

## Effect of Temperature on the Surface Properties of Iron Hydroxide (Am)

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(Received 30th March, 1987)

**Summary:** The surface charge, ionization and complexation of iron hydroxide (Am) in aqueous electrolyte (NaCl) solutions were investigated in the temperature range 25-80°C. The surface charge densities were obtained by fast titration method as a function of pH. Influence of electrolyte concentration on the surface charge density at pH less than the point of zero charge (PZC) decreased as the temperature was increased. Values of PZC and surface ionization and complexation constant ( $pK_{a1}^{int}$ ,  $pK_{a2}^{int}$ ,  $pK_{Cl}^{int}$ ,  $pK_{NA}^{int}$ ) decreased with increasing temperature.  $\Delta H^\circ$  and  $\Delta S^\circ$  for the surface equilibria were also calculated. A simplified model of Davis and Leckie [17] was used to analyse the data. The model described the process reasonably well at low temperatures and at all ionic strengths. However, at higher temperatures, the model broke down due to the over estimation of  $[SOH_2^+ \dots Cl^-]$ .

### Introduction

Iron hydroxide (am) is commonly found in natural aqueous system as a discrete mineral phase and as a surface coating on particulate matter [1]. It plays an important role in controlling the distribution and accumulation of trace metals in many natural water systems [2]. However, iron hydroxide has been extensively characterized for its surface properties i.e. PZC, surface ionization and complexation constants, only at room temperature [3-6]. Therefore, it was considered of interest to study the effect of temperature on its surface properties which would throw light on predicting its adsorption properties at high temperature in many natural and engineering systems.

### Experimental

Iron hydroxide (am) as prepared [4,7] by the dropwise addition of stoichiometric amount of  $CO_3^{2-}$ -free NaOH solution to the acidified (pH ~ 2) solution containing the desired concentration of  $Fe(NO_3)_3$ . The neutralized suspension, containing the precipitate of the iron hydroxide (am), was kept at pH 7 for an hour. Amorphous nature of the hydroxide was confirmed by X-ray diffraction method. The surface area was taken equivalent to  $600 \text{ m}^2 \text{ g}^{-1}$ , considered [5] to be the best estimated value for iron hydroxide (am) [10]. Background electrolyte (NaCl) composition of the suspension were obtained by centrifugation of the appropriate volumes, taken from a stirred suspension and re-dispersing the precipitate in the desired electrolyte solutions. The stock suspension was never used

longer than one week. Iron hydroxide (am) prepared in this way was reproducible adsorbent with well established properties.

Surface charge measurements were performed by the fast titration method. In this method 30 ml of the suspension containing 0.2 g of iron hydroxide (am) in the appropriate background electrolyte concentration was transferred to a double-walled thermostated Pyrex glass cell. pH of the suspension was adjusted to about 4 using  $0.1 \text{ mol. dm}^{-3}$  HCl solution. The suspension was allowed to equilibrate for 2 hours with constant stirring, using magnetic stirrer, at the desired constant temperature. pH was measured ( $\pm 0.005$ ) using precision pH-meter type: OP-205/1 combined with glass and calomel electrodes. The titration experiments were performed at 298, 313, 333 and 353K in 0.1, 0.01 and  $0.001 \text{ mol. dm}^{-3}$  NaCl solutions at each temperature. Titrations were made by the addition of standardized solution of NaOH ( $0.1 \text{ mol. dm}^{-3}$ ) using automatic burette, type: OP-930/1. After each addition (0.2 ml) of strong base the suspension was equilibrated for 3 minutes with constant stirring, at the end of which the pH changes were less than 0.01 units/min. PZC obtained at different temperatures were highly reproducible. The adsorption experiments were performed by taking 30 ml of suspension containing 0.2 g of iron hydroxide (am) in the appropriate background electrolyte concentration, adjusted to the desired pH value with  $0.1 \text{ mol. dm}^{-3}$  NaOH or HCl and allowed to equilibrate for 2 hours with constant stirring. Equi-

librium pH was then measured, suspensions were centrifuged and the supernatants were analysed either for  $\text{Cl}^-$  by Mohr's method or for  $\text{Na}^+$  by flame atomic adsorption spectrophotometry.

