), *I* = 0 M				
		Mn	Co	Zn	Cd
metals hydrolysis reactions[b]					
$[MOH^+] = [M^{2+}][H^+]^{-1}(\gamma_1)^{-2}\gamma_2K$		−10.60	−9.65	−8.96	−10.08
$[M(OH)_2] = [M^{2+}][H^+]^{-2}(\gamma_1)^{-2}\gamma_2K$		−22.20	−18.81	−16.90	−20.36
complexation of metals with salicylic acid[c]					
$[ML] = [M^{2+}][L^{2-}](\gamma_2)^2K$		6.78	7.60	7.85	6.55
$[ML_2^{2-}] = [M^{2+}][L^{2-}]^2(\gamma_2)^2K$		10.95	12.55		
$[MHL^+] = [M^{2+}][L^{2-}][H^+](\gamma_2)^2K$				15.5	16.0
α-$Al(OH)_3$ solubility reactions[d]					
$[AlL^{3+}] = [H^+]^3(\gamma_1)^3(\gamma_3)^{-1}K_S$	8.5				
$[AlOH^{2+}] = [Al^{3+}][H^+]^{-1}(\gamma_1)^{-1}(\gamma_2)^{-1}\gamma_3K$	−4.97				
$[Al(OH)_2^+] = [Al^{3+}][H^+]^{-2}(\gamma_1)^{-3}\gamma_3K$	−9.3				
$[Al(OH)_4^-] = [Al^{3+}][H^+]^{-4}(\gamma_1)^{-5}\gamma_3K$	−23.0				
complexation of Al^{3+} with salicylic acid[c]					
$[AlL^+] = [Al^{3+}][L^{2-}](\gamma_1)^{-1}\gamma_2\gamma_3K$	14.22				
$[Al(L)_2^-] = [Al^{3+}][L^{2-}]^2(\gamma_1)^{-1}(\gamma_2)^2\gamma_3K$	24.96				
$[Al(L)_3^{3-}] = [Al^{3+}][L^{2-}]^3(\gamma_2)^3K$	31.12				

[a] γ_i are activity coefficients of ions of valence ±*i* in aqueous phase; values of γ_i were derived from Dzombak and Morel (*9*). [b] Kotrly and Sucha (*61*). [c] Martell and Smith (*62, 63*) and Smith and Martell (*64*). [d] Stumm and Morgan (*5*).

TABLE 3. Equilibrium Equations and Optimized Constants of Surface Reactions

reaction[a]		log(K), $I = 0$ M[b]			eq no.
		alumina	silica	kaolinite	
surface sites acid−base reactions					
$[{>}\mathrm{AlOH_2^+}] = [{>}\mathrm{AlOH}][\mathrm{H^+}]\exp(-F\Psi/RT)\gamma_1(K_+^{\mathrm{int}})^{-1}$		−6.80 (±0.04)	-	−6.80 (±0.04)	1
$[{>}\mathrm{AlO^-}] = [{>}\mathrm{AlOH}][\mathrm{H^+}]^{-1}\exp(F\Psi/RT)(\gamma_1)^{-1}K_-^{\mathrm{int}}$		−7.68 (±0.04)	-	−7.68 (±0.04)	2
$[{>}\mathrm{SiO^-}] = [{>}\mathrm{SiOH}][\mathrm{H^+}]^{-1}\exp(F\Psi/RT)(\gamma_1)^{-1}K_-^{\mathrm{int}}$		-	−7.79 (±0.06)	−3.52 (±0.04)	3
salicylic acid (H_2L) sorption reactions					
$[{>}\mathrm{Al{-}LH}] = [{>}\mathrm{AlOH}][\mathrm{H^+}]^2[\mathrm{L^{2-}}](\gamma_1)^2\gamma_2K_{\mathrm{LH}}^{\mathrm{int}}$		24.81 (±0.04)			4
$[{>}\mathrm{Al{=}L}] = [{>}\mathrm{Al(OH)_2}][\mathrm{H^+}]^2[\mathrm{L^{2-}}](\gamma_1)^2\gamma_2K_{\mathrm{L}}^{\mathrm{int}}$		24.87 (±0.04)			5
$[{>}\mathrm{Al{-}L^-}] = [{>}\mathrm{AlOH}][\mathrm{H^+}][\mathrm{L^{2-}}]\exp(F\Psi/RT)\gamma_1\gamma_2K_{\mathrm{L-}}^{\mathrm{int}}$		17.67 (±0.03)			6
Metal sorption reactions					
$[{>}\mathrm{AlOM^+}] = [{>}\mathrm{AlOH}][\mathrm{M^{2+}}][\mathrm{H^+}]^{-1}\exp(-F\Psi/RT)(\gamma_1)^{-1}\gamma_2K_{\mathrm{M1}}^{\mathrm{int}}$	Mn	−2.79 (±0.03)		−3.6 (±0.1)	7
	Co	−1.96 (±0.03)		−1.86 (±0.09)	
	Zn	−0.40 (±0.02)		−1.4 (±0.3)	
	Cd	−1.38 (±0.02)		−2.3 (±0.2)	
$[{>}\mathrm{SiOM^+}] = [{>}\mathrm{SiOH}][\mathrm{M^{2+}}][\mathrm{H^+}]^{-1}\exp(-F\Psi/RT)(\gamma_1)^{-1}\gamma_2K_{\mathrm{M1}}^{\mathrm{int}}$	Mn		−6.35 (±0.04)	−3.62 (±0.04)	
	Co		−6.31 (±0.03)	−3.2 (±0.1)	8
	Zn		−3.73 (±0.03)	−3.04 (±0.07)	
	Cd		−5.57 (±0.04)	−2.47 (±0.06)	
$[{>}\mathrm{(SiO)_2M}] = [{>}\mathrm{SiOH}]^2[\mathrm{M^{2+}}][\mathrm{H^+}]^{-2}(\gamma_1)^{-2}\gamma_2K_{\mathrm{M2}}^{\mathrm{int}}$	Zn		−6.61 (±0.02)		9
$[{>}\mathrm{SOMOH}] = [{>}\mathrm{SOH}][\mathrm{M^{2+}}][\mathrm{H^+}]^{-2}(\gamma_1)^{-2}\gamma_2K_{\mathrm{MOH}}^{\mathrm{int}}$					10
ternary surface complexes reactions					
$[{>}\mathrm{AlO{-}M{-}L^-}] = [{>}\mathrm{AlOH}][\mathrm{M^{2+}}][\mathrm{L^{2-}}][\mathrm{H^+}]^{-1}\exp(F\Psi/RT)(\gamma_1)^{-1}(\gamma_2)^2K^{\mathrm{int}}$	Cd	10.86 (0.09)			11
$[{>}\mathrm{Al{-}L{-}M^+}] = [{>}\mathrm{AlOH}][\mathrm{M^{2+}}][\mathrm{L^{2-}}][\mathrm{H^+}]\exp(-F\Psi/RT)\gamma_1(\gamma_2)^2K^{\mathrm{int}}$	Co	21.7 (±0.2)			12
	Cd	23.14 (±0.04)			
$[{>}\mathrm{Al{-}L{-}MOH}]$ (or $[{>}\mathrm{AlO{-}M{-}LH}]$) $= [\mathrm{AlOH}][\mathrm{M^{2+}}][\mathrm{L^{2-}}](\gamma_2)^2K^{\mathrm{int}}$	Co	15.0 (±0.4)			13
	Cd	16.89 (±0.07)			

