

## Adsorption of Organic Acids on Metal Oxides. The Umbrella Effect

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Simultaneous interpretation of electrokinetic and adsorption data for organic ions at metal oxide surfaces is introduced. It is shown that, for the salicylic acid / hematite system, the singly charged salicylate ions react with surface –OH, groups releasing one water molecule. The salicylate ions, when bound to the surface, exhibit a pronounced »Umbrella effect«, *i.e.* each relatively large organic ion covers about four to six surface –OH, excluding them from the further adsorption process. Within the electrical interfacial layer, the salicylate ions are located in the plane near the onset of the diffuse layer. It is demonstrated that the interpretation of adsorption data solely may lead to erroneous conclusions regarding the mechanism of binding and the structure of the interfacial layer. Electrokinetic measurements provide useful information, enabling the solution of the above problem.

### INTRODUCTION

Adsorption of organic acids or the respective anionic species is a subject of numerous publications.<sup>1–4</sup> The equilibrium was commonly interpreted either by a more or less empirical adsorption isotherm or on the basis of the

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This article is dedicated to Professor Egon Matijević on the occasion of his 75<sup>th</sup> birthday.

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Surface Complexation Model (SCM).<sup>1,2</sup> In most cases, the amount of adsorbed molecules increases gradually with their concentration in the bulk of the solution, reaching a plateau enabling the Langmuir isotherm to be employed for the data interpretation.<sup>5</sup> However, the plateau was found to depend on the pH, so a simple application of the Langmuir isotherm would result in the pH dependent value of the area occupied by the adsorbed molecule or ion, and the adsorption equilibrium constant being approximately independent of pH. This finding indicates that at least one requirement was violated when the Langmuir isotherm was used; namely the adsorbed ionic species exhibit a pronounced electrostatic interaction. In principle, the result of such an approach may be interpreted in the following way: the area per molecule may be understood as the area physically occupied by the adsorbed molecule plus the space in which electrostatic repulsion forces prevent the binding of the next ion. In doing so, one still neglects the pH dependent association-dissociation equilibrium in the bulk of the solution. As it will be shown later, the above problems were solved by introducing the electrostatic interaction term into the Langmuir isotherm, as well as the equilibrium concentration of the species that actually adsorb.<sup>6</sup>

A more advanced treatment should include specified surface reactions, *i.e.* binding of adsorbable species to certain surface groups. This approach, known as the Surface Complexation Model (SCM),<sup>3,4,7</sup> requires a knowledge or assumption of the adsorption mechanism on the molecular basis. The interpretation is not simple, since several equilibria take place simultaneously. In addition to protonation and deprotonation of amphoteric surface  $\equiv\text{MOH}$  groups, the binding of organic species, as well as possible counter ion association reactions, should be considered. The situation is even more complicated because the electrostatic potentials affecting the states of charged surface species should be introduced in the relationships describing the surface equilibria. In doing so, one needs to assume a certain structure of electrical interfacial layer (EIL), introduce the concept of capacitors of constant capacitance and use the Gouy-Chapman theory for the diffuse part of the EIL.

## REFINED LANGMUIR ISOTHERM

The Langmuir isotherm may be refined so that it takes into account the dissociation equilibria in the bulk of the solution and also the electrostatic interactions at the surface. The following relationship<sup>6,8</sup> may be used

$$\frac{1}{\Gamma_i} = \frac{1}{\Gamma_{\max}} + \frac{1}{\Gamma_{\max} K_i \exp(-z_i F \phi_d / RT) a_i} \quad (1)$$

where  $\Gamma_i$  is the equilibrium surface concentration of adsorbed species  $i$  while  $\Gamma_{\max}$  is the maximum surface concentration corresponding to saturated surface, related to the area occupied by one adsorbed ion or molecule  $a_M$  by

$$\Gamma = \frac{1}{L \cdot a_m} \quad (L \text{ is the Avogadro constant}) \quad (2)$$