### Results and Discussion

The surface charge density on hydrous oxides is defined by the net uptake of protons by the surface and can be determined from the potentiometric titration data of the suspension on the basis of proton balance/electroneutrality condition: [5,8-12].

$$\sigma_0 = F (H^+ - OH^-) = F/A (C_A - C_B + [OH^-] - [H^+]) \quad (1)$$

where  $\sigma_0$  is the surface charge ( $\text{C.cm}^{-2}$ );  $F$  is Faraday's constant ( $\text{C.eq}^{-1}$ );  $H^+$ ,  $OH^-$  is the equivalent of  $H^+$  or  $OH^-$  ions bound to the hydrous oxide surface ( $\text{eq. cm}^{-2}$ );  $C_A$ ,  $C_B$  are the concentration of strong acid or base after each addition during titration ( $\text{eq. l}^{-1}$ ).

#### Temperature effect on surface charge density:-

The variation of surface charge density ( $\sigma_0$ ), calculated from equation (1) of iron hydroxide (am) as a function of pH for three different concentrations of NaCl is shown in Fig.1. The PZC determined from the point of intersection of the  $\sigma_0/\text{pH}$  curves for different electrolyte concentration lied at  $\text{pH} = 7.85 \pm 0.1$ . The value obtained agreed well with the values reported elsewhere [5,7]. Furthermore, the general shape of the curves (Fig. 1) was typical of the reported  $\sigma_0$ -pH curves for synthetic metal oxides [10,13,14]. The surface charge density ( $\sigma_0$ ) versus pH curves for iron hydroxide (am) in different concentrations of NaCl at 313, 333 and 353 K are shown in Fig.2-4. It is clear that the variation of  $\sigma_0$  with NaCl concentration at high temperature is qualitatively similar to that at 298K. However, as is evident from these curves, the effect of NaCl concentration on  $\sigma_0$  is decreased at high temperatures. The PZC data obtained from the potentiometric titration along with  $1/2 \text{ p}K_w$  and ( $\text{PZC} - 1/2 \text{ p}K_w$ ) are given in Table-1. It is clear that the shift in PZC is in the same direction as the change in  $1/2 \text{ p}K_w$ , the neutral point of water. The magnitude of the shift in PZC (0.91 units) is

larger than the change in  $1/2 \text{ p}K_w$  (0.701 units) between the temperature range 298- 353K. The difference in the observed magnitude of the shift in

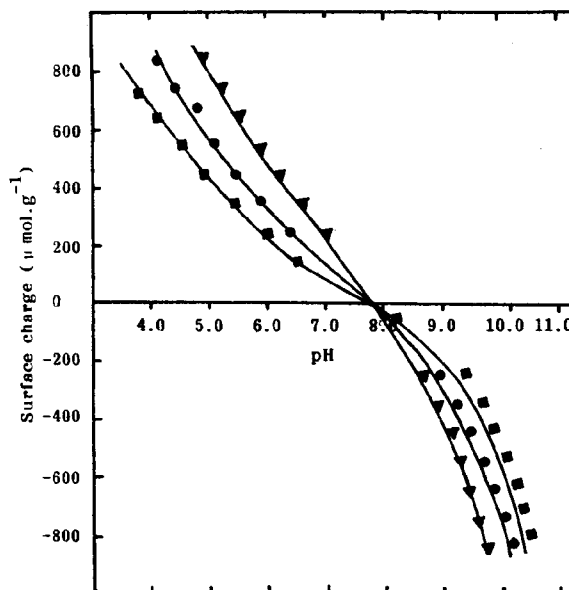


Fig. 1: Variation of the surface charge density ( $\sigma_0$ ) of iron hydroxide (am) as a function of pH at 298K in aqueous solutions of NaCl: (▲)  $0.1 \text{ mol.dm}^{-3}$ ; (●)  $0.01 \text{ mol.dm}^{-3}$ ; (■)  $0.001 \text{ mol.dm}^{-3}$ . Full lines: calculated using Equations (4-12).