[a] γ_i are the activity coefficients in aqueous phase for ions, values of γ_i were derived from Dzombak and Morel (*9*). [b] Values of log(K) were optimized at the ionic strength $I = 0.05$ M (corresponding to the experimental data) and corrected to $I = 0$ M.

listed in Table 2. These constants were corrected at $I = 0.05$ M for calculation. The surface complexation reactions used in modeling data of acid−base titration and data of individual and simultaneous sorption of salicylic acid and trace metals are given in Table 3. All model calculations were performed at the ionic strength $I = 0.05$ M and then the optimized values were corrected to $I = 0$ M (Table 3). Stability constants obtained when modeling particle−salicylic acid and particle−metal systems were used when modeling particle−salicylic acid−metals systems. In systems involving alumina and salicylic acid, reactions representing the solubility of α-$Al(OH)_3$ (Table 2) were included in the equilibrium problem to generate solution complexation of salicylic acid with dissolved aluminum ions.

Results and Discussion

Acid−Base Titration. Figure 1 of the Supporting Information shows the protonic surface charge of silica, alumina, and kaolinite as a function of pH. The point of zero net proton charge (PZNPC) was 7.2 ± 0.1 and 4.5 ± 0.1 for alumina and kaolinite, respectively. For silica, the PZNPC cannot be determined with enough accuracy, because the variation of the protonic surface charge followed a flat curve below pH 6. A similar flat shape of the potentiometric titration curve for silica was found by several authors (*65*−*67*). Values of the PZNPC(s) obtained in this study are compared to values quoted in the literature in the Supporting Information.

Titration data of alumina, silica, and kaolinite were modeled using eqs 1−3 (Table 3), and the speciation of neutral and charged surface sites as a function of pH is depicted in Figure 1. When modeling the titration data for silica, the positively charged silanol groups were ignored since the silica surface presents no positive charge in the pH range explored. This assumption was made in most of the previous studies concerning the modeling of acid−base titration data for silica (*22*, *65*, *67*, *68*). The positively charged silanol groups were

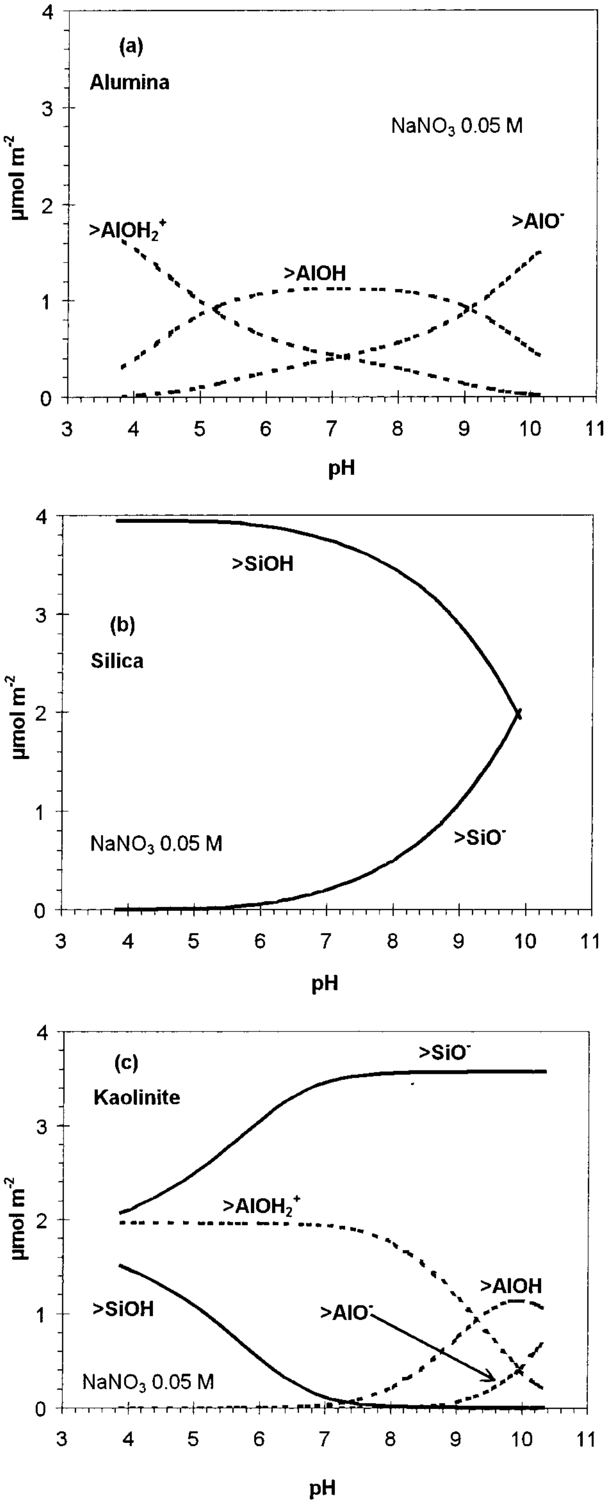

FIGURE 1. Surface site speciation as a function of pH for alumina (a), silica (b), and kaolinite (c). The solid−liquid interface was interpreted using the diffuse layer model, and calculations were performed using the FITEQL program.

