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# Comparison of Different Methods for the Point of Zero Charge Determination of NiO

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**ABSTRACT:** Four methods, fast titration, salt addition, mass titration, and  $\zeta$  potentiometry, were employed to determine the point of zero charge (PZC) and isoelectric point (IEP) of NiO. However, this work mainly focuses on the fast titration method because it limits the release of Ni from the substrate. Furthermore, the fast titration is simple, rapid, and accurate and requires a small quantity of substrate as compared to the salt addition and mass titration techniques. The similarity between the PZC and IEP values rules out the specific adsorption of the bulk electrolyte onto the NiO surface. However, the PZC values shift downward with the increase in Cd ion concentration, which indicates the specific adsorption of Cd onto the NiO. In addition, temperature has a mild effect on the deprotonation constants and PZC of NiO. It was also observed that the thermodynamic parameters favor the deprotonation of NiO.

## INTRODUCTION

Insoluble metal oxides/hydroxides are important class of inorganic ion exchangers and sorbents from water for metals of human health concern. In an aqueous environment, the surface of metal oxides/hydroxides is hydroxylated<sup>1,2</sup> and the hydroxyl groups develop surface electrical charges.<sup>3</sup> Metal oxides are mostly amphoteric,<sup>1</sup> and their surface dissociation may be represented schematically as follows:



where M stands for the solid surface.

The point of zero charge (PZC) is the pH of the suspension at which the net charge on the surface of an insoluble oxide/hydroxide is zero. PZC plays an important role in surface characterization of metal oxides/hydroxides.<sup>3,4</sup> In the environmental science field, PZC determines how easily a substrate can adsorb potentially harmful ions.

Numerous studies<sup>5–10</sup> have determined the PZCs of various metal oxides and hydroxides. Comparison of these studies reveals reports of different PZC values for the same oxide. However, the literature data show that a particular sample of a metal oxide/hydroxide has never a fixed PZC value.<sup>5,6</sup> PZC values are often very divergent; for example, the PZC of aluminum oxide varies from 6.5 to 10 depending on the type of aluminum oxide,<sup>1,11</sup> and PZCs for anatase have been reported in the range of 5.2 to 7.0. Similarly, Schindler et al.<sup>12</sup> and Wieland and Stumm<sup>13</sup> recorded that the PZC for kaolinite varies from 4.0 to 7.5. The values concerning the PZC of Illite clay mineral were also reported to vary from 2.5 to 8.0. This disagreement was attributed to the differences in the origin of samples, to data treatment and to different models used to interpret the experimental data.<sup>14</sup> Experimental methods also account for these discrepancies, as some authors used potentiometric titrations with short equilibration

time while others preferred longer equilibrium times.<sup>15,16</sup> Noh and Schwarz<sup>15</sup> determined the PZC values of TiO<sub>2</sub> in the presence of NaCl solutions. The PZC of TiO<sub>2</sub> was observed to be higher than the PZC measured by the mass titration method.

Several theoretical models have been developed to describe the surface charge properties of the metal oxide/hydroxide. Generally, literature data is available on MnO<sub>2</sub>, Fe(OH)<sub>3</sub>, SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, whereas very little is known about the oxides of divalent metals such as ZnO, CdO, and NiO.<sup>17–19</sup>

This study examines NiO because it is a technologically important material. It has been used as a heterogeneous catalyst and has received considerable attention in recent years for its electronic and magnetic properties.<sup>20,21</sup> Nickel oxide is a very efficient catalyst for many organic and inorganic reactions in the areas of organic synthesis, pharmaceuticals, industrial products, and environmental applications. However, no systematic work<sup>22</sup> has been conducted on the surface charge properties of NiO.

This research compared different techniques to measure the PZC of NiO with a focus on the fast titration method because it limits the release of Ni from the substrate. Fast titration is simple, rapid, and accurate and requires a small quantity of substrate as compared to salt addition and mass titration techniques. During the course of the investigation, we found that the temperature has a mild effect on the deprotonation constants and PZC of NiO. We also observed that the thermodynamic parameters favor the deprotonation process of NiO.

