

## Interfacial Properties of $\alpha$ -FeOOH, Prepared by Two Different Methods

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**Summary:**  $\alpha$ -FeOOH was prepared by two different methods and were designated as sample-1 and sample-2. Point of zero charge (PZC) and surface ionization and complexation constants of both the samples were calculated from the potentiometric titration data of their suspensions in aqueous electrolyte solutions. PZC values of the sample-1 and sample-2 were found to be at pH = 8.4 and 8.2 respectively, which demonstrated a negligible difference. However, the absolute values of their surface charge at the given pH and electrolyte concentration was significantly high for sample-1 as compared with sample-2. This was attributed to the high  $N_s$  values (total number of surface sites) of former sample. Moreover, the numerical values  $\Delta pK_a^{int}$  and  $\Delta pK_{complex}^{int}$  suggested the fact that ionization and complexation reactions were weak in sample-2 as compared with sample-1.

### Introduction

Hydrous oxides of iron are present in soil and sediments in various amorphous and crystalline forms [1-6]. When present in the aqueous environment, they develop pH-dependent surface electrical charges which affect the transport of ionic species in soils and natural aquatic systems. As such, many researchers (7-21) have focused on evaluating the surface characteristic of various oxides and hydrous oxides, so that their behaviour could be predicted under the given environmental conditions. It has been found in most of these studies that besides other factors, the method of preparation of hydrous oxides might have a significant effect on their surface charge properties.

The aim of this work was to investigate the effect of method of preparation on the various surface parameters of  $\alpha$ -FeOOH. This work thus describe the preparation of this oxide by two different chemical methods and their characterization by various physical methods. Furthermore, the method for the estimation of their points of zero charge (PZC) and surface ionization and complexation constants have also been described in detail. The values of these parameters were used to compare the properties of the two solids.

### Results and Discussion

#### Characterization

X-ray diffraction analysis confirmed that both the samples were crystalline in nature and

having the chemical composition of  $\alpha$ -FeOOH. Transmission Electron microscopy showed that both the samples had nearly rod shaped morphological features with different particle sizes (Fig. 1). BET nitrogen adsorption measurements gave the surface area of 26.1 and 7.8  $m^2.g^{-1}$  for sample-1 and sample-2 respectively, which demonstrates the fact that solids of the same chemical composition having different surface areas can be prepared by varying the experimental conditions and the starting materials.

#### Surface charge

Surface charge ( $\sigma_o$ ) of both the samples as a function of pH was estimated from the potentiometric titration data of their suspensions in aqueous solutions of electrolyte (NaCl) using the following equation (14)

$$\sigma_o = F(C_a - C_b + [OH^-] - [H^+])/A \quad (1)$$

where A is the surface area of the solid ( $m^2.g^{-1}$ ), F is the Faraday constant, and  $C_a$  and  $C_b$  are the concentrations of acid and base in  $mol.dm^{-3}$  after addition to the oxide dispersions.

Figure 2 shows surface charge versus pH curves for sample-1. The common-point of intersection of the surface charge/pH curves, corresponding to different concentrations of the electrolyte solution is identified as the point of zero charge (PZC) of this sample. The PZC occurs at pH 8.4 which is reasonably close to the values reported



Fig. 1: Transmission electron micrographs of  $\alpha$ -FeOOH particles: (a) Sample-1, (b) Sample-2. Magnification, 70,000 x.

