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Original Scientific Article

Electrical Interfacial Layer at Hematite/Dicarboxylic Acid Aqueous Interface[†]

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Abstract. The interfacial properties of the system hematite/dicarboxylic acid were investigated in the presence of sodium perchlorate by means of adsorption, zeta potential and surface potential measurements. Maleic and fumaric acid were used as dicarboxylic acids. No significant difference in the surface potential values of hematite with and without the presence of dicarboxylic acids was observed. On the other hand, the zeta potential and the corresponding isoelectric point values obtained after adsorption of fumaric and maleic acids on hematite differ significantly from the zeta potential values of pure hematite. The parameters characterizing the electrical interfacial layer were determined on the basis of simultaneous interpretation of experimental data showing that there are some differences in adsorption behavior of two investigated dicarboxylic acids. The obtained equilibrium constant for adsorption of fumaric acid ($\log K^\circ = 4.9 \pm 0.2$) is higher than the same constant obtained for adsorption of maleic acid ($\log K^\circ = 4.0 \pm 0.1$) and the value of C_1 was in both cases determined as 2.2 ± 0.3 F m^{-2}. (doi: 10.5562/cca2176)

Keywords: hematite, maleic acid, fumaric acid, adsorption, zeta potential, surface potential

INTRODUCTION

The study of adsorption of organic acids on metal oxide and other mineral surfaces is important both from the fundamental and from the application point of view having implications in various fields such as soil chemistry, geochemistry and waste water treatment. Among other organic acids, dicarboxylic acids are particularly interesting because they arise as waste products from several industrial processes. Interaction of fumaric and maleic acids in aqueous solution with synthetic hydroxyapatite was studied by Vega and Colinas.[1] They found that both acids are adsorbed to hydroxyapatite *via* the completely deprotonated carboxylates, but that maleic acid shows stronger adsorption due to its *cis* geometry. They concluded that hydroxyapatite could be applied for selective removal of fumaric and maleic acids from wastewaters. Persson and coworkers[2] studied the adsorption of dicarboxylates (among them of maleate) on nano-sized gibbsite particles by means of quantitative batch adsorption experiments and ATR-FTIR spectroscopy. The main aim of their study was to identify the molecular level bonding mechanisms of the dicarboxylates to gibbsite. They concluded that carboxylates with $z = -2$ (z being the charge number) formed predominantly outer sphere complexes, whereas the importance of inner sphere complexes progressively increased for $z = -1$ and $z = 0$. The inner sphere structures were identified as mononuclear chelates with one oxygen from each carboxylate group bonded to Al(III) at the surface. On the other hand, Yao and Yeh[3] studied the adsorption of fumarate, maleate and succinate on hydrous Al_2O_3 and observed that the adsorption of HX^- is more favorable than adsorption of H_2X or X^{2-} and that the adsorption maximum of maleate was about 10 % higher than that of fumarate. Hwang and Lenhart[4] also investigated hematite/maleic acid system and they concluded on the basis of ATR-FTIR and batch adsorption experiments that both outer-sphere and inner-sphere complexes are simultaneously present, with inner-sphere complexes being favored at low pH. On the other hand, their results suggest that in the case of adsorption of fumaric acid on hematite surface only outer-sphere complexes are formed. Finally, their results show that subtle differences in the structure of adsorbed acids produce important differences in the physicochemical behavior of particles in dilute aquatic systems.

From the above mentioned studies it is obvious that the equilibrium at various solid-liquid interfaces is very often a subject of both experimental and theoretical

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investigations, but various uncertainties still exist. In many cases the interpretation of surface equilibria is based on only one type of experimental data (*e.g.* only adsorption data) and such an approach may lead to erroneous conclusions regarding the mechanism of binding and the structure of the Electrical Interfacial Layer (EIL). We have already shown earlier[5–7] that the introduction of other, additional experimental techniques could provide useful information leading to the more accurate determination of various adsorption parameters, but also to valuable indications about the location of adsorbed species within the EIL and to the binding mechanism. In this article we use such an approach for comparison of parameters obtained in the case of adsorption of two dicarboxylic acids (fumaric and maleic acid) on hematite. For that purpose we performed adsorption, zeta potential and, recently introduced, surface potential measurements by means of single crystal electrodes.[8] Therefore we decided to examine these differences using abovementioned methods and have applied simultaneous interpretation of data.