## MATERIALS AND METHODS

**Materials.** Analytical grade reagents were used in this study. All glassware and polyethylene bottles were rinsed with 10%

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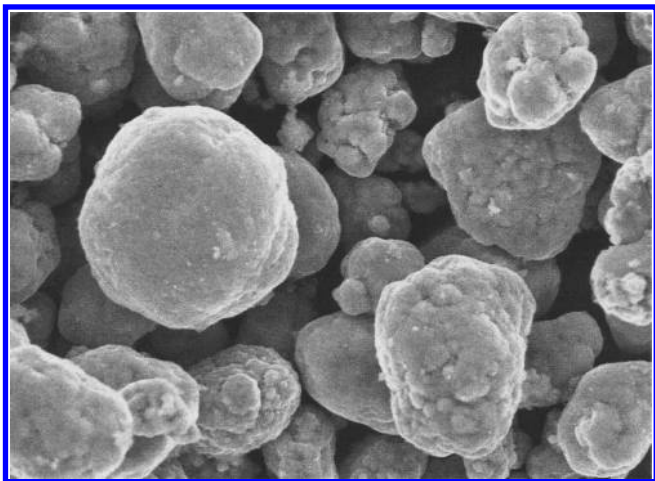


Figure 1. SEM of the virgin sample of NiO.

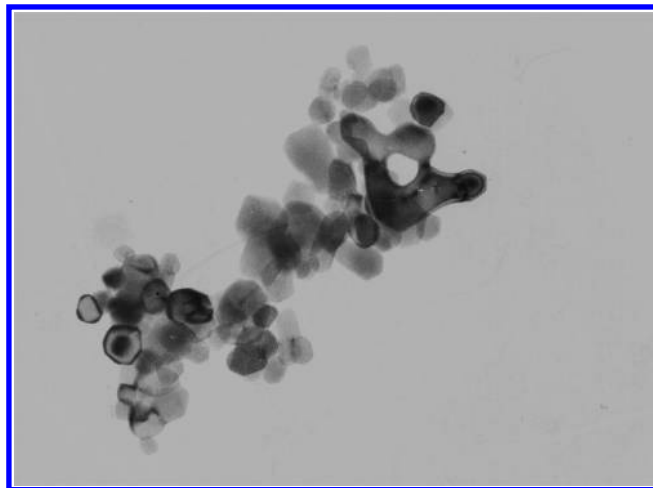


Figure 2. TEM of the virgin sample of NiO.

HNO<sub>3</sub> and deionized water. NiO was purchased from BDH Chemicals Ltd., Poole, England, Product 29235. All PZC experiments were conducted in the presence of nitrogen gas to bubble out carbon dioxide from the system.

**Methods.** *Characterization of NiO.* NiO samples were characterized using X-ray diffractometry (XRD), surface area, thermogravimetric and differential thermal analyses (TGA/DTA), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis, Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). The characterization procedures are similar to those reported elsewhere.<sup>15,22–25</sup>

*PZC by the Salt Addition Method.* PZC values for NiO were determined in  $1 \times 10^{-1}$  M NaNO<sub>3</sub> solution at 303–333 K. In this method, the sample (0.2 g) and  $1 \times 10^{-1}$  M NaNO<sub>3</sub> (40 mL) were mixed in different reaction vessels. The pH of the suspension was then adjusted to an initial pH value of 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11 using either  $1 \times 10^{-1}$  M HNO<sub>3</sub> or  $1 \times 10^{-1}$  M NaOH solutions and an Orion pH-meter model 710 A. Each flask then was vigorously agitated in a shaker bath for 24 h. After settling, the final pH of each suspension was measured very carefully. The  $\Delta$ pH (the difference between final and initial pH) values were then plotted against the initial pH values. The initial pH at which  $\Delta$ pH is zero was taken to be the PZC.<sup>1,26</sup>

*PZC by Mass Titration Method.* NiO mass titration experiments<sup>27</sup> were performed under N<sub>2</sub> atmosphere at constant ionic strength ( $1 \times 10^{-1}$  M) and different temperatures following the method of Noh and Schwarz.<sup>15</sup> Aqueous suspensions containing different amounts of NiO were equilibrated for 24 h and then the pH of each suspension was measured. The PZC was determined from the appearance of a plateau in the pH versus mass of the NiO curve.