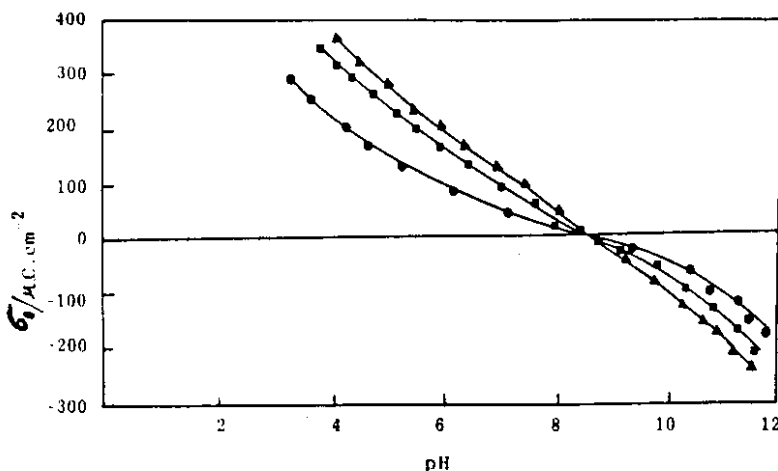


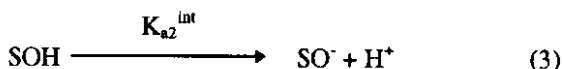
Fig. 2: Surface charge versus pH curves for Sample-1 in aqueous solutions of NaCl: ( $\bullet$ )  $0.001 \text{ mol.dm}^{-3}$ ; ( $\blacksquare$ )  $0.01 \text{ mol.dm}^{-3}$ ; ( $\blacktriangle$ )  $0.1 \text{ mol.dm}^{-3}$ . Solid lines and the legends represent the calculated and experimental values, respectively.

elsewhere for other oxides of iron [12,15]. Furthermore, Figure 2 also depicts that the absolute values of the surface charge increased with the increase in electrolyte concentration. This agrees with the results reported by other workers [12,15-

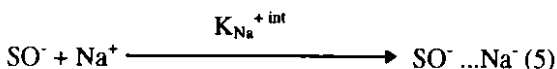
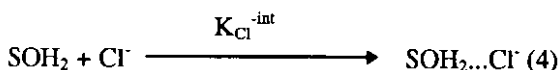
17] for various oxides in aqueous electrolyte solutions.

Effect of electrolyte concentration on the magnitude of the surface charge in aqueous

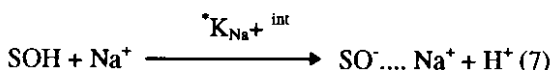
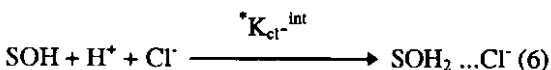
electrolyte solutions can well be explained on the basis of the various reactions taking place at the oxide/electrolyte solution interface. It has been established by various workers [14-17] that the charge development on the hydrous oxides surfaces occur by direct proton transfer on the surface hydroxyl groups according to the following pH dependent surface reactions:



However, the electrolyte ions, if present in the ambient solution, adopt energetically the most favourable option and bind to the surface sites with opposite charge signs as described in the following reaction, for NaCl as the background electrolyte:



The binding of the electrolyte ions with the charged sites may also be described by the following complex ionization reaction, derived from eqns. (2)-(4) as



The surface complex ionization constants, given in eqns (6) and (7) are related to the equilibrium constants described in eqns, (2)-(6) by the following equations, i.e.,

$$*K_{\text{Cl}^-}^{\text{int}} = K_{a1}^{\text{int}} / K_{\text{Cl}^-}^{\text{int}} \quad (8)$$

$$*K_{\text{Na}^+}^{\text{int}} = K_{a2}^{\text{int}} \cdot K_{\text{Na}^+}^{\text{int}} \quad (9)$$

These equilibrium constants, given in eqns (2)-(7) used to characterize the above mentioned ionization and complexation reactions, as described later in this paper.

In fact the electrolyte ions screen the surface charge sites, according to eqns (4) and (5). As such, more surface SOH groups get a chance to generate more surface charged sites [SOH<sub>2</sub>, or SO<sup>-</sup>] according to eqns (2) and (3). Therefore, the increase of concentration of electrolyte in the hydrous oxide suspension suggest a more effective screening of the charged sites and thus resulting high surface charge [24]. This mechanism may thus explain the increase in the absolute values of the surface charge with the increase in electrolyte concentration at the given pH values, as shown in Figure 2.