THEORETICAL

When discussing the models that describe the electrical interfacial layer at the solid/liquid interface the number of postulated layers, *i.e.,* planes that divide these layers and corresponding potentials should be assumed. In the so-called general model three layers and four different planes (with corresponding potentials) are postulated.[9] The interpretation of experimental results presented in this paper is based on the measured surface (Ψ_0) and electrokinetic zeta (ζ) potentials. Surface potential is the potential at the (inner) surface plane, 0-plane. In this plane the charged species are directly bound to the surface. On the other hand, the electrokinetic ζ-potential corresponds to the imaginary slip or shear plane that is located within the diffuse layer and close to the d-plane which is assumed to be the onset of diffuse layer. According to the Gouy-Chapman theory, the relationship between the potential at the onset of diffuse layer and the electrokinetic ζ-potential is given by:

$$\Psi_\mathrm{d} = \frac{2RT}{F}\ln\left(\frac{\exp(-\kappa l_\mathrm{e}) + \tanh(F\zeta/4RT)}{\exp(-\kappa l_\mathrm{e}) - \tanh(F\zeta/4RT)}\right) \qquad (1)$$

where l_e is the distance between d-plane and slip plane, corresponding to the thickness of electrokinetic stagnant layer, while κ is the Debye-Hückel parameter given by:

$$\kappa = \sqrt{\frac{2I_c F^2}{\varepsilon RT}} \qquad (2)$$

where I_c is ionic strength based on (molar) concentration, ε is the permittivity of the medium (solution), while other symbols have their usual meaning.

The surface charge densities of interfacial planes are related to the corresponding surface concentrations of interfacial ions: the surface charge density of the 0-plane and the β-plane (plane where the centers of counterions are located) are denoted σ_0 and σ_β, respectively. The net surface charge density σ_s is equal in magnitude but opposite in sign to that in diffuse layer (σ_d) and in the case of adsorption of *e.g.* organic acids the net surface charge density equals to:

$$\sigma_\mathrm{s} = -\sigma_\mathrm{d} = \sigma_0 + \sigma_\mathrm{a} \qquad (3)$$

where σ_a presents the surface charge due to the adsorbed ions. According to the Gouy-Chapman theory, in the case of (1:1) symmetrical electrolytes the relationship between the surface charge densities (σ_d, σ_s) and the electrostatic potential at the onset of the diffuse layer Ψ_d for planar geometry is given by:

$$\sigma_\mathrm{d} = -\sigma_\mathrm{s} = -\sqrt{8RT\varepsilon I_c}\,\sinh\left(F\Psi_\mathrm{d}/2RT\right) \qquad (4)$$

or

$$\Psi_\mathrm{d} = -\frac{2RT}{F}\,\mathrm{ar\,sinh}\frac{\sigma_\mathrm{d}}{\sqrt{8RT\varepsilon I_c}} \qquad (5)$$

According to the general model, the (inner) Helmholtz layer could be considered as a capacitor with two planes; 0-plane and β-plane. The inner layer capacitance C_1 is assumed to be constant and is commonly defined as:

$$C_1 = \frac{\sigma_0}{\Psi_0 - \Psi_\beta} \qquad (6)$$

In the literature various values of C_1 could be found. For example, Sverjensky[10] predicted the triple layer model capacitances to be between 0.5 and 1.55 F m^{-2} for various metal oxide electrolyte interfaces. Shimizu and coworkers[11,12] calculated the surface-area-normalized capacitance values for hematite electrode/electrolyte (NaCl and NH_4Cl) solution interface to be between 1 and 1.4 μF cm^{-2}. These values are at least one order of magnitude smaller than those obtained *e.g.* by fitting the potentiometric titration data of iron oxide powders. On the other hand, in the case of specific adsorption of different cations and anions higher capacitance values are found. For specific adsorption of Cd(II) ions on hematite Chibowski and Janusz[13] obtained the capacitance of 2.4 F m$^{-2.}$