*PZC by the Fast Titration Method.* Potentiometric titrations<sup>27,28</sup> of nickel oxide were conducted in temperature controlled double walled pyrex cells covered with rubber lids having three holes for a temperature probe, a fine-tipped microburet, and an electrode. In each titration, 40 mL of background electrolyte solution of a different concentration ( $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$ , or  $1 \times 10^{-1}$  M NaNO<sub>3</sub>) containing 0.2 g of nickel oxide was equilibrated with continuous magnetic stirring at the desired temperature (303, 313, 323, or 333 K) for 40 min. The pH of the system was adjusted using  $1 \times 10^{-2}$  M HNO<sub>3</sub>. After 40 min, when the pH had adjusted completely, the suspension was titrated by addition of 0.2 mL of  $1 \times 10^{-2}$  M NaOH

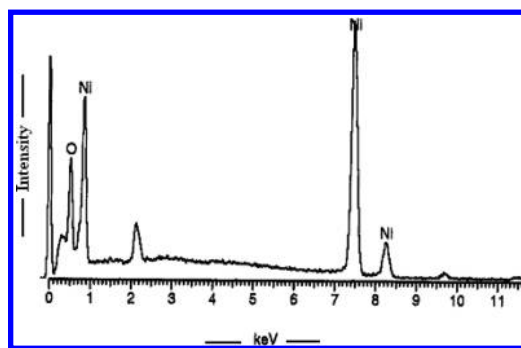


Figure 3. EDX spectrum of the virgin sample of NiO.

delivered by a microburet. The suspension was equilibrated for 2 min with constant stirring after each addition of base, and then the pH was recorded. At the end of the equilibration period, the pH change was less than 0.01 pH units per minute. The electrode was standardized with pH 2.07 and 11.72 buffer solutions.

## RESULTS AND DISCUSSION

**Characterization of NiO.** The XRD measurement showed that the NiO is single-phase with a cubic structure, which is in good agreement with the Joint Committee for Powder Diffraction Standards (JCPDS) card no. 01-1239 for NiO.<sup>29</sup> The NiO surface area determined by the nitrogen adsorption method using the BET equation was  $23 \pm 2$  m<sup>2</sup> g<sup>-1</sup>, which is similar to the literature value<sup>30</sup> and is comparable to the value reported by Tewari and Campbell.<sup>19</sup> The average pore width and micropore volume of NiO were found to be  $1.98 \times 10^2$  Å and  $2.52 \times 10^{-2}$  cm<sup>3</sup> g<sup>-1</sup>, respectively.

SEM in Figure 1 and TEM in Figure 2 revealed that the NiO is spherical, has a porous structure, and is in an aggregated form composed of smaller (2 μm) primary particles. No elements other than Ni and O were detected in the EDX spectrum (Figure 3). As reported in our previous papers,<sup>22,24</sup> the FTIR spectrum has dominant peaks at 3500, 1640, 1350, and 482 cm<sup>-1</sup>, which are the characteristic peaks of NiO.<sup>31</sup> The dissolution study revealed that the amount of Ni released from NiO decreases with increasing pH, and the extent of NiO dissolution is negligible in the pH range 7–11.<sup>22,24,32</sup> NiO

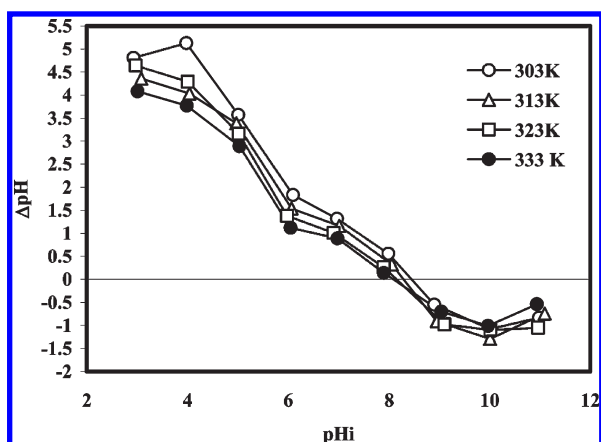


Figure 4.  $\Delta\text{pH}$  versus initial pH of NiO suspensions at different temperatures.