Surface charge/pH curves for sample-2 is shown in Figure 3 which reveals that the PZC of this sample is at pH 8.2 which is nearly the same as that of sample-1. Identical values of PZC of these two samples suggested that due to the presence of Fe atoms in both the solid's matrices, the companion oxygen atoms may have acquired the same electron densities. As such, identical PZC were obtained since the magnitude of the electron density on the oxygen atom in oxide may generally play a significant role in deciding their PZC values. Furthermore, effect of electrolyte concentration on the absolute values of the surface charge of this sample qualitatively followed the same trend as that of sample-1. However, inspection of Figures 2 and 3 reveals that the magnitude of the absolute values of the surface charge at the given pH and electrolyte concentration is low in sample-2 as compared with sample-1. This difference in the magnitude of the surface charge may be explained in terms of the difference in their N<sub>s</sub> values, since the N<sub>s</sub> values of the hydrous oxide may virtually corresponds to the number of active surface hydroxyl groups. The N<sub>s</sub> values of sample-1 and sample-2 were 25.37 and 19.2 μmol.m<sup>-2</sup>, respectively. As such, more surface OH groups may have taken part in the surface charging processes in the former sample and thus resulted high surface charge density at the given pH and electrolyte concentrations. Moreover, the origin of the different N<sub>s</sub> values of these samples is not quite obvious. As such, one might think of in terms of the morphological features of the their crystalline faces. In sample-1 the presence of the possible disordered crystal faces which may have surface OH groups, easily accessible for the acid/base uptake in N<sub>s</sub> determination experiment. As such,

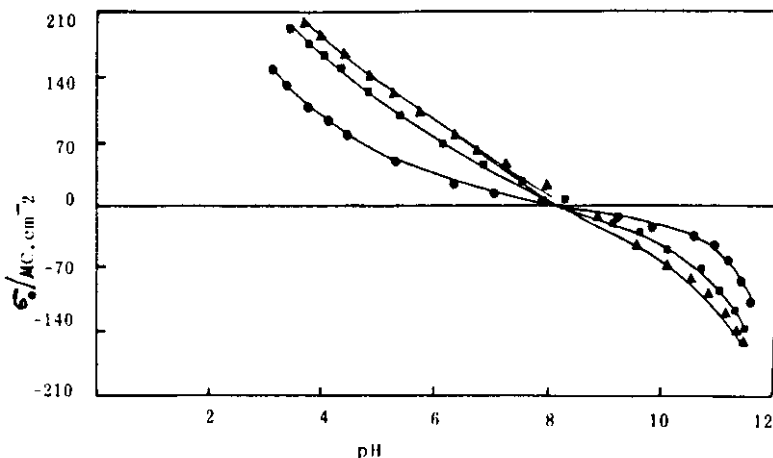


Fig. 3: Surface charge versus pH curves for Sample-2 in aqueous solutions of NaCl: (●) 0.001 mol.dm<sup>-3</sup>; (■) 0.01 mol.dm<sup>-3</sup> (▲) 0.1 mol. dm<sup>-3</sup>. Solid lines and the legends represent the calculated and experimental values respectively.

high values of  $N_s$  and  $\sigma_0$  were obtained for this sample. These results thus suggest the fact that the  $N_s$  value of the hydrous oxides may serve as a valuable guide for the qualitative assessment of their surface charge in aqueous electrolyte solution.

#### Surface ionization and complexation constants

According to eqns. (1) and (2), the surface OH groups of these samples in aqueous solutions may be characterized as diprotic acid  $a \equiv \text{SOH}^+_2$ . Since each loss of proton reduces the charge on the polyacidic surface and affect the acidity of the neighboring group. The acidity constant of the surface thus becomes smaller with increasing the degree of base titration of the oxide suspension. Similarly, this process also affects the binding of the electrolyte anions and cations with charged site, as described in eqns. (4)-(7). However, to estimate the intrinsic surface acidity and complexation constants, described in eqns. (2)-(7). Davis, James and Leckie [14] proposed a method and employed the following equations for the estimation of these constants.

$$\begin{aligned} \text{p}K_{a1}^{\text{int}} &= \text{pH} + \log [\alpha^+/(1-\alpha^+)] + (e \psi_0 / 2.303kT) \\ &= \text{p}Q_{a1} + (e \psi_0 / 2.303kT) \end{aligned} \quad (10)$$

$$\begin{aligned} \text{p}K_{a2}^{\text{int}} &= \text{pH} - \log [\alpha^-/(1-\alpha^-)] + (e \psi_0 / 2.303kT) \\ &= \text{p}Q_{a2} + (e \psi_0 / 2.303kT) \end{aligned} \quad (11)$$