TABLE 4. Calculated Surface Site Densities Using Experimental Data from the Acid−Base Titration of Alumina, Silica, and Kaolinite

	SSA (m^2 g^{-1})[a]	site type	*S*, site density (μmol m^{-2})
alumina	53	>AlOH	1.91(±0.06)
silica	325	>SiOH	3.9(±0.4)
kaolinite	15	>AlOH	1.96(±0.09)
		>SiOH	3.57(±0.08)

[a] Specific surface area measured using the BET method.

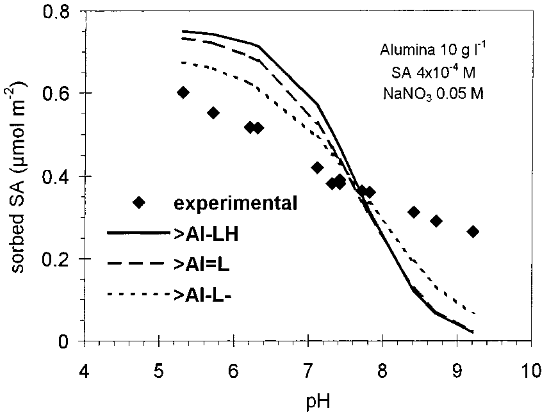

FIGURE 2. Sorption of salicylic acid (SA) onto alumina as a function of pH: (diamonds) experimental data, (lines) model results using different hypotheses on the surface complex types (see the text).

also neglected when modeling the titration data for kaolinite, but the calculation did not converge. Hence, the number of unknown parameters was reduced from five to three (surface density of the aluminol and silanol groups, and one acidity constant for silanol groups) assuming that the acidity constants of the aluminol groups are equal to those obtained for alumina surface sites (*59*). This assumption was also made by Wieland and Stumm (*69*). Values of surface site densities (*S*, Table 4) and acidity constants ($K_+^{\rm int}$ and $K_-^{\rm int}$; Table 3) for alumina, silica, and kaolinite are within the range of data reported in the literature as discussed in the Supporting Information.

Particle−Salicylic Acid Systems. The sorption of salicylic acid in the range of pH 3.5−9 was significant for alumina but not for silica and kaolinite. For alumina, the sorption decreased as the pH increased (Figure 2), following the decrease in the positive surface charge with pH (Figure 1). Hence, ligand exchange with >AlOH$_2^+$ sites seems to be the main sorption process, since the positive surface hydroxyls are thought to be more exchangeable than neutral hydroxyl groups (*33*, *70*, *71*). It is worth noting, for silica, the large abundance of neutral hydroxyl groups (Figure 1), which are potential sites for ligand exchange reactions but which appeared to be inoperative. For kaolinite, the sorbed amount was low but cannot be determined since within the range of analytical error, probably because of its strong negative surface charge (*59*). Other studies have shown a weak sorption of organic acids onto silica and kaolinite (*23*, *28*, *49*).

Modeling of the Alumina−Salicylic Acid System. By testing each of the sorption reactions of salicylic acid (eqs 4−6, Table 3) in turn, the best fit was obtained (Figure 2) with the reaction involving the formation of the anionic monodentate complex (>Al−L$^-$). On the whole, the model did not fit the experimental data well; particularily in the alkaline pH range, the amount of sorbed salicylic acid was underestimated. The values of the intrinsic stability constants of salicylic acid surface complexes ($K_{\rm LH}^{\rm int}$, $K_{\rm L}^{\rm int}$ and $K_{\rm L-}^{\rm int}$) are given in Table 3. The value of p$K_{\rm L-}^{\rm int}$ (17.67) was very close to the value (17.24) determined by Kummert and Stumm (*35*) from acid−base titration data using a graphical method. Furthermore, these authors found the conditional value of p$K_{\rm LH}$ to be equal to 22.64, which is comparable to the intrinsic value found here (24.81).

Particle−Metal Systems. Since the ratio ($r_{\rm S/M}$) of surface site concentration (*S*, Table 4) to the sum of trace metal concentration (*M*, Table 1) is higher than 10^3, competitive sorption effects of trace metals were probably very limited.

