Effect of Temperature and Electrolyte Concentration on the Surface Charge Properties of Fe(OH)₃

[1]Muhammad Irshad, [1]Syed Mustafa, [2]Muhammad Waseem*, [1]Khizar Hussain Shah and [3]Umer Rashid
[1]*National Centre of Excellence in Physical Chemistry, University of Peshawar, Pakistan.*
[2]*Department of Physics, COMSATS Institute of Information Technology 44000, Islamabad Pakistan.*
[3]*Department of Chemistry, Hazara University Mansehra, Pakistan.*
waseem_atd@yahoo.com, m.waseem@comsats.edu.pk*

Summary: Amorphous iron hydroxide was fabricated in the laboratory by precipitation technique. Salt addition and fast titration methods were employed for the determination of zero point charge. The present study is mainly focused on the surface charge, PZC determination from the potentiometric titration data in the temperature range 293 – 323 K and to calculate the thermodynamic parameters during the exchange of surface H^+/OH^- ions. The PZC of the solid was decreased with increasing the temperature of electrolytic solution. The Standard thermodynamic parameters such as ΔH^o and ΔS^o were also determined from Berube and DeBruyn equation, which showed the endothermic nature of potential determining ion H^+/OH^- ions. Further, their freedom in the double layer has lost on account of the electrostatic force of interaction. The positive ΔG^o values are suggesting the nonspontaneous transferring reactions of H^+ and OH^- from the bulk solution to the interfacial region.

Keywords: Potentiometric titration; point of zero charge; surface charge density; thermodynamic parameters; Fe(OH)₃.

Introduction

The appearance of charge on the surface of oxide and the solvent is connected with the proton balance and its equilibrium is determined by acid-base properties of both the surface hydroxyl groups and the solvent molecules. [1-4]. The PZC is a key parameter which explains the behavior of solids in aqueous suspensions where metal oxides/hydroxides develop electrical charges by the process of protonation and deprotonation of the surface proton and hydroxyl groups. This exchange mechanism usually follows the following chemical reactions,

$$SOH + H^+ \rightarrow SOH_2^+ \qquad (1)$$

$$SOH \rightarrow SO^- + H^+ \qquad (2)$$
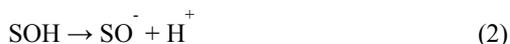
It is perceptible that the surface charge changes with the pH of the solution. As the pH increases, the above equilibrium shift towards the left and the positive charge on the surface of the solids decreases, while the surface of the solid will become more positive when the pH of the aqueous phase decreased. The pH at which the net surface charge approaches to a zero value is defined as PZC. It is the pH at which the net surface charge on oxides/hydroxides becomes zero, which means that at this pH the charge of the positive surface sites is equal to that of the negative ones [5]. Many factors like the nature of sample, degree of hydration, crystallinity, drying and temperature affects the observed PZC value. Generally the PZC ranges from 1-12; however, no system has found a fixed PZC value in the literature [6].

Both temperature and the ionic strength were found to affects the PZC of materials. Temperature is reported to be an important variable which influence greatly the surface ionization and point of zero charge of the oxides and hydroxides [7, 8]. The decrease in PZC of oxides/hydroxides with temperature was reported by Mustafa *et al*. [9, 10] and Valdivieso *et al*. [11].

The PZC is an important parameter used in several applications [12-16]. So far, various methods have been developed for its determination which includes potentiometric titration, mass titration and immersion [17-21]. Microelectrophoresis is also used for the determination of IEP. The IEP is an important parameter and its values are equal to the PZC provided that there is no specific adsorption on the surface of the solid. In present investigation, the PZC of Fe(OH)₃ was determined from the potentiometric titration data in the temperature range 293–323 K.

Results and Discussion

The following techniques were used for studying the surface charge of amorphous Fe(OH)₃.

---

*To whom all correspondence should be addressed.

