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# Surface charge properties of zirconium dioxide

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## Abstract

Zirconium dioxide, commonly known as zirconia, is an interesting material and is receiving growing attention due to its excellent mechanical properties. The solid was characterized for surface area measurements, scanning electron microscopy (SEM), Energy dispersive X-ray diffractometry (EDX) and potentiometric titrations. Surface titrations were carried out at the temperature range 303 to 323K in the presence of different concentrations (0.1, 0.01 and 0.001mol/dm$^3$) of $NaNO_3$ as a background electrolyte. Surface charge density and point of zero charge (PZC) of $ZrO_2$ were determined from the titration data. Salt addition method was also applied to measure the PZC of the solid. The surface charge densities of $ZrO_2$ were observed to increase with increase in temperature but decrease while increasing the concentration of electrolyte. Further, the PZC was found to decrease with the rise in temperature. However, it was found to increase with increase in concentration of the background electrolyte. The thermodynamic parameters such as $\Delta H$ and $\Delta S$ were also determined from the slope and intercept of the linear plot of (pHpzc - ½ $pK_w$) versus reciprocal temperature (1/T). The values of both the $\Delta H$ and $\Delta S$ were found to be negative, while that of $\Delta G$ were positive. From these thermodynamic parameters, it was suggested that the protonation / de-protonation process of $ZrO_2$ is non-spontaneous.

***Keywords**:* Pointentiometric titration; point of zero charge; protonation; deprotonation; surface charge density

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## 1. Introduction

A variety of inorganic materials like zeolites, magnetite, hematite, hydrated aluminum oxide, titanium phosphate, silicon dioxide, zirconium phosphate, zirconia, titanium oxide and others have been reported that can be used as ion-exchangers, catalysts and adsorbents [1]. The importance of these inorganic materials is due to their variety, chemical stability and extraordinary range of chemical and physical properties, including the properties of bulk and surface layer. The properties of surface and interface of these substances usually play an important role in the overall properties and behavior; both in preparation and use. The surface of many mineral oxides is changed when exposed to the external environment. The presence of hydroxide groups on the surface of oxide develops surface electrical charges in aqueous media. The formation of surface charge is actually a proton balance between the oxide surface and the suspension, and its equilibrium is determined by their acid-base properties**.** The nature and magnitude of surface charge depends upon the electrolyte concentration and pH [2, 3]. The pH dependent surface charging of mineral oxide in aqueous media is a very important field of research; therefore, it is necessary to find an important parameter, point of zero charge (PZC) for such systems. The point of zero charge (PZC or pHpzc) is related to adsorption and is the pH of the mineral surface in the aqueous medium at which that surface has a net neutral charge. At PZC, protonated positive surface sites are balanced by an equal number of de-protonated negative surface sites [4, 5].

Several workers reported PZC as a tool for the determination of chemical properties of soil samples and mineral oxides or hydroxides [6]. The study of PZC also plays an important role in the process of ore flotation, adsorption of colloidal particles on the surface, deposition of corrosion products in steam generators and in water-cooled nuclear reactors for transport of radioactivity [5].

Zirconium dioxide is a white crystalline solid which occurs naturally in the form of mineral, baddeleyite, having a monoclinic structure. It is a very interesting material and is receiving growing attention as a result of its wide use as a catalyst, as

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a refractory, an insulator in transistors in future nano-electronic devices, in oxygen sensors, fuel cells, orthopedic implants and prosthetic dentistry for the fabrication of crowns and fixed partial dentures [7].