$\phi_d$  is the electrostatic potential affecting the state of the adsorbed species  $i$  of charge number  $z_i$ , and  $a_i$  is their equilibrium activity in the bulk of the solution, which may be calculated for any pH from the total concentration (after equilibration of the adsorption) and the respective bulk equilibrium constant(s). Consequently,  $K_i$  is the true adsorption equilibrium constant, which corresponds to the thermodynamic one if the bulk activity is used instead of the bulk concentration of adsorbable species. The application of Eq. (1) requires the knowledge of the electrostatic potential of the plane in which adsorbed ions are located. It was shown<sup>6,8</sup> that this potential may be approximated by the potential at the onset of diffuse layer  $\phi_d$  and calculated, using the Gouy-Chapman theory, from the electrokinetic potential

$$\phi_d = (2 RT / F) \ln \frac{\exp(-s\kappa) + \tanh(F\zeta / 4RT)}{\exp(-s\kappa) - \tanh(F\zeta / 4RT)} \quad (3)$$

where  $s$  is the electrokinetic slipping plane separation,  $\kappa$  the Debye-Hückel reciprocal distance, and  $\zeta$  the measured electrokinetic potential. In order to establish the ionic state of the species that actually adsorb, one needs to interpret the adsorption data using all possible assumptions. The procedure is simple; for example, in the case of diprotic acid, one at first assumes that only doubly charged species are bound to the surface ( $z_i = -2$ ) and calculates their pH dependent bulk equilibrium activity. This value should be multiplied by the exponential term,  $\exp(z_i F \phi_d / RT)$ , calculated using the value of  $\phi_d$  as obtained from the measured  $\zeta$  potential by Eq. (3), assuming different values of slipping plane separation  $s$  (from 5 to 20 Å). If the assumption (binding of doubly charged species) is correct, the plot of the reciprocal surface concentration *vs.* reciprocal value of the product  $a_i \exp(z_i F \phi_d / RT)$  should be linear for a proper choice of  $s$ . One repeats the procedure for neutral and singly charged species and, from the assumption that results in linearity, finds the charge number of the species bound to the surface, the area per adsorbed molecule, and the corresponding adsorption equilibrium constant. The nonlinear regression analysis may be also used for this purpose.

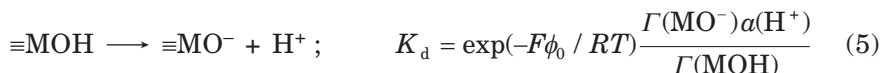
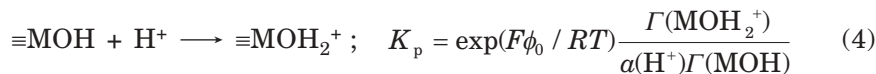
This article presents a further extension of the above procedure based on the Surface Complexation Model. The proposed interpretation will be

demonstrated on the example of adsorption equilibria of salicylic acid ( $H_2L$ ) on hematite.<sup>6</sup> The experimental adsorption and electrokinetic data, taken from Ref. 6, are presented in Figure 1. For this system, the linearity based on Eq. (1) was obtained only in one case, *i.e.* when the adsorption of singly charged anions ( $HL^-$ ) was considered. The best fit was obtained for the electrokinetic slipping plane separation of 15 Å. The surface area occupied by  $HL^-$  ion was found to be  $87 \pm 15 \text{ \AA}^2$ , and the adsorption equilibrium constant was evaluated as  $\log K = 3.5 \pm 0.1$ .

### FURTHER INTERPRETATION IN THE SALICYLIC ACID/HEMATITE AQUEOUS SYSTEM

#### *Surface Potential*

According to the Surface Complexation Model (2-pK concept),<sup>6</sup> the surface charging is due to protonation and deprotonation of amphoteric surface  $\equiv MOH$  groups



The surface charge density in the inner part of the electrical interfacial layer (0-plane) is given by:

$$\sigma_0 = F(\Gamma(MOH_2^+) - \Gamma(MO^-)) \quad (6)$$

while the effective (net) surface charge density takes into account the contribution of specifically adsorbed salicylate ions

$$\sigma_s = F(\Gamma(MOH_2^+) - \Gamma(MO^-) - \Gamma(HL^-)) \quad (7)$$

The above equation is valid at a low ionic strength and in the vicinity of the isoelectric point, since it neglects association of counterions with charged surface groups.