EXPERIMENTAL

Materials

All solutions were prepared using deionised water ($\kappa < 3$ μS cm^{-1}). Chemicals used were: $HClO_4$ (70 %, $\rho \approx 1.67$ g cm^{-3}, $M_r = 100.46$, Riedel de Haën), NaOH (0.1 mol dm^{-3}, Sigma-Aldrich), $NaClO_4$ (≥ 99 % *p.a.*, $M_r = 122.44$, Sigma-Aldrich), maleic acid (p.a, $M_r = 116.07$, Kemika Zagreb), fumaric acid (synthesized at Laboratory of Organic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb), standard buffers pH = 3 (Kemika Zagreb), pH = 7 (Sigma-Aldrich), pH = 10 (Sigma-Aldrich). Hematite particles were a product of Alfa, Johnson Matthey GmbH (Karslruhe, Germany) having a specific surface area of 8.8 m^2 g^{-1} and diameter around 500 nm. The particles were used without further purification.

The electrode was made from a hematite single crystal (SCr) (origin: Vesuvius, Italy). The properties and construction of the SCr electrode were described in more details earlier.[8] After surface potential measurement (in the presence of maleic or fumaric acid) the crystal plane was cleaned by exposure of electrode to NaOH solution ($c \approx 1\times10^{-3}$ mol dm^{-3}) and was sonicated during 1–2 minutes. Procedure was repeated with deionized water instead NaOH solution. After sonication, electrode was washed again with deionized water. The electric resistance of the SCr-hematite electrode was measured directly and was approximately 7 MΩ.

Methods

Batch Adsorption Experiments

Adsorption of maleic and fumaric acid on hematite was studied as a function of pH at 25 °C. Suspensions of hematite particles were prepared by the following procedure: hematite was weighed in the glass tubes which were then filled with 15 mL of suspension solution so that the final mass concentration of hematite was 15 g dm^{-3}. The samples were prepared by adding appropriate volume of stock solution of maleic or fumaric acid, 0.1 mol dm^{-3} perchloric acid and 0.1 mol dm^{-3} NaOH to adjust the pH value and then filled with water up to 25 ml. pH of suspension solution was measured with combined electrode with reference Ag|AgCl|3M KCl (Metrohm 6.0234.100) electrode and 827 Metrohm pH-meter. Suspensions were stirred for 90 minutes and then left overnight so the adsorption equilibrium and separation of the two phases can be achieved. Before filtration of suspensions, equilibrium pH was measured. Suspensions were filtered with Filtrak 390 filter paper with porosity 3–5 μm (Spezialpapierfabrik Niederschlag, Germany). Equilibrium concentration of maleic and fumaric acid was calculated from absorbance measured with Cary UV-Vis Spectrophotometer, Varian. Before spectrophotometric measurements all samples were acidified with $HClO_4$ to a pH ≈ 0.5 to protonate the acids (> 90 %), *i.e.* to convert them to H_2A form. Absorbance values used in the calculation of maleic concentration were measured at $\lambda = 206$ nm and those of fumaric acid were measured at $\lambda = 210$ nm.