The following are the reactions which take place on the surface of zirconia which establish the charge on the ZrOH surface by protonation and deprotonation:

$$ZrOH+H^+ \rightarrow ZrOH_2^+. \quad (1)$$

$$ZrOH \rightarrow ZrO^- + H^+. \quad (2)$$

Thus zirconia particles are either positively or negatively charged with the change in the pH of the solution [8]. The point of zero charge (PZC) of zirconia sample was reported as 5.5 and the isoelectric point (IEP) at pH 5.8. Regazzoni et al. investigated the interfacial properties of mixtures of $ZrO_2$ and Ferric oxide by electrophoretic and potentiometric methods and reported pHpzc values between 6.0 and 6.4 based on their results from three different techniques [9]. Ardizzone and coworkers performed a number of studies of the surface charge on $ZrO_2$ particles and reported pHpzc 7.9 based on potentiometric titration [10]. Palmer et al. studied the adsorption of ions from aqueous solutions on the surface of $ZrO_2$ at a temperature range from 25 to 290 $^{o}$C at various ionic strengths of the background electrolyte NaCl. After various surface titrations they found that the surface charge increase and PZC decrease with an increase in temperature, PZC reaching a minimum of 4.1 by 250 °C [11]. Available literature show the pH of PZC for $ZrO_2$ ranges from 4 to 8, depending on the specific surface properties of the solid [12].

The aim of the present work is to undertake a comprehensive study of the surface charge properties of $ZrO_2$. The main focus is to determine its point of zero charge and the effect of temperature and concentration of background electrolyte on the PZC of $ZrO_2$.

## 2. Experimental

### *2.1. Reagents*

Analytical grade reagents, as received, were used in the present study. All the solutions were prepared in doubly distilled de-ionized water in pyrex glassware. $ZrO_2$ was provided by BDH chemicals (England).

### *2.2. Characterization of zirconium dioxide*

BET surface area was determined by surface area analyzer model Quanta chrome NOVA 1200e (USA) with the method of $N_2$ adsorption. Prior to the analysis, the sample was degassed at a temperature of 77.35 K for 2 h. The morphology of $ZrO_2$ was assessed by SEM of model JSM 5910, JEOL (Japan). To study the elemental distribution on the surface of the oxide, energy dispersive X-ray (EDX analysis was carried out using microanalyzer model INCA-200 (UK).

### *2.3. PZC determination by salt addition method*

The PZC of $ZrO_2$ was determined by salt addition method. 0.2 g of the sample was added to 40 ml of 0.01 M sodium nitrate ($NaNO_3$) solution in titration flasks of 100 ml capacity. The pH of the suspension was adjusted to 2–10 by adding standard nitric acid or sodium hydroxide solutions. The mixture was then kept in an end-to-end water shaker bath for 24 h at 303 K. The final pH value of each suspension was recorded after 24 h of equilibration by using a pH meter model BOECO BT-600 (Germany). The PZC of the sample was calculated by plotting ΔpH (final pH – initial pH) versus pHi.

### *2.4. PZC determination by potentiometeric titration method*

The PZC values of $ZrO_2$ were determined at different temperatures and concentrations of the background electrolyte by the method described elsewhere [13]. Surface titrations of aqueous suspensions of $ZrO_2$ were carried out in double walled pyrex glass cell of 100 ml capacity. The cell was maintained at constant temperature using a thermostatic water bath attached with water circulating pump. To cover the glass cell, a lid with holes for pH meter electrode, and micro burette was used. 40 ml of sodium nitrate solution of appropriate ionic strength having 0.2 g sample of $ZrO_2$ was taken in the cell and was equilibrated for 30 minutes with continuous stirring on a magnetic stirrer. Following equilibration at desired temperature, 2 ml of nitric acid (0.01 M) was then added to the suspension and agitated for 20 minutes. The suspension was titrated against standard solution of sodium hydroxide (0.01 M) added from micro burette of fine capillary. The pH of the suspension was recorded after every 2 minutes till the pH of the solution reached 9. Blank titrations were also performed.

## 3. Results and discussion

### *3.1. Characterization of zirconium dioxide*

The BET surface area of zirconium dioxide was found to be 67 $m^2$/g. The SEM and EDX were also performed (not shown here) and micrograph shows that the solid has no regular shape and size as well as no definite morphology. The EDX analysis confirms the purity of the sample as it represents peaks only for zirconium and Oxygen. Davies et al. also reported similar findings for different samples of $ZrO_2$ [13]. Figure 1 represents the PZC of the solid which was found to be at 3.9. This value is close to that reported elsewhere [11, 12].