$$\begin{aligned} \text{p}^*K_{\text{Cl}^-}^{\text{int}} &= \text{pH} - \log [\text{Cl}^-] + \log [\alpha^+/(1-\alpha^+)] \\ &\quad + (e \psi_0 - e \psi_\beta) / 2.303kT \end{aligned} \quad (12)$$

$$\begin{aligned} \text{p}^*K_{\text{Na}^+}^{\text{int}} &= \text{pH} + \log [\text{Na}^+] - \log [\alpha^-/(1-\alpha^-)] \\ &\quad + (e - e^-) / 2.303kT \\ &= \text{p}^*Q_{\text{Na}^+} + (e \psi_0 - e \psi_\beta) / 2.303kT \end{aligned} \quad (13)$$

where  $\psi_0$  and  $\psi_\beta$  the potentials at the surface plane [o-plane] and the plane of the adsorbed counter electrolyte ions [ $\beta$ -plane] respectively. Moreover,  $\alpha^+$  and  $\alpha^-$  can be defined as,

$$\alpha^+ = \sigma_0 / N_a \quad [\text{for a positive surface}] \quad (14)$$

$$\alpha^- = \sigma_0 / N_a \quad [\text{for a negative surface}] \quad (15)$$

Since the values of the surface potentials [ $\psi_0$  and  $\psi_\beta$ ], as described in eqns. (10)-(13), are unknown in the Ph range employed in this study, with the exception of the PZC, therefore the values of the constants [ $\text{p}K_{a1}^{\text{int}}$ ,  $\text{p}K_{a2}^{\text{int}}$ ,  $\text{p}^*K_{\text{Na}^+}^{\text{int}}$ ,  $\text{p}^*K_{\text{Cl}^-}^{\text{int}}$ ] cannot be obtained right away from these equations. However, these constants can most precisely be estimated by the graphical procedure, using the double extrapolation technique [25]. Following this method, the values of the experimentally determined  $\text{p}Q_{a1}$  and  $\text{p}Q_{a2}$  were

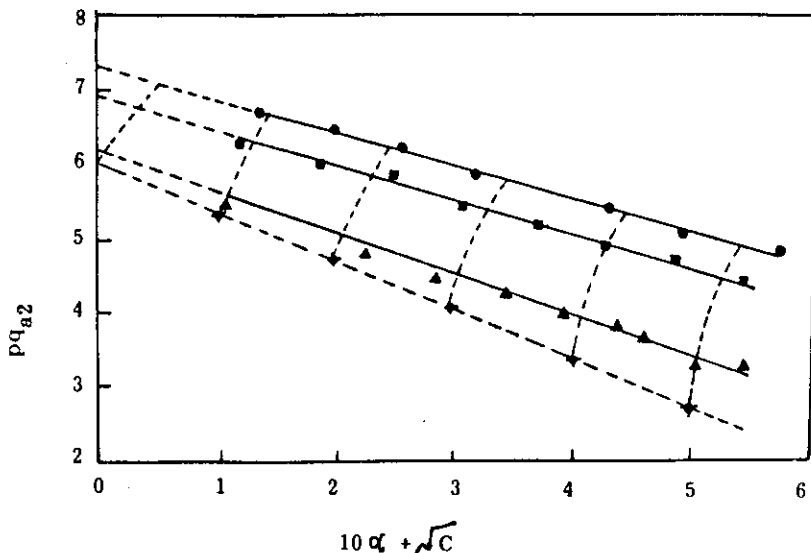


Fig. 4: Variation of  $pQ_{a1}$  as a function of  $\alpha+$  and NaCl concentration for Sample-1 ( $\blacktriangle$ ) 0.001 ; ( $\blacksquare$ ) 0.01; ( $\bullet$ ) 0.1 mol·dm<sup>-3</sup>. The solid lines are experimental ones, whereas the dashed lines and the symbol ( $\blacklozenge$ ) are the extrapolated ones.