Electrokinetic Measurements

The electrokinetic (zeta) potential of hematite particles was measured before and after adsorption of dicarboxylic acids by means of a ZetaPlus Zeta Potential Analyser, Brookhaven Instruments Corporation at 25.0 °C. The instrument uses electrophoretic light scattering and the Laser Doppler Velocimetry method for determination of particle velocity. Zeta potential was calculated from mobility values using the Smoluchowski equation. The measurements in the presence of maleic or fumaric acid were performed after taking 1.5 ml of each supernatant solution and mixing it with small amount of hematite particles because initial concentration of hematite (15 g dm^{-3}) was too high for electrokinetic measurements. Zeta potential of hematite particles in absence of respective acids was measured for suspension of he–matite particles ($\gamma = 100$ mg dm^{-3}) in 1×10^{-3} mol dm^{-3} $HClO_4$ after setting pH values of aliquots with 0.1 mol dm^{-3} NaOH solution. The experiments were performed at 1×10^{-3} mol dm^{-3} ionic strength (*i.e.* concentration of perchloric acid).

Surface Potential Measurements

The potential of the hematite single crystal electrode was measured using the Metrohm 713 pH-meter. The pH was measured with a glass electrode (Metrohm 6.0123.100) using a separate Metrohm 713 pH-meter. The common reference electrode was Ag|AgCl|3M KCl, (Metrohm 6.0729.100) with a salt bridge filled with 0.1 mol dm^{-3} $NaClO_4$. The glass electrode was calibrated with three standard buffers. In the course of measurements the system was thermostated at 25.0 °C and kept under argon atmosphere. In order to determine the electrode potential of hematite in perchloric acid without added maleic or fumaric acid, perchloric acid solution (30 mL, $c = 1\times10^{-3}$ mol dm^{-3}) was titrated with the base ($c = 0.1$ mol dm^{-3}, NaOH). The backward titration (with perchloric acid, $c = 0.1$ mol dm^{-3}) was also performed. The same kind of the cyclic titration was performed in perchloric acid solution ($c = 1\times10^{-3}$ mol dm^{-3}) in presence of maleic or fumaric acid ($c = 1\times10^{-3}$ mol dm^{-3}). The system was gently stirred with a magnetic stirrer.

RESULTS

Adsorption Measurements

Figure 1 displays the effect of the pH on the surface concentration of fumaric and maleic acid on hematite. Typical adsorption isotherm profile consistent with adsorption of singly (–1) charged species is obtained. In both sets of experiments the highest adsorbed amount was observed at pH ≈ 4 which corresponds to the maximum in the speciation diagram (Figure 2) in the case of both investigated dicarboxylic acids. Therefore, in the further interpretation of data the assumption that singly charged species are adsorbed will be taken into account.

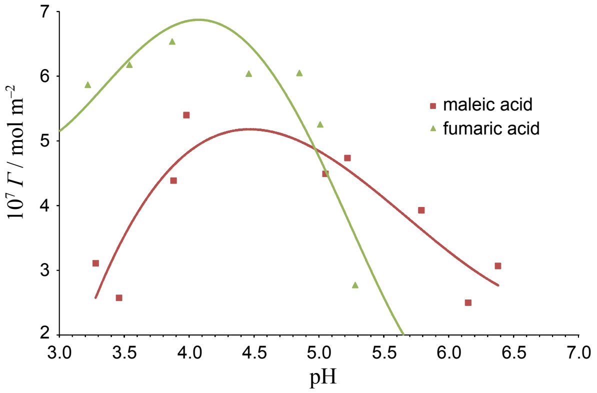

Figure 1. The effect of pH on the surface concentration of maleic (■) and fumaric (▲) acid on hematite at ionic strength of 1×10^{-3} mol dm^{-3}; γ = 15 g dm^{-3}, $[H_2A]_{in} = 1\times10^{-3}$ mol dm^{-3}, t = 25 °C.