Point of zero charge by salt addition method

The PZC of iron hydroxide was determined by salt addition method which has already been reported by Kinniburgh *et al.* [22]. The results were obtained by plotting ΔpH versus pHi shown in the Fig. 1. The PZC of the solid is found to be at pH 5. Kosmulski [23] reported PZC values for AlOOH and hematite at the pH values 5.5 and 5.0 respectively.
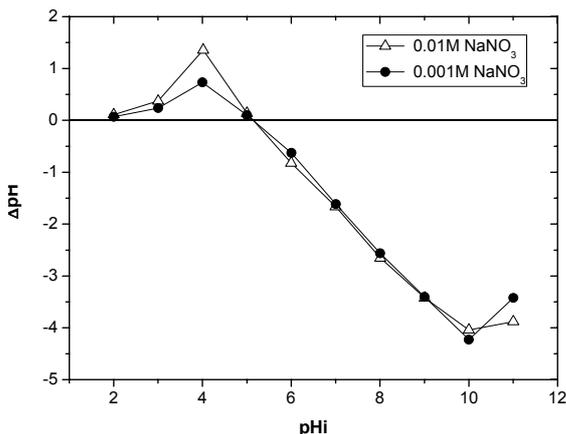

Fig. 1:   PZC of $Fe(OH)_3$ by salt addition method.

It was observed that when the pH values are lower than the PZC, a decrease in pH was observed while adding the sample, which indicates the adsorption of protons by the surface of the solid. Whereas, when the pH values are greater than the PZC, the surface becomes negatively charged. Further, it is also noted from Fig. 1 that the background electrolyte concentration has found no effect upon the PZC of the solid surface, which shows that Na^+ and NO_3^- ions are not adsorbed specifically onto the surface of adsorbent.

Point of zero charge by potentiometric titration method

The PZC values of iron hydroxide at different temperatures were also determined by the potentiometric titration method [24, 25]. The results obtained at different temperatures (293, 303 and 323K) are presented by plotting σ_o versus pH curves as illustrated in Fig. 2-4. Mean surface charge (Q) for the $Fe(OH)_3$ is calculated in different concentrations (0.01 and 0.001M) of background electrolyte ($NaNO_3$) by using the formula

$$Q = C_A - C_B + [OH^-] - [H^+]/m \qquad (3)$$

where C_A (mol/dm^3) and C_B (mol/dm^3) are the concentrations of acid and base added to the suspension, $[OH^-]$ and $[H^+]$ are the concentrations of OH^- and H^+ ions as measured from the pH of the suspension, m is the mass of the $Fe(OH)_3$. The corresponding surface charge is calculated by using the relation

$$\sigma_o = QFS^{-1} \qquad (4)$$

where σ_o ($\mu C/m^2$) is the surface charge density, F (C/mol) the Faraday constant and S (m^2/g) is the specific surface area. In present case, the surface area of $Fe(OH)_3$ was found to be 137 m^2/g which was determined by the BET method of nitrogen adsorption method.
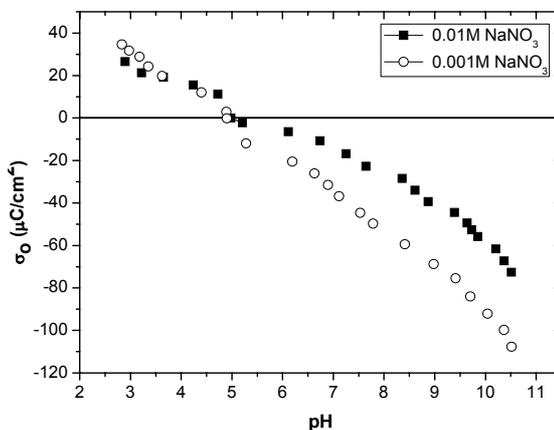

Fig. 2:   Variation of surface charge density of $Fe(OH)_3$ at 293K in different concentration of $NaNO_3$.
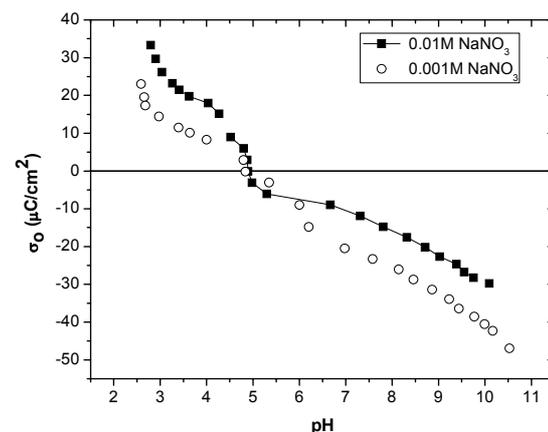