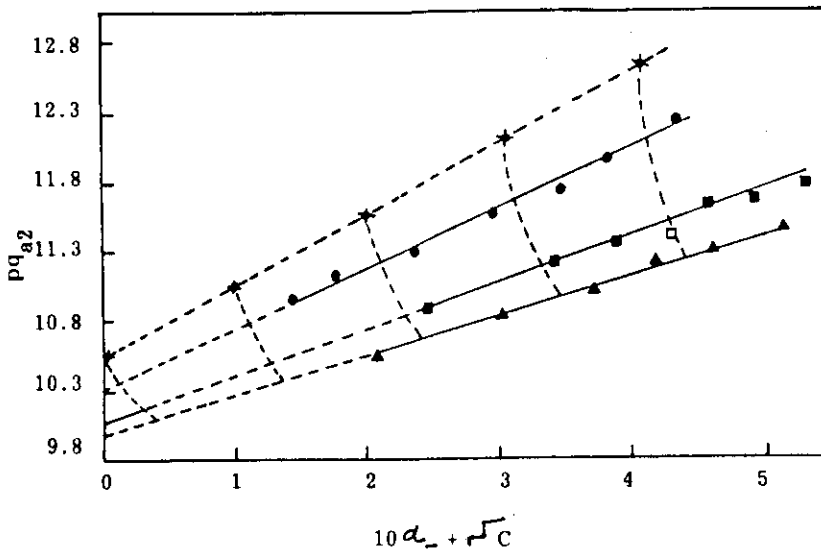


Fig. 5: Variation of  $pQ_{a2}$  as a function of  $\alpha-$  and NaCl concentration for Sample-1; ( $\bullet$ ) 0.001 ; ( $\blacksquare$ ) 0.01; ( $\blacktriangle$ ) 0.1 mol·dm<sup>-3</sup>. The solid lines are experimental ones, whereas the dashed lines and the symbols ( $\blacklozenge$ ) are the extra polated ones.

plotted as a function of  $\alpha+$  and  $\alpha-$  and [NaCl], for both the samples, as shown in Figs (4-7). The lines in these figures were then extrapolated to zero surface charge conditions, and zero electrolyte concentration in order to obtain  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  respectively. The factor 10 in front of  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  respectively. The factor 10 in

front of  $\alpha+$  and  $\alpha-$  and the square root of the NaCl concentration in these figures were chosen for clear graphical representation. Similarly, the values of  $pK_{-Cl}^{int}$  and  $pK_{Na+}^{int}$  were obtained for both the samples by plotting the values of  $p^*Q_{c-1}$  and  $p^*Q_{Na+}$  versus  $\alpha+$  and  $\alpha-$  respectively and extrapolating the lines to zero surface charge

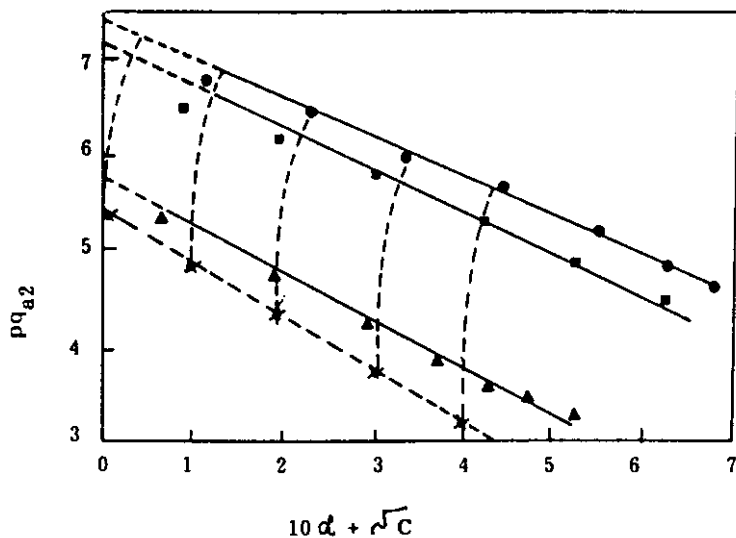


Fig. 6: Variation of  $pQ_{a1}$  as a function of  $\alpha$  and NaCl concentration for Sample-2 ( $\blacktriangle$ ) 0.001 ( $\blacksquare$ ) 0.01; ( $\bullet$ ) 0.1  $\text{mol.dm}^{-3}$ . The solid lines are experimental ones, whereas the dashed lines and the symbols ( $\blacklozenge$ ) are the extrapolated ones.