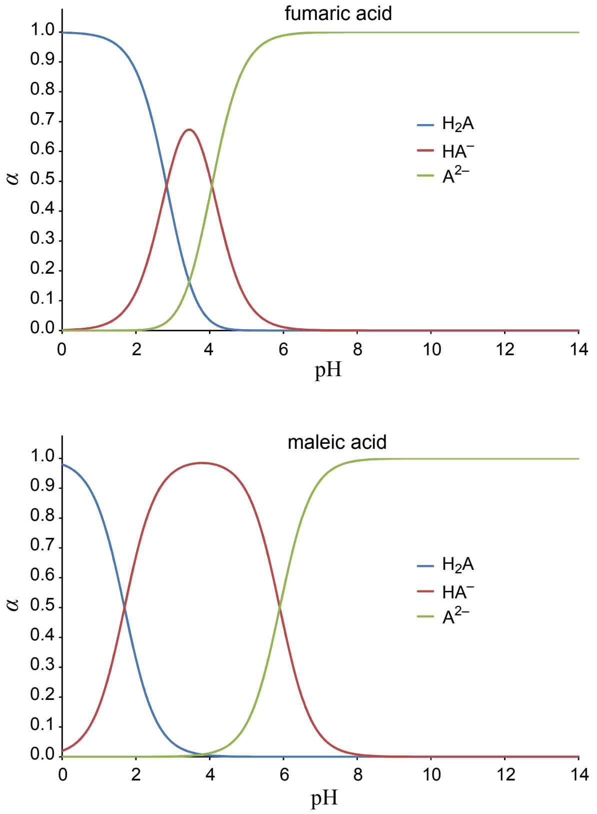

Figure 2. The speciation of fumaric and maleic acid in the bulk of the solution. In the calculations the following values of the dissociation equilibrium constants were used:[14] maleic acid: pK_1 = 1.69, pK_2 = 5.90; fumaric acid: pK_1 = 2.83, pK_2 = 4.06, $[H_2A]_{in} = 1\times10^{-3}$ mol dm^{-3}.

Electrokinetic Measurements

In Figure 3 the influence of pH on the zeta potential of hematite in the absence and in the presence of maleic and fumaric acid is shown. In the absence of dicarboxylic acids (pure hematite dispersion) the isoelectric point of hematite is at pH_{iep} = 6.4 which is in accordance with literature values.[15] In the presence of dicarboxylic acids pH_{iep} is shifted, as expected for the adsorption of negatively charged species, to the lower pH values being pH_{iep} = 4.3 for hematite/maleic acid and pH_{iep} = 4.1 for hematite/fumaric acid system. From these results it could be concluded that the adsorption of fumaric acid shifts the isoelectric point of pure hematite slightly more than the adsorption of maleic acid.

Surface Potential Measurements

Surface potential measurements were performed in order to elucidate the nature of binding of maleic and fumaric acid to hematite surface. The electrode potential of SCr hematite electrode, E, was measured in perchloric acid solution in the absence and in the presence of maleic and fumaric acid as function of pH. The experiments were performed as acid-base titration (perchloric acid solution was titrated with sodium hydroxide solution and the same solution was then titrated with perchloric acid). The hysteresis for alkalimetric titration, *i.e.* titration with base, and acidimetric titration, *i.e.* titration with acid was observed, which is the result of the slow equilibration at the interface.

From the measured electrode potentials of the hematite single crystal electrode surface potentials Ψ_0 were obtained[16] by