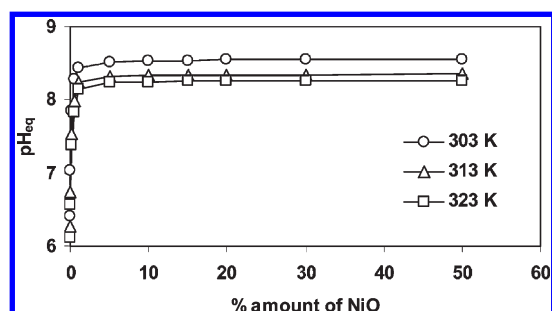


Figure 5.  $\text{pH}_{\text{eq}}$  versus % of NiO at different temperatures.

behaves similarly to CdO and ZnO, as it dissolves slightly in acidic media.<sup>17,18</sup>

**PZC of NiO.** *Salt Addition Method Results.* Addition of NiO to the  $\text{NaNO}_3$  solution changes the pH, which is measured at a fixed ionic strength, as shown in Figure 4. The  $\Delta\text{pH}$  was plotted against the initial pH values, and the PZC is the pH at which  $\Delta\text{pH}$  is zero.<sup>25</sup> In the pH 3–8 range, the  $\Delta\text{pH}$  values are positive with a maximum value at pH 4. The PZC of nickel oxide is 8.45 at 303 K, which is similar to the previously reported PZC<sup>33</sup> and IEP<sup>34</sup> but deviates from the value observed by Tewari and Campbell.<sup>19</sup>

*Mass Titration Method Results.* In Figure 5 the experimental data are plotted in the form of  $\text{pH}_{\text{eq}}$  versus percent of NiO; the  $\text{pH}_{\text{eq}}$  of the suspension increases as NiO increases from 0.001% to 2%. However, after 10% of NiO the pH curves level off. According to Noh and Schwarz,<sup>15</sup> the suspended solid behaves as a pH buffer if increasing quantities of the solid are added into an aqueous electrolyte solution. Then the pH of the suspension becomes closer to the PZC of the material. The PZC of NiO occurs at pH 8.53 at 303 K, which is higher than the PZC value measured by the fast titration method. Moreover, the PZC values obtained from mass titration method at different temperatures are almost similar to the PZC values computed from the salt addition method.

*$\zeta$  Potential Method Results.* The isoelectric point (IEP) of NiO was also determined at 303 K using the  $\zeta$  potentiometer model CAD Nikon Eclipse 50i. The IEP of NiO (Figure 6) is measured as 8.56, which is comparable to the PZC values obtained by mass titration and salt addition. The similarity between the PZC and IEP values shows that no specific adsorption of the bulk electrolyte

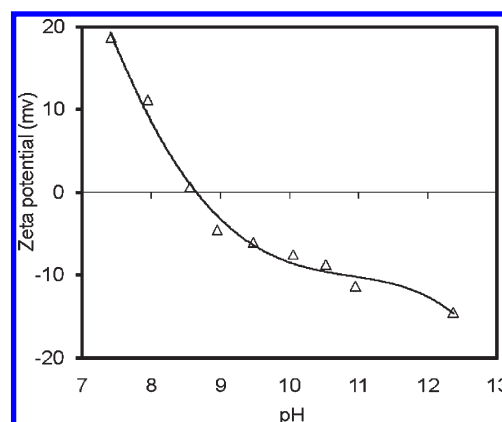


Figure 6. Electrophoretic mobility of NiO as a function of pH in 0.1 M  $\text{NaNO}_3$  at  $303 \pm 1$  K.