The surface charge density in the diffuse layer ( $\sigma_d$ ) is equal in magnitude, but opposite in sign, to the effective surface charge density ( $\sigma_s$ ) and

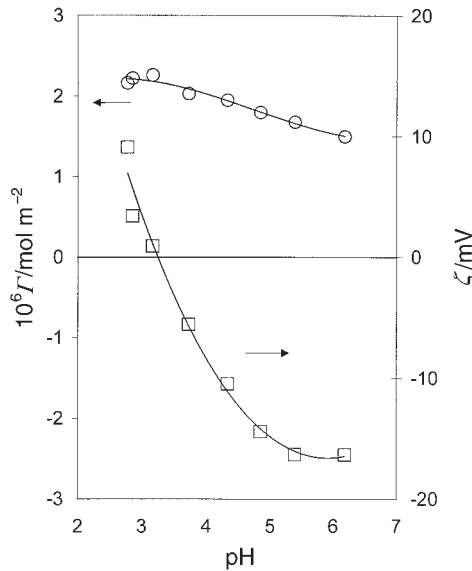


Figure 1. Adsorption of salicylic acid on hematite. The effect of pH on the surface concentration of salicylic acid on hematite (○) and on the electrokinetic potential of hematite particles (□). Mass concentration of hematite was  $200 \text{ g dm}^{-3}$ , initial concentration of salicylic acid  $7.21 \times 10^{-3} \text{ mol dm}^{-3}$ , and temperature  $20 \text{ }^\circ\text{C}$ . The ionic strength of  $I_c = 1.6 \times 10^{-2} \text{ mol dm}^{-3}$  was due to the initial concentration of salicylic acid and addition of NaOH or  $\text{HNO}_3$ , used for pH adjustment. Data were taken from Ref. 6. (Note that low mass concentration of particles was used for electrokinetic experiments).

can be calculated from the electrostatic potential at the onset of the diffuse layer  $\phi_d$  via

$$\sigma_s = -\sigma_d = -\sqrt{8RT\varepsilon I_c} \sinh(\phi_d F / 2RT) \tag{8}$$

Accordingly,

$$\sigma_0 = \sigma_s - F\Gamma(\text{HL}^-) \tag{9}$$

The above equations could be employed for the calculation of the surface charge density in the 0-plane using the value of  $\sigma_s$  obtained from electrokinetic measurements (Eqs. 3, 8) and the measured adsorption density  $\Gamma(\text{HL}^-)$ .

The potential drop between 0-plane and the plane in which adsorbed  $\text{HL}^-$  species are located can be calculated using the concept of the capacitor of the constant capacitance

$$\phi_0 = \frac{\sigma_0}{C_1} + \phi_d \quad (10)$$

Figure 2 represents the pH dependency of  $\phi_0$  and  $\phi_d$  for the hematite/salicylic acid system, as calculated by the above procedure from the data presented in Figure 1. In calculation of  $\phi_0$ , two different values of the capacitance were used;  $C_1 = 1.4$  and  $1.7 \text{ F m}^{-2}$ . As expected, the dependency of  $\phi_0$  on pH shows a »quasi-Nernstian« behaviour.<sup>9-16</sup> The slope was found to depend on the assumed value of  $C_1$ ;  $-46$  and  $-42 \text{ mV/pH}$  for  $1.4$  and  $1.7 \text{ F m}^{-2}$ , respectively. This result agrees with other findings,<sup>6,9,17-20</sup> indicating that the applied  $C_1$  values are reasonable. The choice of the capacitance values will be discussed later.