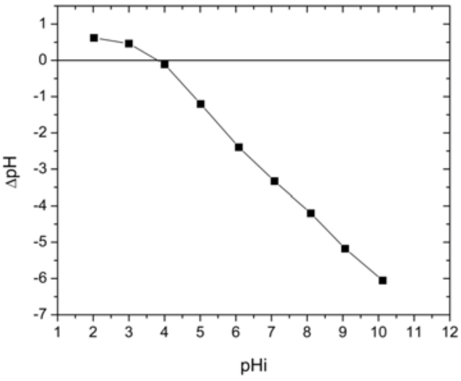

**Fig. 1.** PZC of $ZrO_2$ at 303 K in 0.01 mol /$dm^3$ $NaNO_3$

### *3.2. Potentiometric titration studies of $ZrO_2$*

Figure 2 shows the set of titration curves at 303, 313 and 323 K carried out in the presence of $ZrO_2$ at various ionic strengths of sodium nitrate. From the results, it was observed that the slope increases with the increase in the concentrations of sodium nitrate at specific temperature. Similar trend has also been reported in literature [11].

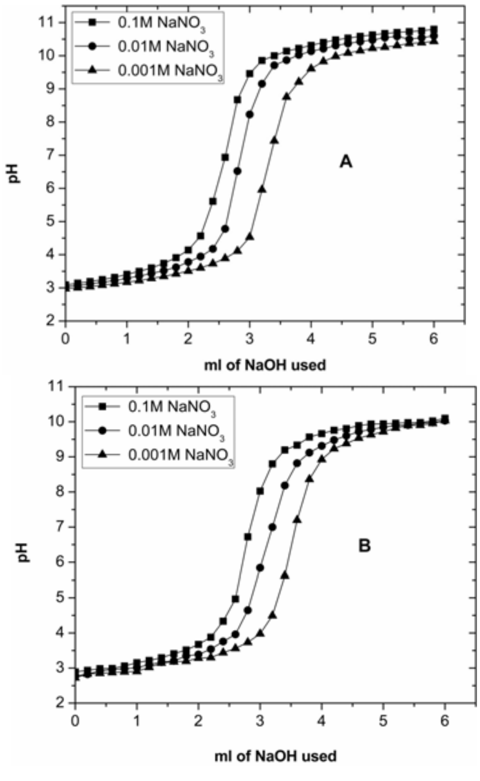

**Fig. 2.** A and B

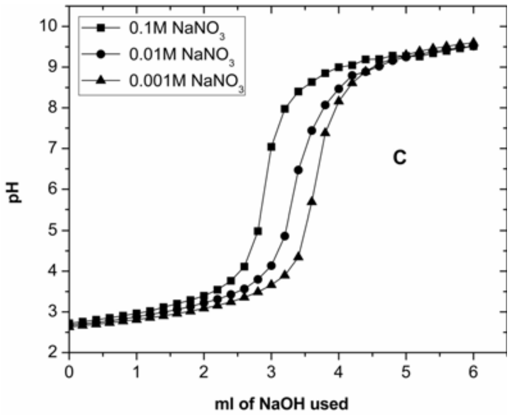

**Fig. 2.** Potentiometric titration curves in presence of $ZrO_2$ at (A) 303 (B) 313 and (C) 323K

Surface titration curves were plotted as pH vs. ml of NaOH observed at different temperatures in the presence of 0.01M sodium nitrate as a background electrolyte (Fig. 3). A shift of the titration curves toward lower pH is observed with increase in temperature in same background electrolyte. This behavior of the curves suggests that the rate of dissociation of proton from the solid oxide surface decreases with the temperature of the electrolytic solution. Similar experiments were also performed in the presence of 0.1M and 0.001M $NaNO_3$ at different temperatures under investigations (not shown here). It is found that both the background electrolyte concentration and temperature have a profound effect on the titration curves. The change in the pH of the suspension from lower to higher values without any breaks indicates that $ZrO_2$ is a cation-exchanger of the weak acid type.