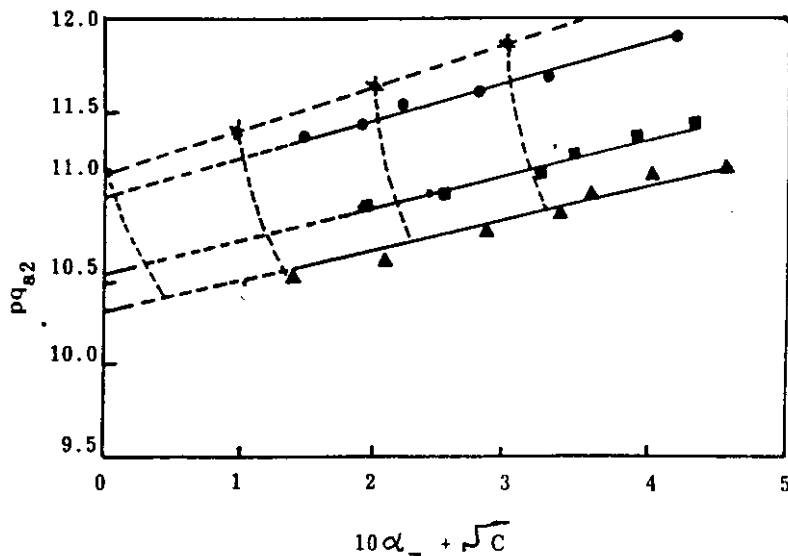


Fig. 7: Variation of  $pQ_{a2}$  as a function of  $\alpha$  and NaCl concentration for Sample-2; ( $\bullet$ ) 0.001; ( $\blacksquare$ ) 0.01; ( $\blacktriangle$ ) 0.1  $\text{mol.dm}^{-3}$ . The solid lines are experimental ones, whereas the dashed lines and the symbols ( $\blacklozenge$ ) are the extrapolated ones.

conditions and 1  $\text{mol.dm}^{-3}$  NaCl solutions. However, these plots have not been included in the text due to brevity. Besides that, the PZC of both the samples were also calculated from the following eqns:

$$(1/2) (pK_{a1}^{\text{int}} + pK_{a2}^{\text{int}}) = \text{PZC} \quad (16)$$

$$(1/2) (p^*K_{\text{cl}}^{\text{-int}} + p^*K_{\text{Na}}^{\text{+int}}) = \text{PZC} \quad (17)$$

All these parameters are summarized in Table-1 and 2 for both the samples. Table-2 reveals that the good agreement between the values of the PZC determined directly from the potentiometric titration data and those calculated from eqns. [16]

Table-1

Sample	$pK_{a1}^{int}$	$pK_{a2}^{int}$	$\Delta pK_2^{int}$	$pK_{ns}^{int}$	$pK_{cr}^{int}$	$\Delta pK_{complex}^{int}$
1.	10.5	6.1	4.4	9.6	6.7	3.1
2.	11.2	5.4	5.8	10.6	6.1	4.5

Table-2

Sample	PZC <sub>calc</sub>	PZC <sub>cal</sub> [Eq.16]	PZC <sub>cal</sub> [Eq.17]
1.	8.40	8.30	8.25
2.	8.20	8.30	8.35

and [17] supporting the method which adopted for the estimation of the constants used in these equations. Similarly, Table-1 reveals that the high values of  $pK_a^{int}$  and  $p^*K_{complex}^{int}$  for sample-2 as compared with sample-1 suggest the fact that both the surface ionization and complexation are weaker in the former sample. In other words, in sample-2 the fraction of the ionized sites are less and those of the neutral sites, remaining on the surface at equilibrium, are large.

#### Validity of the site binding model

Using the basic concept of the site-binding model (14), an attempt was made in this study to model the electrical double layer at the solid-solution interface for both the samples. As mentioned earlier, the electrolyte ions, when present in the oxide dispersion bind to the oppositely charged sites in the  $\beta$ -plane of the electrical double layer and generate the surface potential of  $\psi_\beta$ . As such, the total surface charge ( $\sigma_o$ ) at any electrolyte concentration can be estimated from the following,

$$\sigma_o = (\psi_o - \psi_\beta), C_i \quad (18)$$

where  $C_i$  is the inner layer capacitance of the electrical double layer. The values of  $(\psi_o - \psi_\beta)$  were estimated from eqn 12 and 13, whereas that  $C_i$  were calculated according to the method of Smit and Holten (20) by using eqns [19,20];