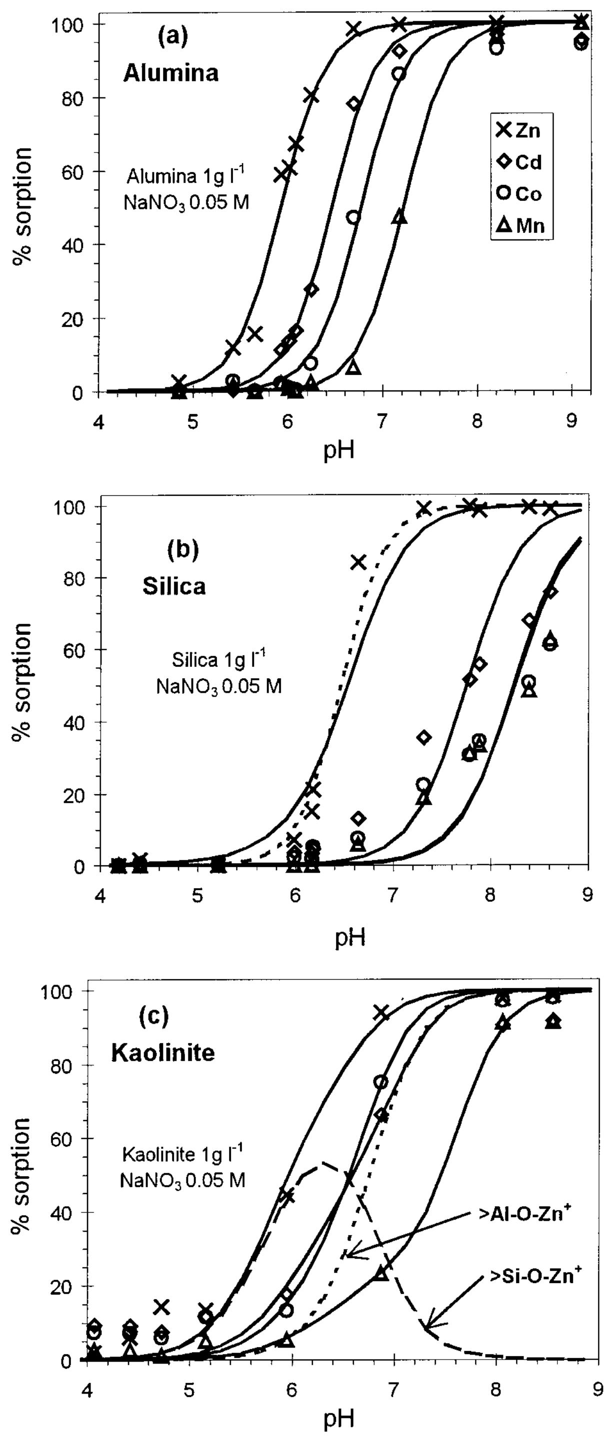

FIGURE 3. Sorption of Zn, Cd, Co, and Mn onto alumina (a), silica (b), and kaolinite (c) as a function of pH. The concentration of trace metals is given in the Table 1; (symbols) experimental data, (solid line) model result using inner-sphere complex $>SOM^+$. For silica (b) in the case of Zn, the dashed line represents the model result using the bidentate complex $(>SiO)_2M$. For kaolinite (c) in the case of Zn, $>AlOZn^+$ and $>SiOZn^+$ complexes are distinguished.

Figure 3 shows the sorption of Zn, Cd, Co, and Mn onto alumina (a), silica (b) and kaolinite (c) as a function of pH. The sorption of Mn, Co, Zn, and Cd onto alumina and kaolinite presented a sorption edge within a narrow pH range (less than two pH units). For silica, the sorption occurred over a wider pH range, except for Zn. For alumina and silica, the sorption of trace metals has been shown to be controlled by chemical coordination reactions (inner-sphere complexes) with the surface hydroxyl groups (*15, 17, 21, 22*). In the present study, this was particularly evident for alumina, for which the sorption occurred at a pH at which the surface was positively charged. This suggested that the chemical affinity of metals for the surface overcame the electrostatic repulsive surface potential. Sorption onto silica followed the variation of the negative silanol groups (Figure 1), which appeared more reactive than neutral silanol groups. In the case of kaolinite, the results of the sorption can be distinguished according to the pH range: (i) Below pH 6, the sorption was small, despite the fact that negative silanol groups were predominant (Figure 1). In this pH range, the sorption is probably partially controlled by cation exchange (*16*), but chemical coordination with surface hydroxyl groups cannot be discounted. (ii) Above pH 6, the sorption shifted in a pH range for which the neutral aluminol sites became more and more abundant, whereas negative silanol groups, although predominant, remain constant. Hence, sorption of Zn, Cd, Co, and Mn onto kaolinite seems to be controlled by chemical coordination with neutral aluminol groups.

The range of pH at which the sorption occurs depends on the concentration of available surface sites and the concentration of the adsorbate (*6, 7, 9*). The pH edges move toward the acidic pH range as the $r_{S/M}$ ratio increases (*9*). In this study, the amount of a given trace metal sorbed onto alumina, silica, and kaolinite cannot be directly compared, since the total amount of surface sites (calculated from the data of Table 4) was different for each substrate. However, for a given pH, alumina removed Cd, Co, and Mn more extensively than did silica, despite a lower $r_{S/M}$ (1.12×10^3 and 1.41×10^4, respectively). Therefore, silanol groups appeared to be less reactive than aluminol groups. As usually observed, the four trace metals behave differently with regard to their affinity with the substrates. Among properties of the four metals such as hydrolysis, soft and hard acid, and ionic potential, the affinity of the metals for the solid surfaces seems to be related to hydrolysis: the affinity increases with increasing first hydrolysis constants (Table 2).

Modeling of the Particle–Metal Systems. Testing the sorption reactions for metals in turn (eqs 7–10, Table 3), the better fit of experimental data for alumina, silica, and kaolinite was obtained using the surface complex $>SOM^+$ (Figure 3), except for Zn onto silica. Due to a high $r_{S/M}$ ratio, changes in the trace metal concentrations from 1 pM to 1 μM had no effect on optimized parameters (*59*). The $>SOM^+$ complex was extensively used in modeling the sorption of divalent cations onto Al and Si oxides (*9–11, 15*). For Zn onto silica, the better fit of the experimental data was obtained when considering the $(>SiO)_2M$ complex (Figure 3b, dashed line). A similar result was obtained by Lützenkirchen (*70*) for Zn sorption onto quartz. For silica, the optimized stability constant of the $>SiOCd^+$ complex for Cd was very close to the value obtained by Schindler et al. (*19*). For kaolinite, the model distinguished the surface complexation of metals with aluminol and silanol groups ($>AlOM^+$ and $>SiOM^+$, respectively). Data are shown only for Zn (Figure 3d), the results for Cd, Co, and Mn being similar. The sorption occurred first via complexation with silanol groups in the pH range below 6.5 and mainly with aluminol groups above this pH.

Particle–Salicylic Acid–Metal Systems. Compared to free-organic-ligand systems at a given pH, the apparent effect of salicylic acid upon trace-metal sorption could be classified into three types depending on the substrate and the metal (Figures 4–6): (i) both an increase and a decrease, depending on pH, (ii) a decrease only, and (iii) no apparent effect. In the following section, for each substrate, the trace-metal sorption in the presence of salicylic acid is discussed on the basis of these behaviors.