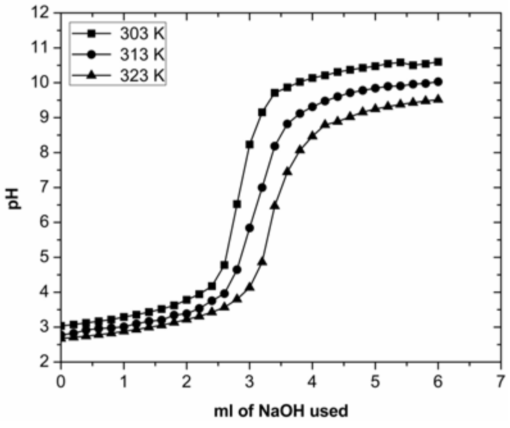

**Fig. 3.** Surface titration curves at various temperature in the presence of 0.01M $NaNO_3$

Mean surface charge, Q was first calculated to evaluate the surface charge density of the solid. The following equations are used:

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

$$\sigma_o = QF/S. \quad (4)$$

### 3.3. Effect of temperature on the PZC of $ZrO_2$

Surface titration curves of $ZrO_2$ showing the effect of temperature on the PZC of $ZrO_2$ are shown in Fig. 4. It is evident from the data that the PZC of $ZrO_2$ decreases with increase in temperature. These curves show that at a given pH, the negative surface charge increases with a rise in temperature. It is due to an increase in proton release from the surface of zirconia. From the aforementioned discussion it is inferred that de-protonation process of $ZrO_2$ is endothermic in nature As a result of deprotonation, the surface of $ZrO_2$ acquire a negative charge, which is counter-balanced by $Na^+$ ions present on the surface. The PZC values of $ZrO_2$ are found to decrease from 4.2 to 3.6, while increasing the temperature from 303 to 323 K in the same ionic strength of background electrolyte. Similarly in 0.01mol /$dm^3$ $NaNO_3$ the PZC for the oxide is found to decrease from 3.9 at 303 K to 3.4 at 323 K and in 0.001 mol /$dm^3$ $NaNO_3$ it decreases from 3.6 at 303 K to 3.2 at 323 K. Similar results have been found by Tewari and McLean for alumina and magnetite [14], Mustafa et al. for Iron hydroxide (amp) [15], Tewari and Campbell for nickel oxide (NiO) [16] and $Co_3O_4$ and Machesky et al. for rutile [17]. Further, the charge densities at different temperatures and at different concentrations of sodium nitrate were found to cross the pH line at the PZC point (point at which $\sigma_o = 0$). The results of these observations are summarized in Table 1.

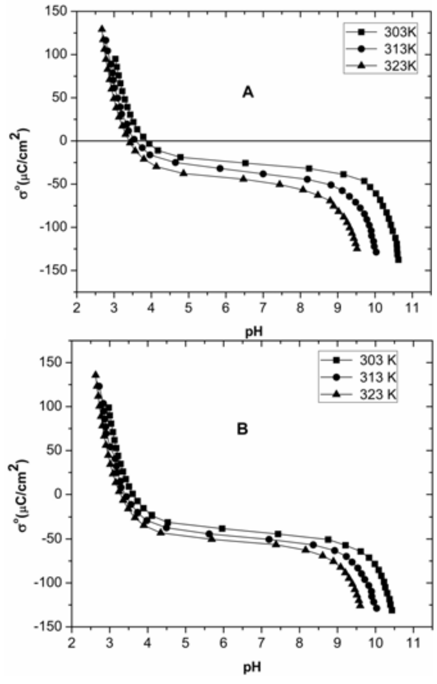

**Fig. 4.** Surface charge density vs. pH of $ZrO_2$ in (A) 0.01 and (B) 0.001 mol /$dm^3$ $NaNO_3$

**Table 1.** PZC of $ZrO_2$ at different temperatures and different ionic strengths of $NaNO_3$

| Observed PZC of $ZrO_2$ | | | |
|---|---|---|---|
| Temp. (K) | 0.1 mol/$dm^3$ $NaNO_3$ | 0.1 mol/$dm^3$ $NaNO_3$ | 0.1 mol/$dm^3$ $NaNO_3$ |
| 303 | 4.2 | 3.9 | 3.6 |
| 313 | 3.8 | 3.6 | 3.4 |
| 323 | 3.6 | 3.4 | 3.2 |