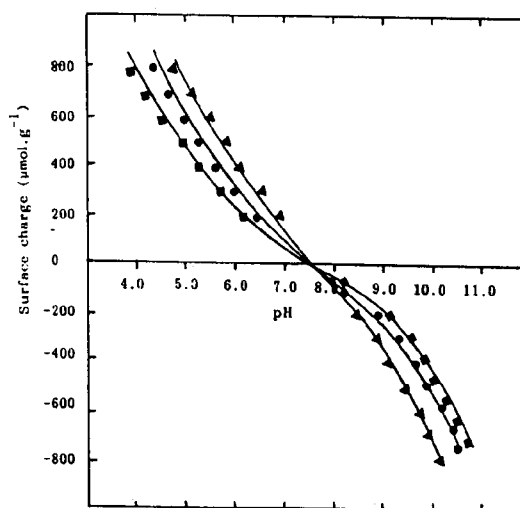


Fig. 2: Variation of the surface charge density ( $\sigma_0$ ) of iron hydroxide (am) as a function of pH at 313K in aqueous solutions of NaCl: (▲)  $0.1 \text{ mol.dm}^{-3}$ ; (●)  $0.01 \text{ mol.dm}^{-3}$ ; (■)  $0.001 \text{ mol.dm}^{-3}$ . Full lines: calculated using Equations (4-12).

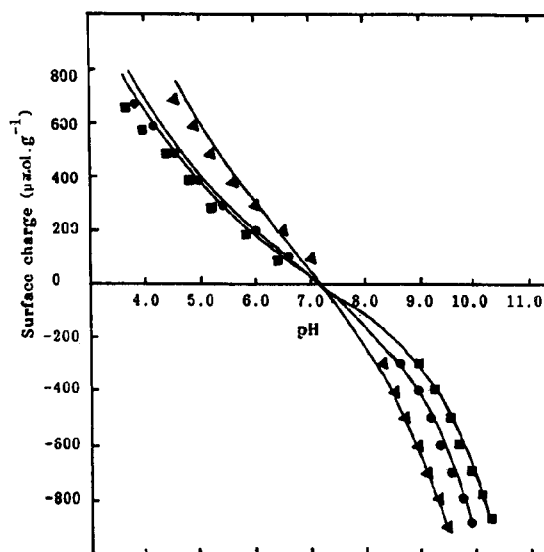


Fig. 3: Variation of the surface charge density ( $\sigma_0$ ) of iron hydroxide (am) as a function of pH at 333K in aqueous solutions of NaCl: (▲) 0.1 mol.dm<sup>-3</sup>; (●) 0.01 mol.dm<sup>-3</sup>; (■) 0.001 mol.dm<sup>-3</sup>. Full lines: calculated using Equations (4-12).