Fig. 3:   Variation of surface charge density of $Fe(OH)_3$ at 303K in different concentration of $NaNO_3$.
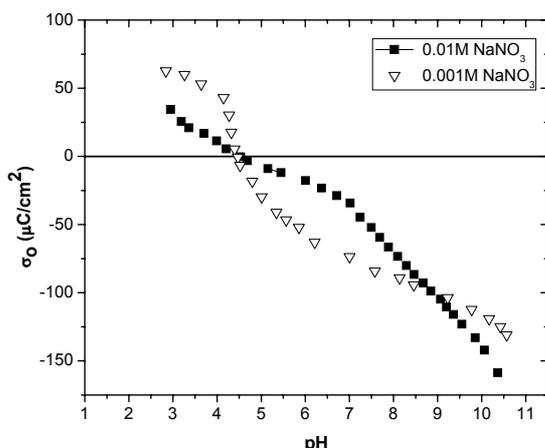
Fig. 4: Variation of surface charge density of Fe(OH)$_3$ at 323K in different concentration of NaNO$_3$.

It can be seen from the Fig. 2-4 that the surface charge densities at different temperatures and concentrations of NaNO$_3$ was found to cross the pH line at the PZC point. These figures further expose the effect of Na$^+$ cations in the charging mechanism of the Fe(OH)$_3$ is greater than the corresponding effect of NO$_3^-$ anions. This behavior is clear as it results in the shifting of surface charge density curves which points towards the shielding effect of the NO$_3^-$ anions at higher concentrations. The effect of Na$^+$ ions on the charging mechanism is however, enhanced with rise in the temperature of the electrolytic solution.

The PZC values determined from the titration curves are reported in Table-1. From this table it can be seen that the PZC of the solid decreases while increasing the temperature from 293 to 323 K. Mustafa *et al* [26] found the PZC of iron hydroxide at pH 4 which is close to the PZC values observed in the present study.

Table-1: PZC of Fe(OH)$_3$ at different temperatures and concentrations.

Temperature (K)	0.01M NaNO$_3$ Observed PZC	0.001M NaNO$_3$ Observed PZC
293	4.98	4.90
303	4.89	4.84
323	4.70	4.47

Thermodynamic Parameters of H$^+$/OH$^-$ Adsorption

For double layer formation on the surface of oxide or hydroxide, Berube and Ball [27] had derived the thermodynamic relationship in the form,

$$4.6R \, [pH_{PZC} - 1/2pK_w] = \Delta S - \Delta H/T \qquad (5)$$

where ΔH is the standard differential heat transfer of potential determining H$^+$ and OH$^-$ ions from the bulk solution to the interfacial region, ΔS is the difference in standard ionic entropy of hydration of H$^+$ and OH$^-$ ions at PZC, R is the gas constant and T is the absolute temperature and PZC is the point of zero charge of the hydroxide.

The quantity pH$_{PZC}$ -1/2 pK$_w$ should decreases with the increase in temperature. The data obtained in the present investigation for hydroxide fit very well in equation (5) and the plots of pH$_{PZC}$ -1/2 PK$_w$ against reciprocal temperature (T^{-1}) give a straight line with R^2 > 0.97 as shown in Fig. 5. The values of ΔH and ΔS were calculated from the slop and intercept are given in the Table-2. The positive value of ΔH not only shows the endothermic nature of the process but also the special structuring effects of the solvent in the interfacial region. The value of ΔH for Fe(OH)$_3$ was found to be 18.67 kJ/mol which is in closed agreement with the value reported by Kallay *et al* [28]. The negative value of ΔS shows an increased interaction of the ions with the hydroxide surface which indicates that due to charge formation; H$^+$ and OH$^-$ ions have mobility in the double layer. The value of ΔS is found to be -16.35 J/mol.K, which is close to the value (-11.93 J/mol. K) reported by Halter while studying the surface acidity constants of Al$_2$O$_3$ at different temperatures [29].
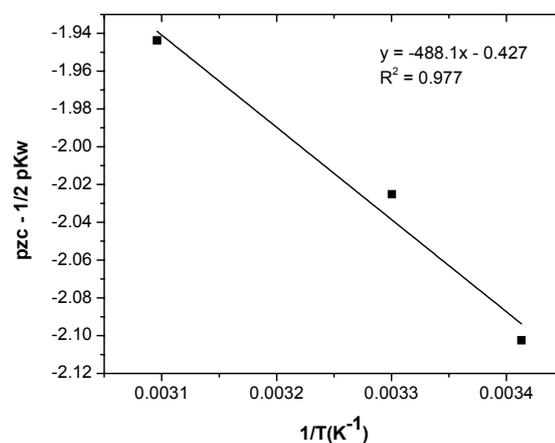