$$\Psi_0 = E - E_{cal} \tag{7}$$

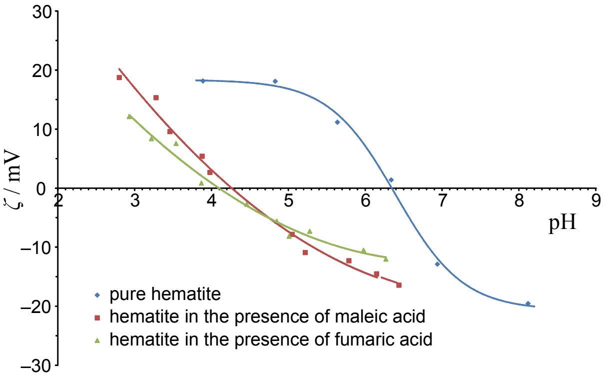

Figure 3. Electrokinetic (zeta) potential of hematite particles (γ = 100 mg dm^{-3}) as function of pH in perchloric acid solution ($c = 1\times10^{-3}$ mol dm^{-3}) before (♦) and after adsorption of maleic (■) or fumaric acid (▲) ($c = 1\times10^{-3}$ mol dm^{-3}). pH value of suspension was changed by adding sodium hydroxide solution (0.1 mol dm^{-3}) at 25.0 °C.

where the value of E_{cal} includes all potential differences in the measuring circle, except the one at the crystal/solution interface. Once the value of E_{cal} is known, surface potentials can easily be obtained from the measured electrode potentials *via* Equation (7). In fact, one sets the zero value of surface potential at pH_{pzp} which was approximated by the isoelectric point pH_{iep} of pure hematite (determined from electrokinetic measurements to be $\text{pH}_{\text{iep}} = \text{pH}_{\text{pzp}} = 6.4$) assuming that at low ionic strength the point of zero potential coincides with the isoelectric point. The same value of $\text{pH}_{\text{pzp}} = 6.4$ was used as the basis for calculation of surface potentials in the presence of maleic and fumaric acid, since it is known[17] that association of various ions shifts pH_{iep} more significantly than pH_{pzp}, and E_{cal} value was calculated accordingly. In Figure 4 surface potential values determined in the abovementioned way are presented as arithmetic mean of surface potentials calculated from both titration curves (alkalimetric and acidimetric) for all three examined cases. The surface potential of hematite is found to decrease with pH, indicating that the surface becomes less positively or more negatively charged. The slope of the Ψ_0(pH) function is found to be lower than the Nernstian slope.[17,18]

From the results shown in Figure 4 it could be concluded that the presence of maleic and fumaric acid influences the surface potentials in similar manner and that no significant difference in the curves obtained in the presence and in the absence of fumaric acids was observed. Taking into account these results, as well as the results of zeta potential measurements, it could be assumed that it is more probable that adsorption of dicarboxylic acids takes place in the d- and not in the 0-plane. Therefore, in the interpretation of the data the assumption of the adsorption in the d-plane will be used.

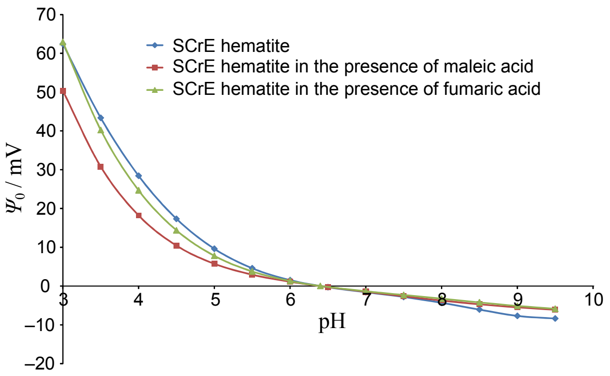

Figure 4. The dependence of surface potential (Ψ_0) of hematite on pH in perchloric acid solution ($c = 1 \times 10^{-3}$ mol dm^{-3}) in the absence (◆) and in the presence of maleic (■) and fumaric (▲) acid at 25 °C. Equilibration time: 20 min. Surface potential values were calculated from electrode potentials *via* Equation (7).