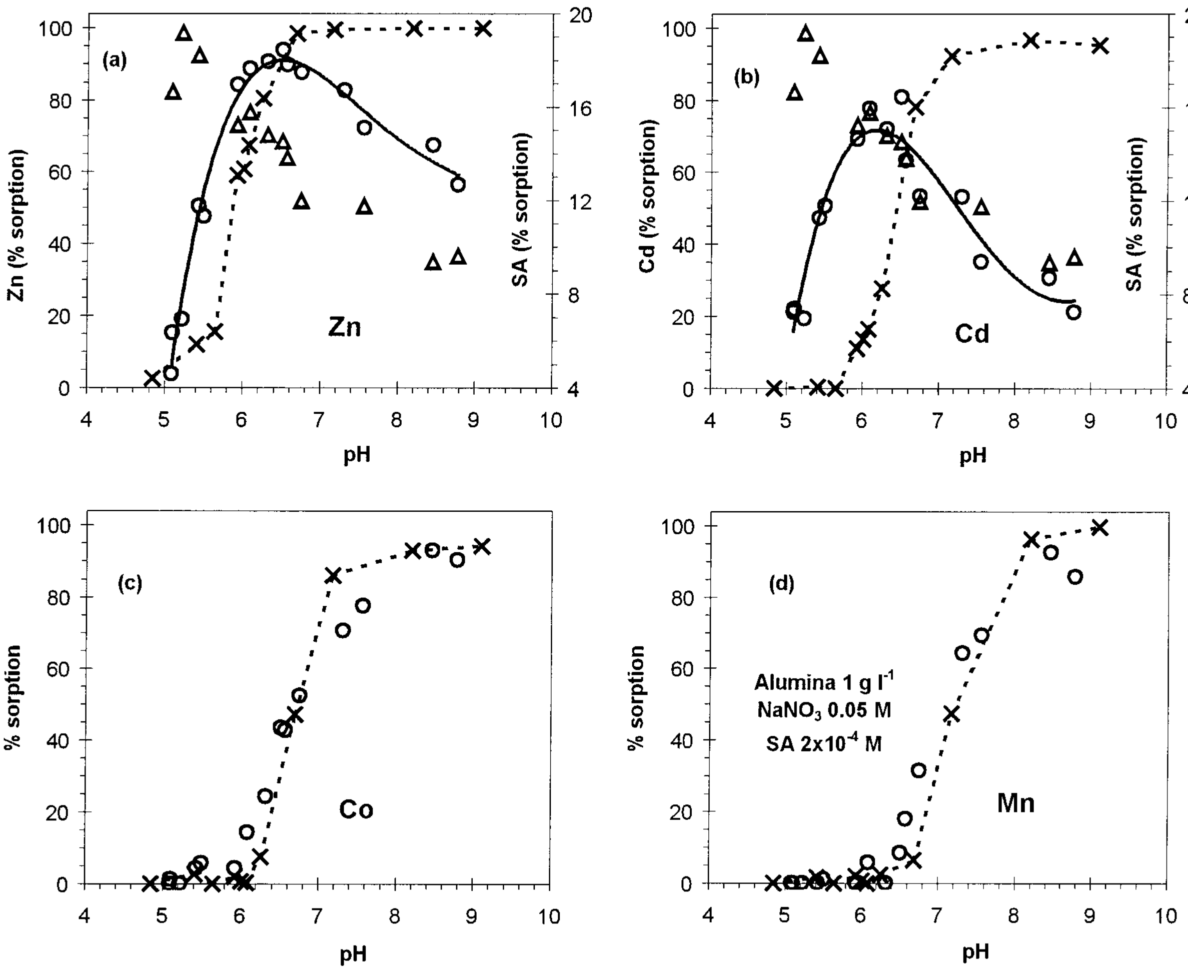

FIGURE 4. Trace-metal sorption onto alumina versus pH in the presence of salicylic acid (SA); Zn (a), Cd (b), Co (c), and Mn (d); (circle plus solid line) trace-metal sorption in the presence of SA, (triangle) salicylic acid sorption (shown for Zn and Cd only), (cross plus dotted line) trace-metal sorption in the ligand-free system added for comparison. All curves are the best fitted eye-drawn curves.

Alumina. The sorption of the salicylic acid decreased with increasing pH in a similar proportion to that observed for the particle−salicylic acid system (Figure 4). However, data cannot be directly compared because the concentrations of solid and salicylic acid were not the same for the two systems. The sorption edges of Zn and Cd in the presence of salicylic acid had similar shapes. For these elements, compared to the ligand-free system, two opposite behaviors were observed: (i) the sorption increased in the low pH range (<6.5), whereas (ii) it decreased continuously above pH 6.5. In the low pH range, the increase in sorption of Zn and Cd in the presence of sorbed salicylic acid suggested that ligand-like (>Al−L−M) ternary surface complexes were formed in addition to metal−surface complexes. Ligand-like ternary surface complexes are promoted in this pH range since $>AlOH_2^+$ groups can easily exchange with salicylic acid (*33, 71, 72*). In the high pH range, the decrease in sorption of Zn and Cd in the system containing salicylic acid results from their competitive complexation with the dissolved salicylic acid (for which the complexing ability increased with pH), on one hand, and the functional surface groups (including sorbed salicylic acid), on the other hand. Such an increase and a decrease in the trace-metal sorption in the presence of organic ligands have also been found for other systems: Cu onto γ-Al_2O_3, in the presence of natural humic substances (*50*); Co onto goethite, in the presence of EDTA (*48−49*); likewise, for the sorption of Ni, Cu, Zn, Cd, and Pb onto γ-Al_2O_3, in the presence of EDTA (*16*). In contrast to Zn and Cd, the sorption of Mn and Co was only weakly influenced by the presence of the salicylic acid in terms of net effect (Figure 4c,d). Hence, neither the sorbed fraction nor the dissolved fraction of salicylic acid seemed to have a significant affinity for Mn and Co. Particularly, in the alkaline pH range, the difference between Co and Zn cannot be explained by the stability constants of the dissolved complexes of those metals with salicylic acid, which are very close (Table 2).