Fig. 5: Plot of PZC-1/2pK$_w$ as a function of T^{-1} for Fe(OH)$_3$ in 0.01mol.dm^{-3} NaNO$_3$ solution.

Table-2: Thermodynamic parameters H$^+$ and OH$^-$ adsorption on Fe(OH)$_3$.

Temperature(K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
293	23.46		
303	23.62	18.67	-16.35
323	23.95		

In present work, the values of ΔG calculated from the thermodynamic relationship (Eq.6) are close to the values reported by Mustafa *et al.* while studying the surface charge properties of Fe_2O_3 in aqueous and alcoholic mixed solvents [30].

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

The positive values of ΔG were found to increase with the increase in temperature, suggesting a decrease in the affinity of the hydroxide towards the potential determining (H^+ and OH^-) ions. This further suggests that the mechanism for the transferring of H^+ and OH^- ions from the bulk solution to the interfacial region is non spontaneous.

Experimental

$Fe(NO_3)_3$ provided by the Scharlau, NaOH by BDH and $NaNO_3$ and HNO_3 were purchased from MERCK. All the chemicals used were of analytical grade having $\geq$ 99.7% purity and were used as received. All the solutions were prepared in double distilled water. $NaNO_3$ solutions having concentration of 0.01 and 0.001M were used as background electrolyte. The pH of the suspension was carefully adjusted with the required amount of standard NaOH and HNO_3 solutions.

Preparation of $Fe(OH)_3$

$Fe(OH)_3$ was prepared by drop wise addition of NaOH and $Fe(NO_3)_3$ solution in a 3:1 ratio. The resulting suspension was aged for three hours at pH 7. The pH of the suspension was adjusted with the help of standard NaOH and HNO_3 solutions by Orion pH meter model 710A. After 24 hours the suspension was decanted and pH of the suspension was adjusted at 7 again. It was then washed with double distilled water and filtered. The solid thus obtained was dried at 105 ^{o}C and ground to fine powder. Finally, the powder was stored in polyethene bottles for further investigations.

PZC by Salt Addition Method

30 ml of 0.01 and 0.001M $NaNO_3$ solutions were taken in 50 ml titration flasks. The pH values of the solutions were adjusted 2 – 11 by using NaOH and HNO_3 solutions. Afterward, 0.2 g of the sample was added to each of the flasks and was shaken for 24 hours in an end to end shaker bath model DAIHAN WSB-30 at a shaking speed of 120 rpm. After equilibration, the final pH of the suspension was noted, and the difference between the initial and final pH (ΔpH) was then plotted against pHi to get the PZC of the solid.

PZC by Potentiometric Titration Method

Potentiometric titration of $Fe(OH)_3$ was conducted in thermostated double-walled Pyrex cell of 100ml capacity with a rubber lid having holes for electrode and microburette. 30 ml of 0.01M $NaNO_3$ as a background electrolyte solution containing 0.2 g sample was equilibrated for 40 min with continuous magnetic stirring, at the desired temperatures (293, 303 and 323 K). Then 1.5 ml of 0.1M HNO_3 was added and the suspension was agitated for 20 minuets more. The new pH value of the suspension was recorded which was then titrated by the addition of 0.2 ml of 0.05M NaOH, delivered by a micro burette of very fine tip. Following each addition of the titrant, the pH of the suspension was recorded every two minutes till it reaches the pH value of 10.5. Similar practice was performed by using 0.001M $NaNO_3$ as a background electrolyte.

Conclusions

The point of zero charge of $Fe(OH)_3$ is found to be in the range 4.47-5.00, which decreases with the increase in temperature from 293 to 323K. The PZC data of the $Fe(OH)_3$ was calculated by using Berube and De-Bruyn equation. The positive value of ΔH and the negative ΔS value show that the sorption of potential determining ions H^+/OH^- is endothermic in nature where the freedom of the metal cations on the surface of the solid is restricted. The ΔG values are found to be positive and an increase in the values with the rise in temperature indicates a decrease in the affinity of the hydroxide towards the potential determining ions.