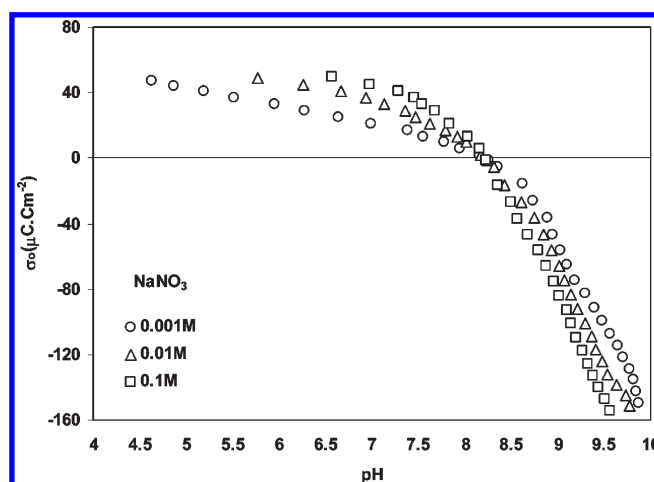


Figure 7. Surface charge density ( $\sigma_o$ ) as a function of pH for NiO in different concentrations of  $\text{NaNO}_3$  solutions at  $303 \pm 1$  K.

onto the NiO surface occurs. The observed IEP is close to the value (8.25) recorded by Moon et al.<sup>35</sup> and lies in the range of 7.80–11.30 reported by Tewari and Campbell,<sup>19</sup> Rao and Finch,<sup>36</sup> and Parks.<sup>5</sup>

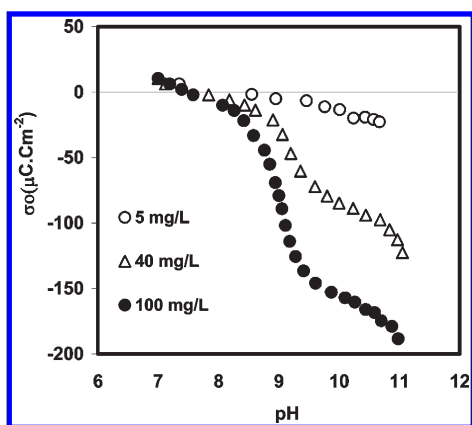
*Fast Titration Method Results.* The surface charge on the NiO was determined<sup>27</sup> from the potentiometric titration data using the following equation:

$$\sigma_o = \frac{F(C_a - C_b) + [\text{OH}^-] - [\text{H}^+]}{mS} \quad (3)$$

where  $\sigma_o$  is the surface charge density ( $\mu\text{C cm}^{-2}$ );  $F$  is the Faraday constant ( $\text{C mol}^{-1}$ );  $C_a$  and  $C_b$  are the concentrations ( $\text{mol dm}^{-3}$ ) of acid and base after addition to the nickel oxide solution;  $[\text{OH}^-]$  and  $[\text{H}^+]$  represent the adsorption densities of  $\text{OH}^-$  and  $\text{H}^+$ , respectively, as measured from the pH of the solution; and  $m$  and  $S$  refer to the mass (g) and surface area ( $\text{m}^2 \text{g}^{-1}$ ) of NiO, respectively.

The surface charge densities ( $\mu\text{C cm}^{-2}$ ) are plotted versus the pH of the suspension, as shown in the representative Figure 7. The surface charge densities do not vary significantly with the increase in background electrolyte concentration from  $1 \times 10^{-3}$  to  $1 \times 10^{-1}$  M  $\text{NaNO}_3$ . The adsorption densities also seem to be insensitive to  $\text{NaNO}_3$  concentration, which indicates the





**Figure 8.** Surface charge density ( $\sigma_0$ ) as a function of pH for NiO in different concentrations of  $\text{Cd}^{2+}$  solutions at  $303 \pm 1$  K.

nonspecific adsorption of  $\text{Na}^+$  and  $\text{NO}_3^-$  onto the surface of NiO. As reported elsewhere, the specific adsorption of cations and anions would shift the PZC toward lower and higher values, respectively.<sup>37</sup> The potentiometric titration curves of the metal oxide/electrolyte systems measured for different ionic strengths have a common intersection point (CIP) which corresponds to the PZC. However, there are systems where a CIP exists but the surface charge at this point does not equal zero ( $\text{PZC} \neq \text{CIP}$ ). In the case of specific adsorption, the PZC may not be equal to the CIP. However, it was observed in the present case that the  $\sigma_0$ -pH curves intersect at a common point irrespective of the electrolyte concentration. As evident from Figure 7, both the PZC and CIP are located at pH 8.25 at 303 K.