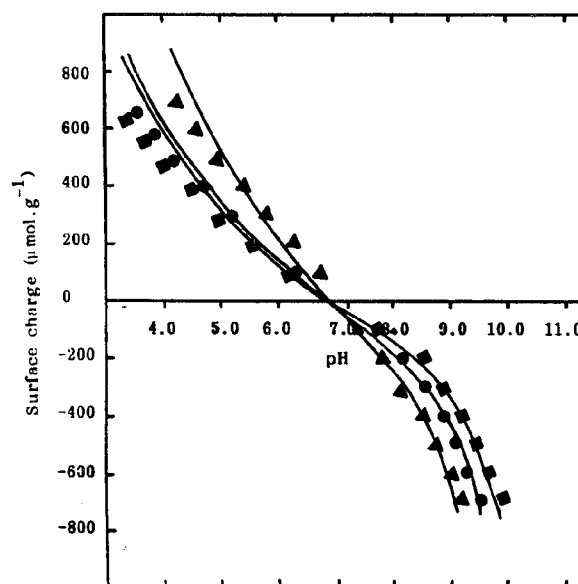


Fig. 4: Variation of the surface charge density ( $\sigma_0$ ) of iron hydroxide (am) as a function of pH at 353K in aqueous solutions of NaCl: (▲) 0.1 mol.dm<sup>-3</sup>; (●) 0.01 mol.dm<sup>-3</sup>; (■) 0.001 mol.dm<sup>-3</sup>. Full lines: calculated using Equations (4-12).

Table 1: Point of zero charge of iron hydroxide (am) at various temperatures

T(K)	PZC	1/2pK <sub>w</sub>	PZC-1/2 pK <sub>w</sub>	ΔG* (kJ.mol <sup>-1</sup> )	δΔS* (J.K <sup>-1</sup> .mol <sup>-1</sup> )
298	7.85	7.000	0.850	-9.699	14.82
313	7.55	6.768	0.782	-9.372	12.21
333	7.22	6.509	0.711	-9.066	9.50
353	6.94	6.299	0.641	-8.664	6.81

PZC compared to the shift in the neutral point, therefore, suggests that the relative affinity of the potential determining ions ( $H^+$ ,  $OH^-$ ) for the hydroxide surfaces varies with the increase in temperature. Similar changes in the affinity of  $H^+$  and  $OH^-$  for the  $Ni(OH)_2$  and  $Co(OH)_2$  surfaces with temperature were observed by Tewari and Combell [15]. The magnitude of the shift in PZC with temperature observed in the present study is of the same order as that observed by Berube and De Bruyn [16] for the rutile/solution interface. Further, Berube and De Bruyn [16] have derived a ther-

modynamic relationship for the variation of PZC with temperature which is given by:

$$4.6R(PZC - 1/2 pK_w) = \Delta S^* - \Delta H^*/T \quad (2)$$

where  $\Delta H^*$  is the standard differential heat of transfer of  $H^+$  and  $OH^-$  ions from the bulk solution to the interfacial region,  $\Delta S^*$  is the difference in standard ionic entropy of hydration of  $H^+$  and  $OH^-$  ions at the PZC, R is the gas constant and T is the absolute temperature.

The data obtained in the present investigation fit Equation (2) and the quantity  $(PZC-1/2pK_w)$  varies linearly with  $1/T$ . Values of  $\Delta H^*$  and  $\Delta S^*$  estimated from the slope and intercept of the linear plot in Fig. 5 are  $-14.93 \text{ kJ mol}^{-1}$  and  $-17.73 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively. Value of  $\Delta H^*$  closely resemble with that obtained from Magnetite in  $\text{KNO}_3$  solutions by Blesa *et al.* [12] but the value of  $\Delta S^*$  is much less than that obtained for Magnetite in the same studies ( $-50 \text{ JK}^{-1} \text{ mol}^{-1}$ ). The value of  $\Delta S^*$  obtained is reasonable, as compared to oxides, hydroxides generally form disordered structure by  $\text{H}_2\text{O}$  penetration. The adsorption process requires penetration for the potential determining ions ( $\text{H}^+$ ,  $\text{OH}^-$ ) into the inner region of this relative orderly liquid phase, which in the present case closely resembles that of the bulk. Similar differences in behaviour of oxides and hydrous oxides were also noted by Tewari and Cambell [15].

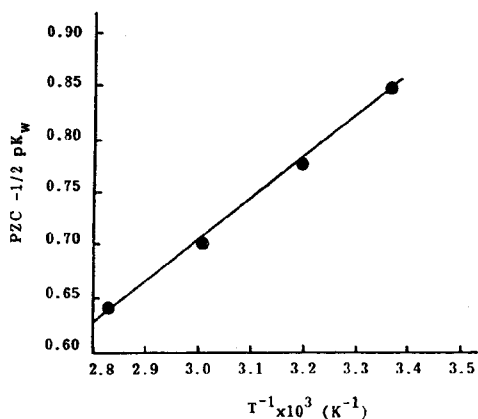


Fig. 5: Plot of  $\text{PZC} - 1/2 \text{ pK}_w$  as a function of  $T^{-1}$  for iron hydroxide (am) in NaCl solutions.