$$(dp^*Q_{C1}/d\alpha^+) = - (eN_s/2.3kT)/C_i \quad (19)$$

$$(dp^*Q_{Ns}/d\alpha^-) = - (eN_s/2.3kT)/C_i \quad (20)$$

The values of  $(\psi_o - \psi_\beta)$  and  $C_i$  thus calculated for both the samples at different electrolyte concentrations were substituted in eqns. [18] and the values of surface charge were calculated. The calculated values were compared

with the experimental values as shown in Figs (1 and 2). Good agreement between the calculated and the experimental values indicates the validity of the site-binding model for the two samples of  $\alpha$ -FeOOH, prepared in this study by the two different methods.

#### Experimental

All the chemical used were of analytical grades and were employed without further purification. All the solutions were prepared in doubly distilled water using pyrex glass vessels.

#### Preparation of $\alpha$ -FeOOH

$\alpha$ -FeOOH was prepared by the following two different methods and were designated as sample-1 and sample-2 in the text.

#### Sample-1

For preparing this sample 0.01 mol.dm<sup>-3</sup> solution of iron(III) sulfate solution was refluxed for 15h, during which time a colloidal suspension of iron(II) hydroxide was formed [22]. As such, the suspension was then cooled to room temperature and the solid was separated from the mother liquor by filtration, using membrane filter. The solid was washed several times with doubly distilled water in order to remove any residual impurities. The solid was then redispersed in 200 cm<sup>2</sup> of 0.1 mol.dm<sup>-3</sup> ammonium hydroxide solution, allowed to stay for 1h with constant stirring and then centrifuged. The same process was repeated several times by using fresh ammonium hydroxide solution each times, till no sulfate was detected in the centrifugate of the sample. The solid was finally washed with sufficient amount of doubly distilled water till the washing became neutral. The solid was then dried in an oven at 60°C and stored in a sealed bottle before employing for further investigation.

#### Sample-2

This sample was prepared by the dropwise addition of 250 cm<sup>3</sup> 2.5 mol.dm<sup>-3</sup> solution of potassium hydroxide to a 200 cm<sup>3</sup> of 1 mol.dm<sup>-3</sup> solution of iron(III) nitrate with constant stirring using a magnetic stirrer with a teflon coated magnetic bar [23]. The reaction mixture was then aged for 24h at 60°C. The solid thus formed at the

end of the aging period was separated from its mother liquor by filtration and washed first with 0.1 mol.dm<sup>-3</sup> solution of ammonium hydroxide and then with sufficient amount of doubly distilled water until the washing was neutral. The solid was then dried at 60°C and stored in a sealed glass bottle.

#### Characterization

Both sample-1 and sample-2 were characterized by x-ray diffractometry (JEOL x-ray diffractometer with Mn-filtered Cu-K $\alpha$  radiations), transmission electron microscopy (JEOL-100 CY) and quantasorb surface analyzer (Quantachrome Corporation).

#### Potentiometric titration

Potentiometric titration of the samples were performed under similar experimental conditions. In each case, 0.4g of the solid was dispersed in 100 cm<sup>3</sup> of 0.001 mol.dm<sup>-3</sup> NaCl solution in a glass stoppered titration flask in an ultrasonic bath. The content of the flask was then transferred to a double-walled vessel with a lid having holes for the electrode and nitrogen purging, pH of this dispersion was adjusted to about 3.1 by using standardized 0.1 mol.dm<sup>-3</sup> HCl solution and its temperature was adjusted to 25°C by circulating water through the double walled jacket of the reaction vessel from a thermostated water circulating bath. The oxide dispersion was then allowed to stay for one hour with constant stirring using a magnetic stirrer in the presence of purging nitrogen gas. Titration was then proceeded by the addition of aliquotes of 0.1 cm<sup>3</sup> of 0.1 mol.dm<sup>-3</sup> standardized NaOH solution to the oxide dispersion at the interval of 10 minutes each till ~ pH 11 of the dispersion was obtained. Similar titration experiments were performed on the dispersions of both the samples in 0.01 and 0.1 mol.dm<sup>-3</sup> NaCl solutions. All the pH measurements were made with Orion, Model 900A, digital pH-meter, equipped with a combination glass electrode.

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