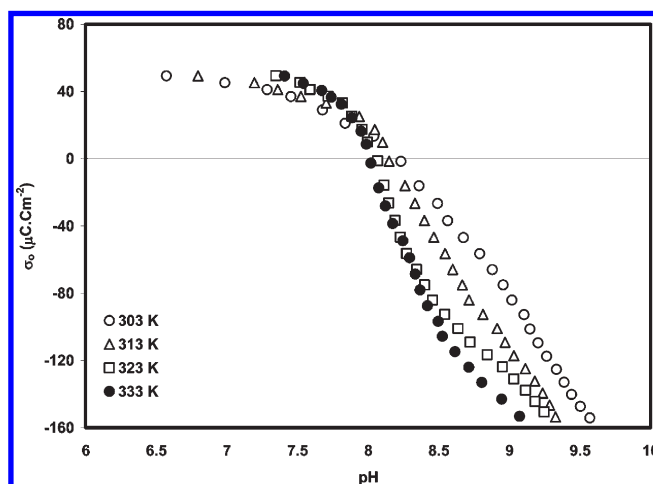
Our findings strongly support the conclusion made by several authors<sup>1,38</sup> that the background electrolyte is inert but are contrary to the results of Jablonski et al.<sup>39</sup> in which the PZC of aluminum oxide shifted from 8.10 to 8.50 as  $\text{Na}_2\text{SO}_4$  concentration increased from  $1 \times 10^{-3}$  to  $1 \times 10^{-1}$  M. These authors attributed this PZC increase to the specific adsorption of  $\text{SO}_4^{2-}$  to the  $\text{AlOH}_2^+$  group of aluminum oxide. A similar shift was observed in the PZC of  $\gamma\text{-Al}_2\text{O}_3$  due to the specific adsorption of  $\text{NO}_3^-$  anions.<sup>38</sup> The observed PZC value (8.25) of NiO is consistent with those reported by Ludwig and Casey<sup>33</sup> for NiO, Mustafa et al.<sup>17</sup> for  $\text{ZnO}$ , and is smaller than the one reported by Tewari and Campbell<sup>19</sup> for NiO. This difference in the PZC may be because of the nature, purity, hydrolysis, and sample preparation history, aging, experimental protocol, or crystallinity of the sample. All these parameters have a pronounced effect on the PZCs of insoluble metal oxides/hydroxides.<sup>40</sup>

The PZC of NiO in the presence of different concentrations of Cd was also investigated at 303 K. As can be seen in Figure 8, the concentration of Cd has a substantial effect on the PZC of NiO, which is 8.13, 7.64, and 7.48 at 5, 40, and  $100 \text{ mg L}^{-1}$  Cd, respectively. The downward shift in the PZC values with the increase in Cd concentration indicates its specific adsorption onto the NiO surface. This behavior is in agreement with the specific adsorption of Cd and Zn ions at the  $\text{Fe}_2\text{O}_3$  surface.<sup>41</sup>

**Comparison of Different Methods.** Classical methods were used to locate the PZC of NiO; Figures 4–7 present the experimental curves corresponding to the different techniques. A close inspection of the data (Table 1) shows that the mass titration and salt addition yield PZC values of 8.53 and 8.45 at 303 K, which are similar in magnitude to the IEP (8.56) of NiO measured by a  $\zeta$  potentiometer. However, the fast and blank

**Table 1.** Effect of Temperature on the PZC of NiO as Determined by Different Techniques in the Presence of 0.1 M  $\text{NaNO}_3$  Solution

temperature (K)	salt addition	mass titration	blank titration	fast titration	calculated PZC
303	8.45	8.53	8.17	8.25	8.33
313	8.28	8.32	8.12	8.14	8.24
323	8.15	8.24	8.04	8.06	8.18
333	8.09	8.19		8.02	8.08