The free energy change  $\Delta G^*$  of the process can be computed using equation:

$$\Delta G^* = RT \ln (a_{\text{H}^+} / a_{\text{OH}^-}) \text{PZC} \quad (3)$$

The right hand side of Equation (3) is an entropic contribution,  $T \Delta S^*$ , which is either equal to or greater than  $\Delta S^*$ . As was pointed out by Blesa *et al.* [13] for most of the oxides  $\Delta H^* = T \delta \Delta S^* = 0$ , leading to  $\delta \Delta S^* = \Delta S^* - \Delta S^{*0} = 0$ . This kind of behaviour ( $\delta \Delta S^* = 0$ ) indicates an absence of the structuring effect of solvent in the interface. How-

ever, in the present investigation (Table 1) positive values of  $\delta \Delta S^*$  are obtained which decrease with the increase in temperature. Comparing the value at 298K with that of Magnetite ( $-46 \text{ JK}^{-1} \text{ mol}^{-1}$ ) [12], as expected, the structuring effect of the solvent in the interfacial region is much less in the iron hydroxide (am)/solution interface. If it is assumed that the dielectric constant of the interfacial water is lower than the bulk water, then at low temperature a decrease in the ionization of water leads to the positive values of  $\delta \Delta S^*$ . However, with the increase in temperature, the dielectric constant of the interfacial region comes closer to that of the bulk, resulting in a decrease in the values of  $\delta \Delta S^*$ .

#### Evaluation of the Surface Ionization and Complexation Constants:

The titration/adsorption data was used to determine surface ionization and complexation constants ( $\text{pK}_{\text{al}}^{\text{int}}$ ,  $\text{pK}_{\text{a2}}^{\text{int}}$ ,  $\text{pK}_{\text{cl}}^{\text{int}}$ ,  $\text{pK}_{\text{Na}^+}^{\text{int}}$ ) according to the methods of Davis *et al.* [17,18]. The involvement of the complex formation in the charging mechanism of the surface is evident from the fact that the intercept  $\text{pQ}_{\text{a1}}$  ( $\alpha_+ = 0$ ) and  $\text{pQ}_{\text{a2}}$  ( $\alpha_- = 0$ ) in Fig.6-7 are dependent upon the concentration of the NaCl. The values of the constants so determined are given in Table-2. The corresponding enthalpy and entropy changes calculated from  $\text{pK}$  versus  $T^{-1}$  plots are given in Table-3.

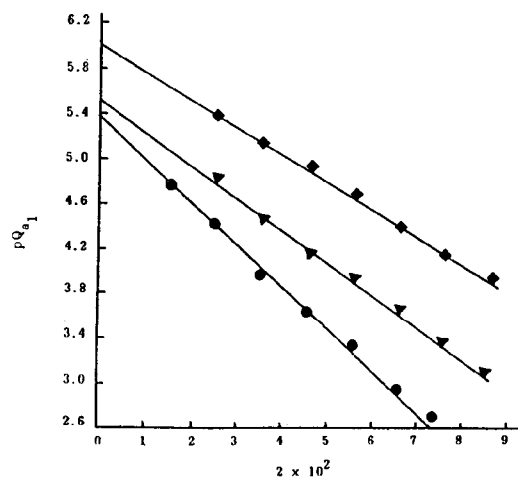


Fig. 6: Plot of  $\text{pQ}_{\text{a1}}$  as a function of surface fractional ionization ( $\alpha_+$ ) for iron hydroxide (am) at 298K in NaCl solutions: (■)  $0.1 \text{ mol.dm}^{-3}$ ; (▲)  $0.01 \text{ mol.dm}^{-3}$ ; (●)  $0.001 \text{ mol.dm}^{-3}$ .