The PZC of $ZrO_2$ is found in the range 4 to 8 [5]. The primary factor for this large range of experimentally observed PZC values near room temperature is that the sample of $ZrO_2$ is amorphous. The decrease in PZC shows that the surface of the solid progressively becomes more negatively charged at high pH and more positively charged at lower pH. Figure 5 shows a relationship of PZC of $ZrO_2$ with temperature which depicts a linear increase in PZC with an increase in temperature. Alternatively, the Fig. shows that the PZC of $ZrO_2$ decreases linearly with decreasing 1/T [18]. It is found that with a rise in temperature, the ionization constant of water changes and hence it may result in the change in PZC of the $ZrO_2$ surface.

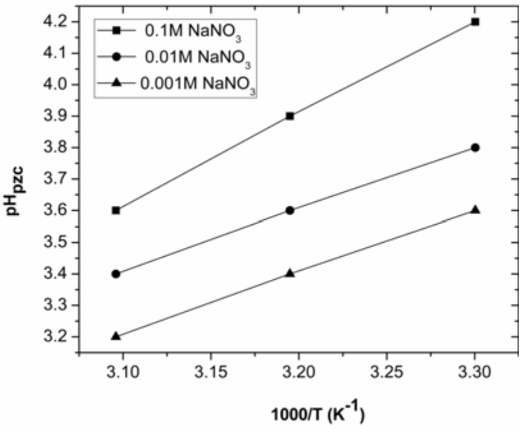

**Fig. 5.** Relationship of $pH_{pzc}$ of $ZrO_2$ with temperature in different concentrations of $NaNO_3$

### 3.4. Effect of background electrolyte concentration on the PZC of $ZrO_2$

The effect of concentration of background electrolyte on the potentiometric titration curves of $ZrO_2$ at different temperatures is shown in Fig. 6. It can be seen that in the charging mechanism of the $ZrO_2$, the effect of sodium ions ($Na^+$) is greater than the corresponding effect of nitrate ions ($NO_3^-$). It shows that shielding effect of the $NO_3^-$ ions increases as its concentration rises. The $Na^+$ ions effect on the charging mechanism, however, is enhanced with the increase in temperature. These curves also show that the PZC of $ZrO_2$ increase with an increase in the concentration of the background electrolyte. Further, the observed PZC decreases from 4.2 to 3.6 at 303 K, 3.8 to 3.4 at 313 K and 3.6 to 3.2 at 323 K with the decrease in the concentration of the background electrolyte. Thus, increase in the ionic strength of the background electrolyte shifts the PZC to the basic region, indicating a higher association affinity for negative ions compared to positive ions.

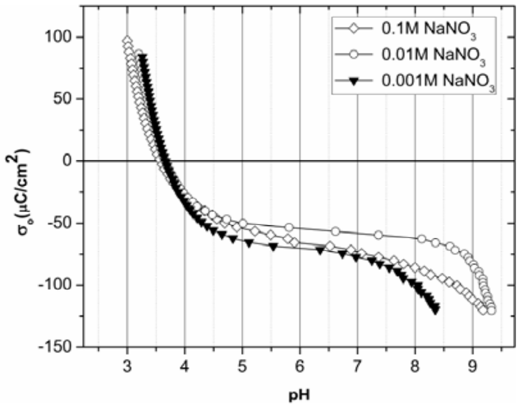

**Fig. 6.** Effect of background electrolyte on the PZC at 313 K

### *3.5. Thermodynamics parameters of surface protonation/ deprotonation*

To evaluate the thermodynamics parameters, the following equations are used [19].