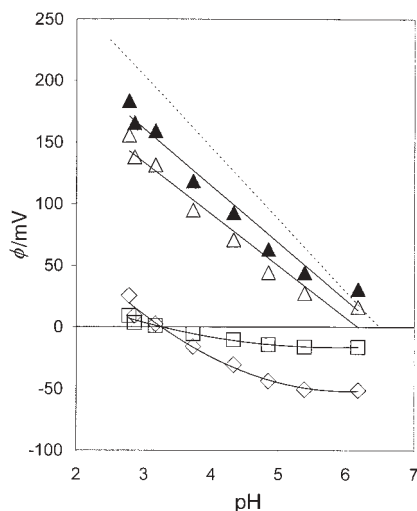


Figure 2. Adsorption of salicylic acid on hematite. Potentials in the interfacial layer as a function of pH ( $s = 15 \text{ \AA}$ ); measured  $\zeta$ -potentials ( $\square$ ), calculated  $\phi_d$  ( $\diamond$ ) and  $\phi_0$  ( $\blacktriangle$ ,  $\triangle$ ). The dashed line represents the theoretical Nernstian slope at  $20 \text{ }^\circ\text{C}$  of  $-58.2 \text{ mV}$ . In calculations of  $\phi_0$ , two limiting values of  $C_1$  were used:  $C_1 = 1.4 \text{ F m}^{-2}$  ( $\blacktriangle$ ) and  $C_1 = 1.7 \text{ F m}^{-2}$  ( $\triangle$ ).

*Concentration of Surface Species*

Once  $\phi_0$  is known, one can calculate surface concentrations of positive and negative surface sites as follows. At the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) in the absence of specific adsorption:  $\phi_0 = 0$  and  $\Gamma(\text{MOH}_2^+) = \Gamma(\text{MO}^-)$ , so that

$$\text{pH}_{\text{pzc}} = 0.5 \log (K_p/K_d) \quad (11)$$

According to Eqs. (4) and (5), the ratio  $\Gamma(\text{MOH}_2^+)/\Gamma(\text{MO}^-)$  could be calculated from the values of surface potential  $\phi_0$  for any pH by

$$\frac{\Gamma(\text{MOH}_2^+)}{\Gamma(\text{MO}^-)} = \frac{1}{\alpha_{\text{pzc}}^2(\text{H}^+)} \exp(-2\phi_0/RT) \alpha^2(\text{H}^+) \quad (12)$$

Once this ratio is known one can simply calculate the charge density of negative sites by the following relationship, obtained by rearranging Eq. (6),

$$\Gamma(\text{MO}^-) = \frac{(\sigma_0/F)}{(\Gamma(\text{MOH}_2^+)/\Gamma(\text{MO}^-)) - 1} \quad (13)$$

The density of positive surface sites is then given by

$$\Gamma(\text{MOH}_2^+) = (\sigma_0/F) - \Gamma(\text{MO}^-) \quad (14)$$

The results of calculations are presented in Figure 3. In the calculations, both assumed values of the capacitance were used. It is clear that, in the presence of adsorbed monovalent salicylate ions, the concentration of negative surface groups  $\text{MO}^-$  is almost negligible.

*Binding Mechanism and the »Umbrella Effect«*

Up to this point, the mechanism of binding salicylic acid onto hematite surface was not discussed, since the interpretation did not require such an assumption. The spectroscopy data suggested several possible structures of surface complexes in the salicylic acid / hematite system.<sup>21-23</sup> The proper choice was enabled by considering the results of adsorption and electrokinetic data as presented in this study. Since singly charged salicylate ions are bound to the surface, one can conclude that the following surface reaction is responsible

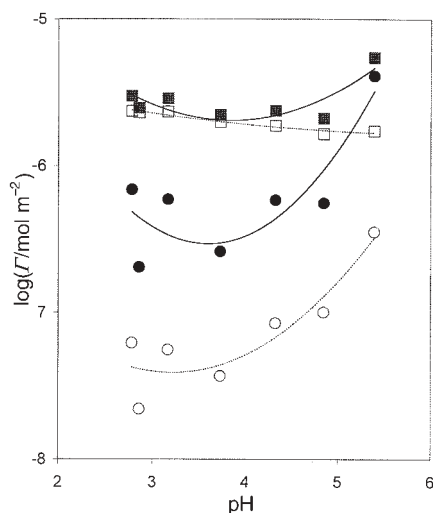
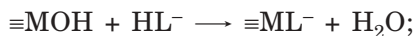


Figure 3. Adsorption of salicylic acid on hematite. Surface concentrations of positive  $\text{MOH}_2^+$  (■, □) and negative  $\text{MO}^-$  (●, ○) surface sites. Two limiting values of  $C_1$  were used in calculation:  $C_1 = 1.4 \text{ F m}^{-2}$  (■, ●) and  $C_1 = 1.7 \text{ F m}^{-2}$  (□, ○).