**Figure 9.** Surface charge density ( $\sigma_0$ ) as a function of pH for NiO in 0.1 M  $\text{NaNO}_3$  solutions at different temperatures.

titration techniques measure the PZC values to be at pH 8.25 and pH 8.17, respectively. The similarity among the salt addition, mass titration, and  $\zeta$  potentiometer is probably due to their same equilibration time (24 h) as compared to the fast and blank titration techniques, which have faster equilibrium times (2 min). Moreover, all the classical techniques yield the PZC value for NiO in the range of 8.53–8.17 at 303 K (Table 1). The observed differences in the PZC values of NiO by different methods are almost comparable in magnitude with those reported by Bourikas et al.<sup>27</sup> for  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$  while using several techniques for the determination of their PZC values.

**Effect of Temperature on PZC.** The influence of temperature on the PZC of NiO is shown in Figures 4, 5, and 9 and Table 1. The data illustrate that the  $\text{pH}_{\text{PZC}}$  of NiO decreases as the temperature increases, which indicates desorption of protons from the NiO surface. This decrease in PZC values may also be assigned to changes in the ionization of water with the increase in temperature.<sup>28–30</sup> With the use of the salt addition method, when the temperature is raised from 303 to 333 K, the PZC of NiO decreases from 8.45 to 8.09, whereas in the potentiometric titration it changes from 8.25 to 8.02. Furthermore, the magnitude (small) of the PZC decrease is comparable to those reported elsewhere<sup>1,26</sup> for other metal oxides/hydroxides. A similar decreasing trend in PZC with temperature also was observed with the mass titration technique. Tewari and McLean<sup>42</sup> and Mustafa et al.,<sup>28</sup> who determined the effect of temperature on the PZC of  $\gamma\text{-Al}_2\text{O}_3$ , have made similar suggestions.

**Surface Ionization Constants.** Metal oxides/hydroxides develop a surface electrical charge in aqueous solution because

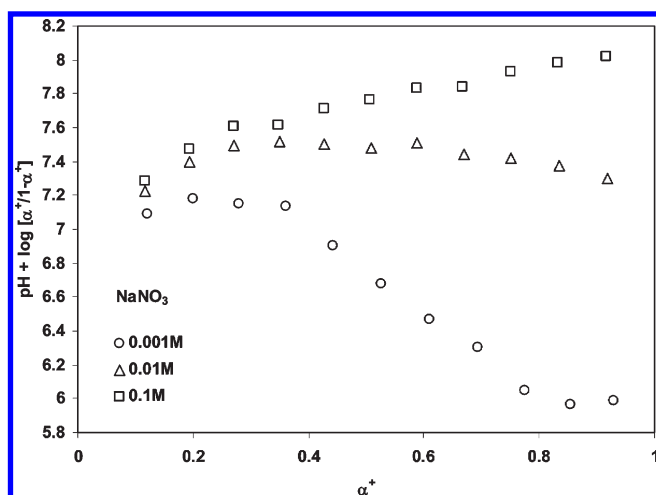


Figure 10. Plots of  $\text{pH} + \log [\alpha^+ / 1 - \alpha^+]$  versus  $\alpha^+$  for NiO in different concentrations of  $\text{NaNO}_3$  solutions at  $303 \pm 1$  K.

Table 2. Calculated PZC and Dissociation Constants ( $\text{pK}_1$  and  $\text{pK}_2$ ) for NiO in the Presence of Different Concentrations of  $\text{NaNO}_3$  Solutions at  $303 \pm 1$  K

$\text{NaNO}_3$ concn (M)	$\text{pK}_1$	$\text{pK}_2$	calculated PZC = $1/2(\text{pK}_1 + \text{pK}_2)$
$1 \times 10^{-3}$	6.60	10.38	8.49
$1 \times 10^{-2}$	6.52	10.34	8.43
$1 \times 10^{-1}$	6.36	10.30	8.33

of the amphoteric dissociation of surface hydroxyl groups after hydration of the surface.<sup>2,3</sup> The surface charge on NiO may be interpreted by a 2 pK model according to the following reactions:



where  $\text{NiOH}_2^+$ ,  $\text{NiOH}$ , and  $\text{NiO}^-$  refer to the positive, neutral, and negative groups on the NiO surface, respectively, and  $\text{H}_s^+$  represents the concentration of surface protons.