**Table 2: Surface ionization and complexation constants for iron hydroxide (am) at various temperatures.**

T(K)	$pK_{a1}^{int}$	$pK_{a2}^{int}$	$^*pK_{Cl}^{int}$	$^*pK_{Na+}^{int}$	$\log K_{Cl}^{int}$	$\log K_{Na+}^{int}$
298	5.38	10.76	7.00	9.04	1.62	1.72
313	5.14	10.46	6.71	8.76	1.57	1.70
333	4.81	10.12	6.32	8.44	1.51	1.68
353	4.58	9.84	6.04	8.18	1.46	1.66

**Table 3: Enthalpies and entropies of surface ionization and complexation for Iron Hydroxide (am) NaCl solutions**

Surface reaction	$\Delta H^\circ$ (kJ.mol. <sup>-1</sup> )	$\Delta S^\circ$ (J.K. <sup>-1</sup> .mol. <sup>-1</sup> )
$SOH^+_{\cdot 2} = SOH + H^+$	29.313	-4.544
$SOH = SO^- + H^+$	33.247	-94.181
$SOH^{+2} + Cl^- + SOH^+_{\cdot 2} \dots Cl^-$	5.793	11.551
$SO + Na^+ = SO^- \dots Na^+$	-2.143	25.784

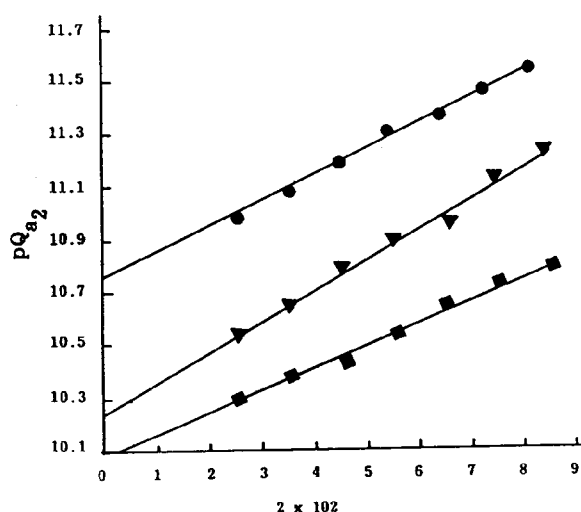


Fig. 7: Plot of  $pQ_{a2}$  as a function of surface fractional ionization ( $\alpha$ ) for iron hydroxide (am) at 298K in NaCl solutions: (■) 0.1 mol.dm<sup>-3</sup>; (▲) 0.01 mol.dm<sup>-3</sup>; (●) 0.001 mol.dm<sup>-3</sup>.

It is clear from Table-2 that all of the  $pK$  values decrease with increasing temperature. The same trend was observed by Blesa *et al.* [12] for the  $pK$  values of Magnetite in  $KNO_3$  solutions. Further, the decrease in the value of  $pK_{a1}^{int}$  and  $^*pK_{Cl}^{int}$  is more pronounced than in  $pK_{a2}^{int}$  and  $^*pK_{Na+}^{int}$ . This can be due to the closer movement of chloride ions as compared to sodium towards the iron hydroxide (am) surface. The pronounced effect of chloride ions was also observed by Maroto [19]. It can also be noted that  $\Delta pK_{a1}^{int}$  ( $= pK_{a2}^{int} - pK_{a1}^{int}$ ) decreases while  $\Delta pK_{complex}$  ( $= ^*pK_{Na+}^{int} - ^*pK_{Cl}^{int}$ ) increasing slightly with the increase in temperature, indicating a slight decrease in the influence of NaCl in the charging mechanism of the iron hydroxide (am) surface.

The negative enthalpy change accompanying the formation of the ion pairs (Table-3) also points towards their diminishing effect, while the temperature is raised. Further, as expected enthalpy change

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