$$4.6R\left[pH_{PZC}-\frac{1}{2}PK_w\right]=\Delta S-\frac{\Delta H}{T} \qquad (5)$$

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

Figure 7 shows that the data obtained in the present investigation fit well in the equation (5). In the present work, a decrease in the quantity ($pH_{PZC}$ – ½ $pK_w$) is observed when the temperature is increased from 303 to 323 K. Similar results are reported elsewhere [14, 18]. The negative values of ΔH and ΔS observed for $ZrO_2$ show that the sorption process is exothermic in nature and the exchange of $H^+$ and $OH^-$ ions takes place in proper order through solid aqueous interface (Table 2). It is evident from the negative value of ΔH that the heat of hydration of the $H^+$ ion being more exothermic for the overall process of the dissociation of the exchanger. This accounts for the distinct surface structure of $ZrO_2$ in the double layer systems. This further depicts that due to the higher hydrophilic nature of the surface, the water molecule will be bound to the surface oxygen of $ZrO_2$ by H-bond and will result in a surface water layer similar to that in the bulk phase.

The positive values of ΔG are found to increase with the temperature of the solution [16, 20]. The free energy values thus show less affinity of $ZrO_2$ towards $H^+$ and $OH^-$, ions which suggests that the transferring reactions of $H^+$ and $OH^-$ from the bulk solution to the interfacial region were non spontaneous.

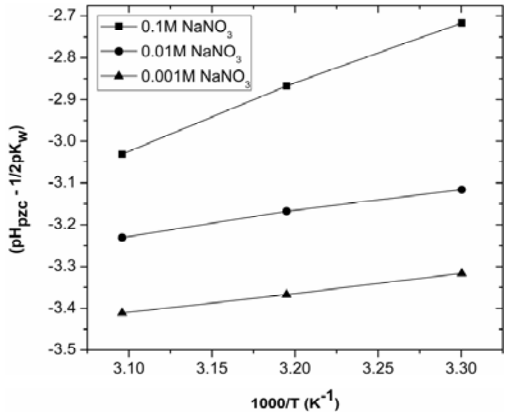

**Fig. 7.** Plot of (pHpzc - ½ $pK_w$) versus 1/T for $ZrO_2$ in different concentrations of $NaNO_3$

**Table 2.** Derived thermodynamic functions for $ZrO_2$

| $NaNO_3$ Concentration | Temperature (K) | ΔG (kJ/mol) | ΔH (J/mol) | ΔS (J/mol K) |
|---|---|---|---|---|
| 0.1mol /$dm^3$ | 303 | 31.43 | -58.78 | -297.77 |
| | 313 | 34.41 | | |
| | 323 | 37.39 | | |
| 0.01 mol /$dm^3$ | 303 | 36.08 | -21.36 | -189.62 |
| | 313 | 37.98 | | |
| | 323 | 39.88 | | |
| 0.001 mol /$dm^3$ | 303 | 37.89 | -17.86 | -184.03 |
| | 313 | 39.73 | | |
| | 323 | 41.57 | | |

## 4. Conclusions

From the above discussion it can be concluded that the background electrolyte concentration and temperature of the system have a profound effect on the titration curves and with increase in temperature, a shift towards lower pH is observed in the presence of same background electrolyte. The variation in the pH of the suspension from lower to higher values without any breaks has been observed in the titration curves depicting that $ZrO_2$ is a weak acid type cation-exchanger. The PZC of $ZrO_2$ is found to increase when the concentration of the background electrolyte increases at a particular temperature. The negative surface charge of $ZrO_2$ increases while PZC decreases with the increase in temperature from 303 K to 323 K at a given pH. The negative value of standard enthalpy, $\Delta H$ observed for $ZrO_2$ show that the sorption process is exothermic in nature. The negative values of standard entropy change, $\Delta S$, illustrate that the potential determining ions are less hydrated at the solid liquid interface. The positive $\Delta G$ values suggest that the dissociation process in non-spontaneous. Moreover, the increase in $\Delta G$ values with a rise in temperature indicates that the deprotonation process is relatively favorable at low temperature.

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