The present work inquired about many applications as the study of PZC is an important parameter which plays a key role in the process of ore flotation, adsorption of colloidal particles on the surface of various oxides, deposition of corrosion products in steam generators and in water-cooled nuclear reactors for transport of radioactivity.

References

1. C. H. Lia, C. Y. Chen, B. L. Wei and S. H. Yeh. *Water Research*, **36**. 4943 (2003).
2. M. Abdulkarim, N. Darwish, Y. Magdy and A. Dwaidar. *Engineering in Life Sciences*, **2**, 161 (2002).

3. K. Lackovic, M. L. Angove, J. D. Wells and B. B. Johnson. *Journal of Colloid and Interface Science,* **257**, 31 (2003).

4. S. Mustafa, P. Shahida, A. Naeem and B. Dilara, *Langmuir* **18**, 2254 (2002).

5. J. Park, and J. R Regalbuto, *Journal of Colloid and Interface Science*, **175**, 239 (1995).

6. M. Kosmulski, *Langmuir* **13**, 6315 (1997).

7. M. A. Blesa, N. M. Figliolia, A. J. G. Maroto and A. E. Regazzoni, *Journal of Colloid and Interface Science*,**101**, 410 (1984).

8. S. Mustafa, I. Haq and S. Y. Hussain, *Journal of the Chemical Society of Pakistan,* **11**, 200 (1989).

9. S. Mustafa, I. Ahmad and D. Begum. *Journal of Surface Science and Technology*, **7**, 51 (1991).

10. S. Mustafa, P. Shahida, A. Aftab and B. Dilara, *Adsorption Science and Technology*, **15**, 10 (1997).

11. A. L. Valdivieso, J. L. R. Bahena, S. Song and R. H. Urbina, **298**, 1 (2006).

12. G. Sposite, *Environmental Science and Technology*, **32**, 2815 (1998).

13. C. M. Eggleston, G. A. Jordan, *Geochimica et Cosmochima Acta*, **62**, 1919 (1998).

14. W. A. Spieker and J. R. Regalbuto, *Chemical Engineering Science*, **56**, 3491 (2001).

15. B. N. Shelimov, J. F. Lambert and M. Didillon, *Journal of. Molecular Catalysis* A*: Chemical*, **158**, 91 (2000).

16. M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chemical Review*, **95**, 69 (1995).

17. J. S. Noh and J. Schwarz, *Journal of Colloid and Interface Science*, **130**, 157 (1989).

18. G. D. Lyklema and C. H. Rochester, Eds. Academic Press: New York, Chapter 5, (1983).

19. P. Tewari and A. Campbell, *Journal of Colloid and Interface Science*, **55**, 531 (1982).

20. Y. G. Berube and P. L. De Bruyn, *Journal of Colloid and Interface Science*, **27**, 305 (1968).

21. G. A. Parks, *Chemical Review*, **65**, 177 (1965).

22. D. G. Kinniburgh, J. K. Styres and M. L. Jackson, *Journal of Soil Science Society America*, **40**, 796 (1976).

23. M. Kosmulski, *Journal of Colloid and Interface Science*, **337**, 439 (2009).

24. J. A. Davis, R. O. James and J. O. Leckie, *Journal of Colloid and Interface Science*, **63**, 480 (1978).

25. G. A. Parks and P. L. DeBruyn, *Journal of Physical Chemistry*, **66**, 967 (1962).

26. S. Mustafa, B. Dilara, Z. Neelofer, A. Naeem and S. Tasleem, *Journal of Colloid and Interface Science*, **204**, 284 (1998).

27. B. Ball, *Journal of Colloid and Interface Science*, **30**, 424 (1969).

28. N. Kallay, S. Zalac and G. Stefanic, *Langmuir*, **9**, 3457 (1993).

29. W. E. Halter, *Geochimica et Cosmochimica Acta*, **63**, 3077 (1999).

30. S. Mustafa, S. Tasleem, A. Naeem, *Journal of Colloid and Interface Science*, **275**, 523 (2004).