(15)

$$K(\text{HL}^-) = \exp(-F\phi_d / RT) \frac{\Gamma(\text{ML}^-)}{\Gamma(\text{MOH})\alpha(\text{HL}^-)}$$

In the literature, different variations are found of the Surface Complexation Model applied to the binding of organic ions on metal oxides.<sup>1-4</sup> The differences are reflected in the mechanisms of surface reactions and postulated structures of the electrical interfacial layer. The same mechanisms are sometimes expressed by differently written reaction equations. For example, the equation



(16)

is equivalent to Eq. (15), resulting in the same values of the equilibrium parameters. The only difference is the state of the water molecule. In Eq. (15), the water molecule is released from the surface complex, and since the process takes place in an aqueous environment, the formulation of the equilibrium conditions remains the same.



For the case of adsorption of relatively large ions, one should consider the fact that a bound organic molecule does not cover only the surface site to which it is chemically bound, but also several adjacent surface sites. This »Umbrella effect« should be significant in the case of salicylate ions and is reflected in the summation of surface sites. The following equation takes into account the fact that one adsorbed salicylate ion excludes  $f$  neutral  $\equiv\text{MOH}$  species preventing them from being active in the adsorption process

$$\Gamma_{\text{tot}} = \Gamma(\text{MOH}) + \Gamma(\text{MOH}_2^+) + \Gamma(\text{MO}^-) + f \Gamma(\text{ML}^-) \quad (17)$$

where  $\Gamma_{\text{tot}}$  denotes the total surface concentration of active sites.

### *Evaluation of the Capacitance*

By dividing the equilibrium expressions for the binding of protons (4) and of salicylate ions (15), and by introduction of the capacitance (10), one obtains

$$\ln \frac{\Gamma(\text{MOH}_2^+) \cdot \alpha(\text{HL}^-)}{\Gamma(\text{ML}^-) \cdot \alpha(\text{H}^+)} + \frac{2\phi_a F}{RT} = \ln \frac{K_p}{K(\text{HL}^-)} - \frac{(\Gamma(\text{MOH}_2^+) - \Gamma(\text{MO}^-))F^2}{C_1 RT} \quad (18)$$

By plotting the LHS of Eq. (18) as the function of  $(\Gamma(\text{MOH}_2^+) - \Gamma(\text{MO}^-))$ , one should get the straight line yielding the ratio of  $K_p/K(\text{HL}^-)$  (intercept) while the slope provides the value of the capacitance  $C_1$ . This approach requires the application of an iterative procedure, since the necessary data on  $\Gamma(\text{MOH}_2^+)$  and  $\Gamma(\text{MO}^-)$  (Figure 3) depend on the chosen value of  $C_1$ . The interpretation showed that  $C_1$  lies between 1.4 and 1.7  $\text{F m}^{-2}$ , while  $\ln(K_p/K(\text{HL}^-))$  could be only roughly estimated as having the value between 5 and 7.

### *Protonation Equilibrium Constant and the »Umbrella Coefficient«*

From Eqs (4) and (17), one may derive the following expression

$$\frac{\exp(-\phi_0 F/RT)}{\Gamma(\text{MOH}_2^+)} (\Gamma_{\text{tot}} - \Gamma(\text{MOH}_2^+)) = \frac{1}{K_p} + f \frac{\Gamma(\text{HL}^-) \exp(-\phi_0 F/RT) \alpha(\text{H}^+)}{\Gamma(\text{MOH}_2^+)} \quad (19)$$