Silica. No sorption of salicylic acid was detected, as for the particle−salicylic acid system. Therefore, it is assumed that no ternary complexes were formed. At a given pH, compared to the organic-ligand-free system, the sorption of Mn, Co, Zn, and Cd decreased in the presence of salicylic acid (Figure 5). It is worth noting that (i) the sorption of Cd was totally inhibited over the pH range investigated, and (ii) compared to the alumina, the sorption of Mn and Co onto silica was significantly affected. Therefore, given the effect of salicylic acid upon trace-metal sorption onto alumina and silica, silanol groups appeared once again to be weaker ligands than aluminol groups.

Kaolinite. No sorption of the salicylic acid was detected. Once more, no or few ternary complexes were expected. Compared to the organic-ligand-free system, the sorption of metals was only significantly reduced for Cd and to a lesser extent for Zn (Figure 6) at the highest pH investigated (7.5). Unfortunately, in the presence of salicylic acid, no data on the metal sorption above pH 7.5 are available. Given the accuracy of the trace metal measurement, and taking into account the results obtained with the other substrates, it

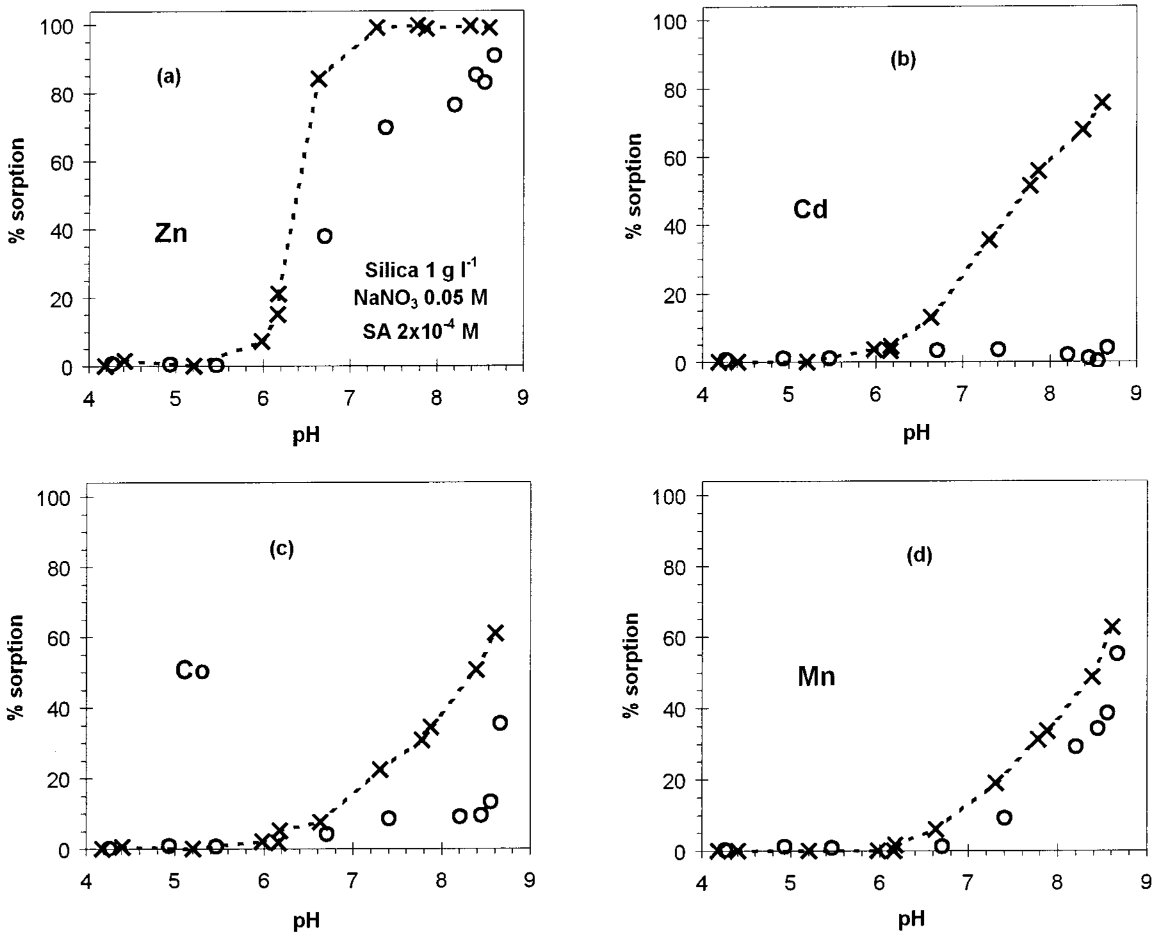

FIGURE 5. Trace-metal sorption onto silica versus pH in the presence of salicylic acid (SA): Zn (a), Cd (b), Co (c), and Mn (d); (circle) trace-metal sorption in the presence of SA, (cross plus dotted line) trace-metal sorption in the ligand-free system added for comparison.

seems reasonable to assume that the data obtained in the alkaline pH range for the kaolinite would be indicative of the overall trend in the alkaline pH range. In the acidic pH range, the absence of modification of the trace-metal sorption in the presence of salicylic acid indicated that the kaolinite behaved more like silica than alumina. This is mainly due to the absence (or very slight amount) of sorbed salicylic acid. However, in the alkaline pH range, the sorption onto the kaolinite appeared intermediate between that obtained for the alumina and the silica. Indeed, compared to silica, the sorption of Mn and Co on the kaolinite appeared to be unmodified and the sorption of Cd was reduced but not inhibited. This suggests that the limited change in the metal sorption onto the kaolinite was controlled by a higher reactivity of aluminol groups than silanol groups with respect to the dissolved salicylic acid complexation.

Modeling of the Particle−Salicylic Acid−Metal Systems. Systems considered in the present modeling were chosen to exemplify one of each type of net effect on trace-metal sorption in the presence of salicylic acid (SA).