INTERPRETATION

The interpretation of the experimental data, performed according to the Surface Complexation Model, was based on the following procedures:

$$\zeta \xrightarrow{l_e} \Psi_{\text{d}} \xrightarrow{\text{G.C.}} \sigma_{\text{s}}(=-\sigma_{\text{d}}) \xrightarrow{-zF\Gamma_{\text{a}}} \sigma_0 \quad (8)$$

$$\Psi_0 \xrightarrow{\sigma_0} C_1 \quad (9)$$

The first step in the interpretation was the calculation of Ψ_{d} from the measured ζ-potential (Equation 1) assuming different values of the distance between d-plane and electrokinetic slip plane l_e in the range from 0 to 25 Å by step of 5 Å. No significant effect of the choice of l_{e} value on the final results was found and therefore the value of $l_{\text{e}} = 5$ Å was used in further calculations. Surface charge density σ_{s} ($= -\sigma_{\text{d}}$) was then calculated from Ψ_{d} potential *via* Equation (4).

In the next step of the interpretation procedure one calculates σ_0 from σ_{s} and σ_{a}, where σ_{a} is equal to $zF\Gamma_{\text{a}}$ (Γ_{a} presents the adsorbed amount of maleic or fumaric acid as obtained from adsorption experiments, Figure 1). The charge number z was taken to be –1 which is in accordance with adsorption results (see the comparison with speciation).

Now, taking into account σ_0 values obtained *via* the procedure (8), in the parallel procedure (9) the value of capacitance C_1 could be estimated from the measured Ψ_0 values and from calculated σ_0 values. In that way the capacitance C_1 was estimated to be relatively high, *i.e.* 2.2 ± 0.3 F m^{-2} for both hematite/maleic and hematite/fumaric acid aqueous interface. Since the value of C_1 is a specific characteristics of species bound to the surface it is not surprising that examined acids behave differently with respect to *e.g.* inorganic counterions.[10–13] The obtained results are also in accordance with the results we obtained earlier for cadmium/goethite aqueous interface.[19]

In the final step of the interpretation procedure the equilibrium constants of adsorption were calculated for both dicarboxylic acids taking into account the assumptions that adsorbed ions are located in d-plane (deduced from zeta and surface potential measurements) and that charge number of adsorbed species is –1 (deduced from adsorption measurements). Therefore, we used the modified Langmuir isotherm[5] in the form

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\max}} + \frac{1}{K^\circ \exp\left(-z\psi_{\text{d}}F/RT\right)\Gamma_{\max}c_{\text{eq}}} \quad (10)$$

where c_{eq} is the equilibrium concentration of adsorbable species.

From the interpretation based on Equation (10) the value of maximum adsorbed amount $\Gamma_{\max}$ was estimated to be 5.2×10^{-7} mol m^{-2} and 6.3×10^{-7} mol m^{-2} for maleic and fumaric acid, respectively. Hwang[20] also obtained higher maximum adsorbed amount for fumaric acid (1.62×10^{-6} mol m^{-2} at pH = 4.1) than for maleic acid (1.41×10^{-6} mol m^{-2} at pH = 4.2). Such a difference between the maximum adsorbed amounts obtained in these two studies could be due to the various hematite samples (*i.e.* different method of preparation, particle size and isoelectric point).

The corresponding thermodynamic equilibrium constants are determined as $\log K° = 4.0 \pm 0.1$ and $\log K° = 4.9 \pm 0.2$ for adsorption of maleic and fumaric acid, respectively.

CONCLUSION

The comparison of experimental results obtained from adsorption, zeta potential and surface potential measurements of pure hematite with the corresponding measurements after adsorption of maleic and fumaric acid could give valuable information about the parameters at hematite/dicarboxylic acid aqueous interface. No significant difference in the surface potential values of single crystal hematite electrode with and without the presence of dicarboxylic acids in the examined pH region was observed. On the other hand, the adsorption of both maleic and fumaric influenced the zeta potential values. The simultaneous interpretation of adsorption, zeta potential and surface potential data on the basis of the Surface Complexation Model leads also to the values of the parameters in the electrical interfacial layer such as equilibrium constant of adsorption and the capacitance C_1. The obtained results suggest that simultaneous interpretation of adsorption, surface and zeta potential measurements could give valuable information about the investigated electrical interfacial layer.

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