which could be used to evaluate the  $K_p$  and  $f$  values. One plots

$$\frac{\exp(-\phi_0 F / RT)}{\Gamma(\text{MOH}_2^+)} (\Gamma_{\text{tot}} - \Gamma(\text{MOH}_2^+)) \text{ vs. } \frac{\Gamma(\text{HL}^-) \exp(-\phi_0 F / RT) \alpha(\text{H}^+)}{\Gamma(\text{MOH}_2^+)}$$

and the slope should correspond to a number ( $f$ ) of neutral  $\equiv\text{MOH}$  species, covered and deactivated by one adsorbed salicylate ion. In addition, the intercept provides the  $K_p$  value, which may be then used to obtain the value of the deprotonation equilibrium constant ( $K_d$ ), using Eq. (11). Such a plot is displayed in Figure 4 and the results are in agreement with the expectations. Several values of the total surface concentration of surface active groups were used in calculations. In the literature,<sup>18</sup> one may find the values of  $\Gamma_{\text{tot}}$  between 1 and  $2 \times 10^{-5}$  mol  $\text{m}^{-2}$ , so calculations were performed with three values of  $\Gamma_{\text{tot}}$  and two limiting values of the capacitance, as obtained previously. The results presented in Table I show that  $f = 6 \pm 1$ , *i.e.* that the salicylate ion is bound to one neutral  $\equiv\text{MOH}$  group but covers approximately four to six others. These groups are no longer active in the adsorption process. The number of  $\equiv\text{MOH}$  groups under the »umbrella« is reasonable if one considers the size of the salicylate ion. It is also in accordance with the interpretation based on the Langmuir isotherm, yielding the area per adsorbed ion of about  $90 \text{ \AA}^2$ . According to the intercept (Figure 4), the

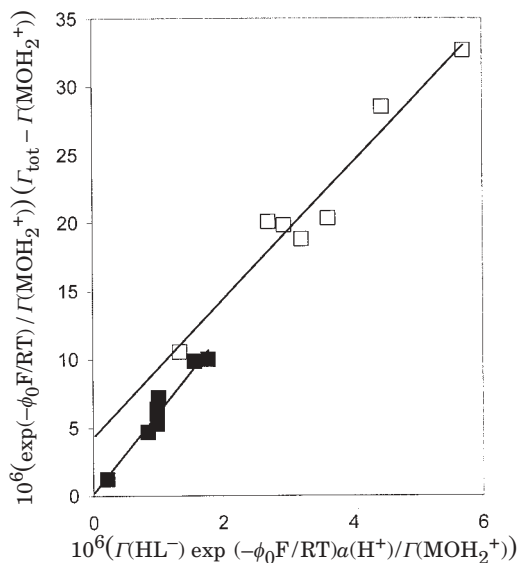


Figure 4. Adsorption of salicylic acid on hematite. Data from the experiment shown in Figure 1 as interpreted by Eq. (19). Two limiting values of  $C_1$  were used in calculation:  $C_1 = 1.4 \text{ F m}^{-2}$  (■) and  $C_1 = 1.7 \text{ F m}^{-2}$  (□);  $\Gamma_{\text{tot}} = 1.5 \times 10^{-5} \text{ mol m}^{-2}$ .

TABLE I

Values of  $f$  and  $K_p$  determined on the basis of Eq. (19) for limiting values of  $C_1$  and  $\Gamma_{tot}$ . Experimental data were taken from Ref. 6.

$10^5 \Gamma_{tot}$ mol m <sup>-2</sup>	$C_1 = 1.4 \text{ F m}^{-2}$		$C_1 = 1.7 \text{ F m}^{-2}$	
	$f$	$10^{-6} K_p$	$f$	$10^{-5} K_p$
1	3.67	—	3.01	3.46
1.5	5.9	6.85	5.03	2.33
2	8.15	2.86	7.06	1.76

equilibrium constant of protonation  $K_p$  is  $2 \times 10^5 - 7 \times 10^6$ , this result is within the range of the values obtained by the potentiometric measurements in the absence of specific adsorption,<sup>18</sup> *i.e.* by interpretation of  $\sigma_o(\text{pH})$  functions. The equilibrium constant of deprotonation  $K_d$  can be obtained from  $K_p$  and  $\text{pH}_{\text{pzc}}$  ( $= 6.5$ ), *via* Eq. (11), and is obtained as  $7 \times 10^{-7} - 2 \times 10^{-8}$ .