Cd−SA−Alumina. This system exemplifies the case of an increase of the sorption in the acidic pH range and a decrease of the sorption in the alkaline pH range, compared to the sorption in the organic-ligand-free system (Figure 4b). As shown in Figure 7a, by using the ligand-like >Al-L-Cd$^+$ ternary complex (eq 12, Table 3) as suggested above, the model fitted with the experimental data well in the acidic pH range but not in the alkaline pH range. However, similar fits were obtained when using one of the other ligand-like or metal-like ternary complexes (eqs 11 and 13, Table 3). The stability constants of these ternary complexes are given in Table 3. In the acidic pH range, the model indicated that Cd is sorbed mainly through ternary surface complexes. In the alkaline pH range, the model appeared unable to simulate the decrease in the Cd sorption, but it is worth noting that the abundance of the ternary surface complexes is close to that of the overall sorbed Cd. To a first approximation (see below), this suggested that either Cd−surface complexes (>AlO−Cd$^+$) were overestimated (due to a masking effect of sorbed salicylic acid) or dissolved Cd−salicylic acid complexes were underestimated.

Zn−SA−Silica. This system exemplifies the case of a decrease of the sorption compared to the organic-ligand-free system (Figure 5a). Modeling of this system was performed using only the effect of dissolved complexes (ZnLH and ZnL), since the absence of the salicylic acid sorption allowed us to consider that no surface ternary complexes were formed. As for alumina, the model was unable to simulate the decrease in the Zn sorption in the presence of salicylic acid (Figure 7b). For the silica, in the absence of ternary complexes or sorbed salicylic acid, the difference between experimental and calculated data was suspected to be due to an underestimation of dissolved Zn−salicylic acid complexes.

Co−SA−Alumina. This system exemplifies the case where a weak net effect on the trace-metal sorption was observed despite the occurrence of the sorbed salicylic acid (Figure 4c). Using the ligand-like >Al-L-Co$^+$ ternary complex (eq 12, Table 3), the model showed that the contribution of this complex was small (Figure 7c). This indicated a low affinity of the sorbed salicylic acid for Co. The model fitted the experimental data well in the acidic pH range, but a significant

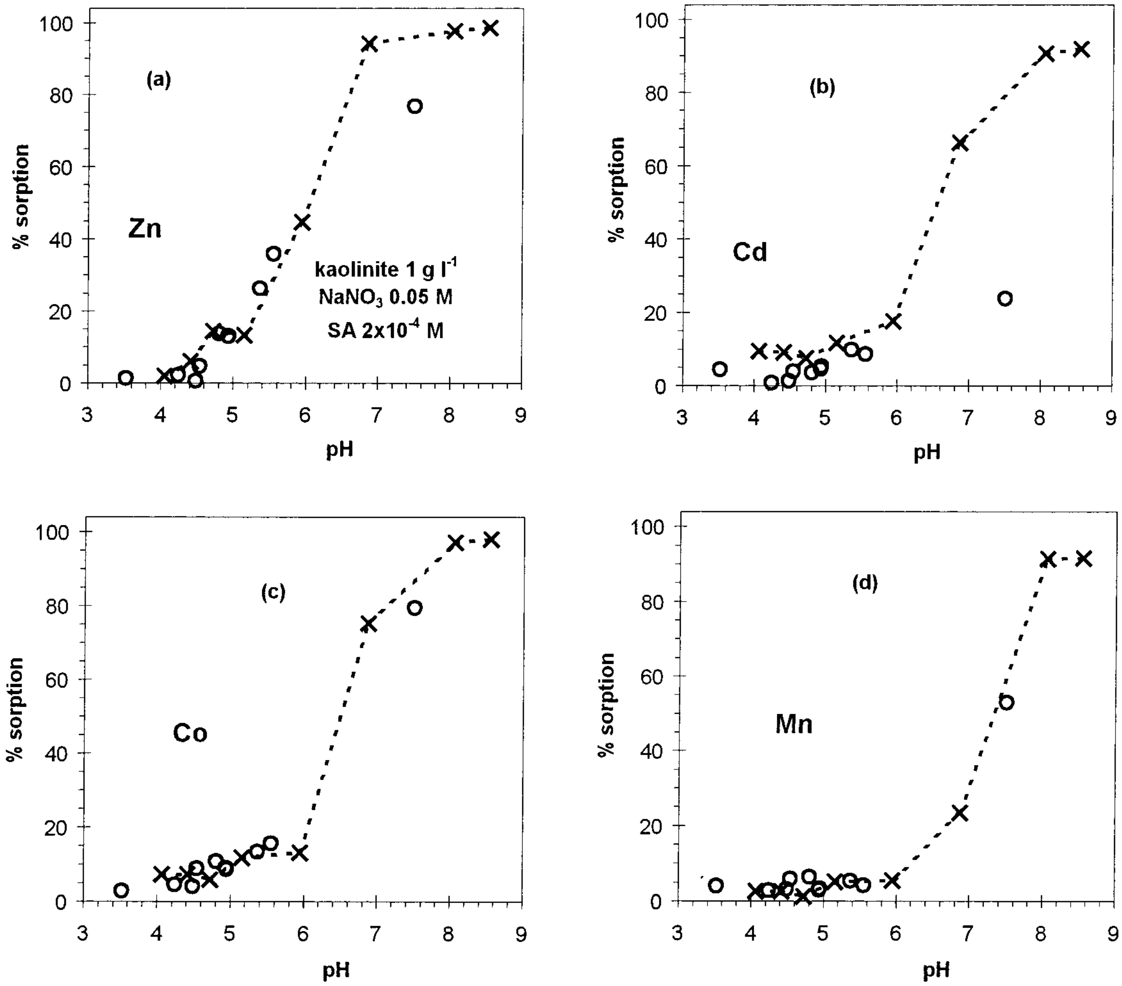

FIGURE 6. Trace-metal sorption onto kaolinite versus pH in the presence of salicylic acid (SA): Zn (a), Cd (b), Co (c), and Mn (d); (circle) trace-metal sorption in the presence of SA, (cross plus dotted line) trace-metal sorption in the ligand-free system added for comparison.

discrepancy was observed at higher pH. Once again, metal–surface complexes ($>$Al–O–Co$^+$) were overestimated, or the complexation of Co with the salicylic acid in solution was not sufficiently strong to reduce the sorption.