*Equilibrium Constant of the Binding of Salicylate Ions*

Once the concentrations of all the surface species, and also the electrostatic potentials affecting the state of adsorbed ions, are known, one can readily calculate the equilibrium constant for the binding of salicylate ions *via* Eqs. (15) and (17). However, in doing so, one needs to use certain values of  $C_1$ ,  $\Gamma_{tot}$  and of the »umbrella« coefficient  $f$ . Table II presents the results of calculations using the limiting values of  $C_1$  and  $\Gamma_{tot}$ , applying different values of  $f$ . Some assumptions resulted in negative values of the adsorption equilibrium constant and they were excluded. The obtained positive values of  $K(\text{HL}^-)$  are in the range of 100–1000.

TABLE II

Values of  $K(\text{HL}^-)$  calculated from Eqs. (15) and (17) for different assumed  $f$  and limiting values of  $C_1$  and  $\Gamma_{tot}$ . Experimental data were taken from Ref. 6.

$10^5 \Gamma_{tot}$ mol m <sup>-2</sup>	$C_1 = 1.4 \text{ F m}^{-2}$			$C_1 = 1.7 \text{ F m}^{-2}$		
	1	1.5	2	1	1.5	2
$f = 2$	440	162	100	339	147	94
$f = 3$	—	218	118	821	191	110
$f = 4$	—	339	145	—	275	133
$f = 5$	—	1300	189	—	535	168
$f = 6$	—	—	276	—	—	232
$f = 7$	—	—	626	—	—	379
$f = 8$	—	—	—	—	—	—

### *Nonlinear Regression of Adsorption Data*

The large number of adjustable parameters governing the interfacial equilibria may lead to erroneous conclusions regarding the mechanism of binding and the structure of the interfacial layer if only adsorption data are used in interpretation. For example, even the most simple case of metal oxides in neutral electrolyte solutions may be successfully interpreted by different theoretical models.<sup>24</sup> If, in addition, the adsorption of organic acid ions takes place, the situation is more complicated, since one should assume a certain mechanism of binding and a more complicated structure of the interfacial layer. Consequently, one is faced with numerous reasonable choices and more than one may agree with the measured adsorption data. The only solution is to interpret simultaneously two sets of independent experimental data, such as adsorption and electrokinetic results.

In the case of adsorption of salicylic acid on hematite one may assume different reaction mechanisms and various structures of the interfacial layer. For this purpose, conventional nonlinear regression analysis was used. In the first step, the model based on the results of this study was employed, *i.e.* binding of singly charged salicylate ions was assumed together with the reaction mechanism (Eq. 15). It was also assumed that the adsorbed ions are exposed to the electrostatic potential approximately equal to the potential at the onset of the diffuse layer. The nonlinear regression showed fair agreement of the measured and calculated values for both adsorption and electrokinetic data. However, when the same reaction mechanism (Eq. 15) was postulated, but the adsorbed salicylate ions were assumed to be located in the 0-plane (the same plane as for  $\equiv\text{MOH}_2^+$  and  $\equiv\text{MO}^-$  groups), the calculated  $\phi_{\text{d}}$ -potential and measured  $\zeta$ -potential substantially disagreed. This finding is demonstrated in Figure 5, showing that interpretation of adsorption data without considering electrokinetics may result in acceptance of an unrealistic model, predicting completely different values of some other parameters, such as for example the electrokinetic potentials. Therefore, if one did not consider electrokinetic measurements, the interpretation would provide an unrealistic answer. In addition, one may assume several other models that would fit the adsorption data, and the choice of the proper one may be based on the quality of the fit. However, comparison with another type of measurements would provide a more accurate answer.

### CONCLUSION

This article demonstrates what a powerful tool is the interpretation of simultaneous measurements providing two types of information. Namely, the adsorption data combined with electrokinetic measurements gave an in-

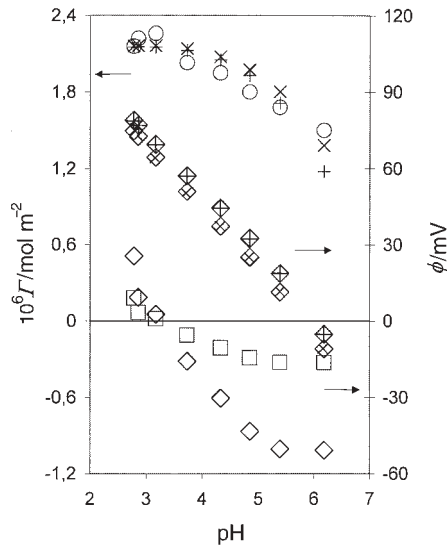


Figure 5. Adsorption of salicylic acid on hematite. Comparison of experimental adsorption ( $\circ$ ) and electrokinetic data ( $\square$ ), taken from Ref. 6, and  $\phi_d$  potentials ( $\diamond$ ) presented in Figure 4 with calculated values of the surface concentration ( $+$ ,  $\times$ ) and  $\phi_d$  potentials ( $\oplus$ ,  $\otimes$ ). The values of parameters used in calculations were obtained by nonlinear regression analysis of adsorption data, disregarding electrokinetic results. The parameters used were:  $\Gamma_{\text{tot}} = 1.6 \times 10^{-5} \text{ mol m}^{-2}$ ,  $K_p = 5 \times 10^5$ ,  $K_d = 2 \times 10^{-7}$ ,  $K_{\text{ads}} = 100$ ,  $f = 6$ ,  $C_1 = 1.2 \text{ F m}^{-2}$  ( $+$ ,  $\diamond$ );  $\Gamma_{\text{tot}} = 1.6 \times 10^{-5} \text{ mol m}^{-2}$ ,  $K_p = 3 \times 10^5$ ,  $K_d = 1.2 \times 10^{-7}$ ,  $K_{\text{ads}} = 180$ ,  $f = 6$ ,  $C_1 = 1.4 \text{ F m}^{-2}$  ( $\times$ ,  $\otimes$ ).

sight into the mechanism of surface binding of salicylate ions and enabled determination of relevant equilibrium parameters. For the examined hematite / salicylic acid system, the binding of singly charged salicylate ions to the neutral surface  $\equiv\text{MOH}$  group was established. Due to the size of the organic ion, about four to six other surface groups are under the »umbrella«, and are consequently excluded from the adsorption process. Another possibility was also explored; the adsorbed salicylate ions changed the equilibria of protonation and deprotonation of  $\equiv\text{MOH}$  groups so that values of individual constants  $K_p$  and  $K_d$  were also estimated.

The nonlinear regression analysis based on several different theoretical models agreed with the adsorption data, but the electrokinetic measurements enabled the proper choice of the mechanism of binding the salicylate ions and of the structure of the interfacial layer.

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**SAŽETAK****Adsorpcija organskih kiselina na kovinske okside. Efekt kišobrana**

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Prikazana je simultana interpretacija elektrokinetičkih i adsorpcijskih podataka za organske ione na površini kovinskih oksida. Za sustav salicilna kiselina / hematit pokazano je da se jednostruko nabijeni salicilatni ioni vežu na površinske –OH skupine, izdvajajući pritom jednu molekulu vode. Salicilatni ioni vezani za površinu pokazuju izražen »efekt kišobrana«, tj. svaki razmjerno veliki organski ion pokriva oko četiri do šest površinskih –OH skupina onemogućujući ih pritom u daljnjem adsorpcijskom procesu. Unutar električnog međusloja, salicilatni su ioni smješteni u plohi blizu početka difuznog sloja. Pokazano je da interpretacija samo adsorpcijskih podataka može dovesti do pogrešnih zaključaka o mehanizmu vezivanja i strukturi električnog međusloja. Elektrokinetička mjerenja pridonose rješenju tog problema.