Results of the modeling of the particle–salicylic acid–metal systems have indicated that ternary surface complexes were operative for those in which the amount of sorbed metals was increased compared to organic-ligand-free systems. However, systems for which the amount of sorbed trace metals was decreased in the presence of salicylic acid were not satisfactorily simulated. Many reasons can be invoked to explain why the model failed to simulate the decrease in the sorption in the alkaline pH range. Among them, we will discuss the contribution of the three main parameters taken into account in describing particle–organic ligand–metal systems: the trace metal–ligand complexation in solution, the number of reactive surface sites, and the trace metal–surface complexation.

(i) The amount of metal–ligand complexes in solution appeared underestimated. This is particularly relevant in the case of silica, for which no salicylic acid sorption is expected and thus salicylic acid directly competes with surface sites for metal complexation. Therefore, the stability constants of the dissolved metal–salicylic acid complexes would be different in the presence of a solid phase compared to those obtained for free-solid-phase systems. When optimizing this constant in the case of the Zn–SA–silica system the model fitted the experimental data well, but the constants became questionable, since they were 10^4 higher than those given in the literature (Table 2).

(ii) Due to a suspected masking effect by the sorbed salicylic acid, the number of surface sites determined from the acid–base titration would be overestimated. When optimizing the number of reactive surface sites (*S*, Table 4), the model fitted the Co–SA–alumina and the Zn–SA–silica data well, and the number of reactive surface sites had to be reduced by a factor 10. However, in the case of the Cd–SA–alumina system, no change of the fit shown in Figure 7a was obtained, even if the number of surface sites is recuced by a factor of 10^2.

(iii) Besides the formation of ternary complexes that we previously discussed, the stability constants of the surface metal complex determined for the particle–metal systems would be different in the presence of salicylic acid. When optimizing these constants, the model generated more ternary surface complexes but worse fits than those shown in Figure 7a and c were obtained.

Finally, the interpretation of the surface complexation using the DLM would be not valid when the system presents particles and both organic ligands and metals. However, the question remains as to why the model was able to simulate experimental data in the acidic pH range but not in the alkaline pH range.

As was shown by the experimental work on, and the modeling of, some systems involving trace metals, model substrates, and a simple organic ligand, the presence of the organic ligand acts as a probe for determining the relative reactivity of different types of surface sites with trace metals.

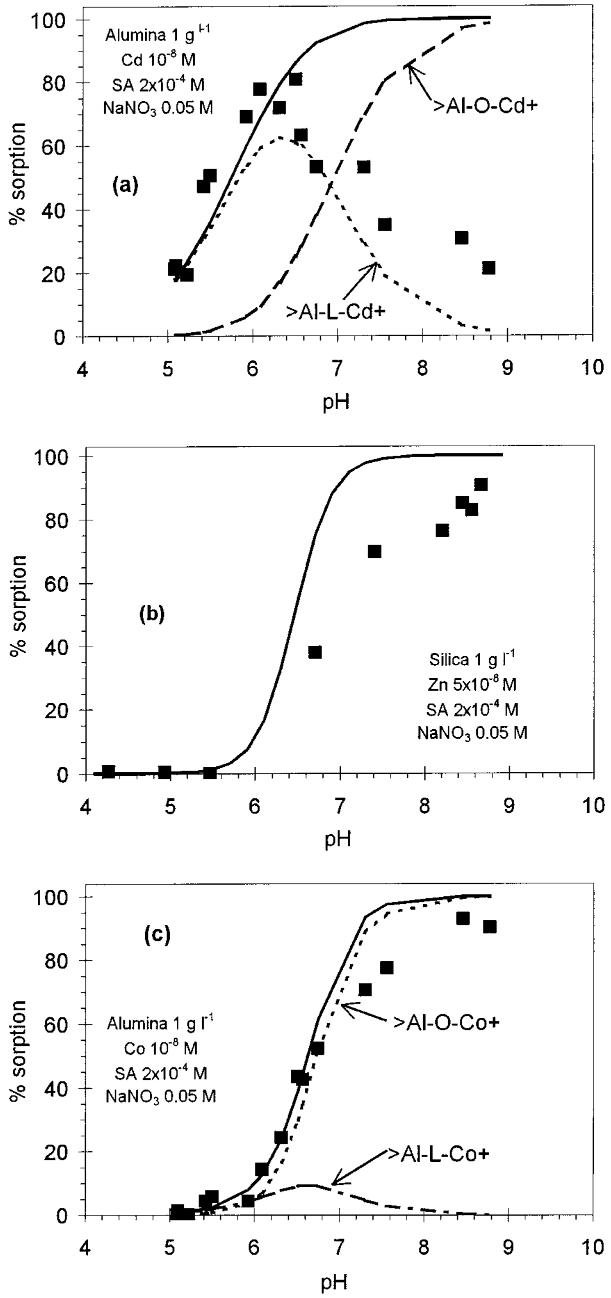

FIGURE 7. Experimental data and modeling results of trace-metal sorption in the presence of salicylic acid (SA) versus pH: (a) sorption of Cd onto alumina, (b) sorption of Zn onto silica, (c) sorption of Co onto alumina; (square) experimental data, (solid line) model result (total sorbed). Dashed lines in panels a and c are the abundance of surface−metal or ternary complexes. For Zn onto silica (b), only the effect of the inner sphere surface complex $>$SiOZn$^+$ and the effect of the ZnLH and ZnL complexes in solution have been taken into account (no ternary complex involved).

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Supporting Information Available

A more detailed description of (i) solid phase pretreatements, (ii) mineral phase compositions and measurement of the specific surface area, and (iii) acid−base tritation. This material is available free of charge via the Internet at http://pubs.acs.org.

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