The intrinsic NiO acidity constants  $\text{pK}_1$  and  $\text{pK}_2$  were determined from potentiometric titration data by applying the triple layer model (TLM) of Davis et al.<sup>1,17</sup> in the form

$$\text{pK}_1 = \text{pH} + \log \left[ \frac{\alpha^+}{1 - \alpha^+} \right] + \left[ \frac{F\Psi_o}{2.3RT} \right] \quad (6)$$

$$\text{pK}_2 = \text{pH} - \log \left[ \frac{\alpha^-}{1 - \alpha^-} \right] + \left[ \frac{F\Psi_o}{2.3RT} \right] \quad (7)$$

where  $\alpha^\pm = \sigma^\pm / \sigma_m$ ,  $\sigma_m$  is the maximum surface charge density;  $\sigma^+$  and  $\sigma^-$  represent the surface charge densities ( $\mu\text{C cm}^{-2}$ ) below and above the PZC of nickel oxide, respectively;  $F$  is the Faraday constant ( $\text{C mol}^{-1}$ );  $\Psi_o$  is the potential mean in the plane of the surface;  $R$  is the gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ); and  $T$  is the absolute temperature (K).

The plots of  $\text{pH} \pm \log [\alpha^\pm / 1 - \alpha^\pm]$  versus  $\alpha^\pm$  were extrapolated to  $\alpha^\pm = 0$  using Microsoft Excel 5 to determine

Table 3. Calculated PZC and Dissociation Constants ( $\text{pK}_1$  and  $\text{pK}_2$ ) for NiO in the Presence of 0.1 M  $\text{NaNO}_3$  Solutions at Different Temperatures

temp (K)	$\text{pK}_1$	$\text{pK}_2$	calculated PZC = $1/2(\text{pK}_1 + \text{pK}_2)$	observed PZC
303	6.36	10.30	8.33	8.25
313	6.24	10.23	8.24	8.14
323	6.18	10.18	8.18	8.06
333	6.06	10.10	8.08	8.02

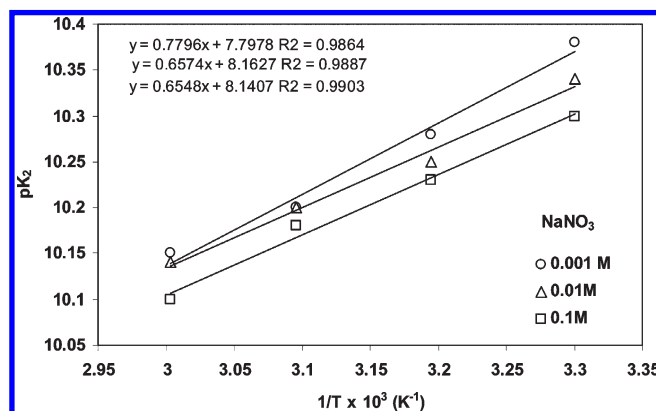


Figure 11.  $\text{pK}_2$  versus  $1/T$  for NiO in different concentrations of  $\text{NaNO}_3$  solutions.

the values of the acidity constants, as shown in Figure 10. The calculated values of the NiO acidity constants at different  $\text{NaNO}_3$  concentrations and temperatures are listed in Tables 2 and 3, respectively. The background electrolyte concentration has a mild effect on the first acidity constant ( $\text{pK}_1$ ) of NiO (Table 2). However, it has no effect on the second acidity constant ( $\text{pK}_2$ ) of the NiO. As expected, a change in the ionic strength would not disturb the NiO surface charge considerably because of the nonspecific adsorption of both the cation and anion. The  $\text{pK}_1$  and  $\text{pK}_2$  values are consistent with those reported for other metal oxides/hydroxides.<sup>6</sup>

Both  $\text{pK}_1$  and  $\text{pK}_2$  values (Table 3) decrease as temperature increases, which consequently results in a decrease in  $\alpha^+$  and  $\alpha^-$ . Thus, as temperature rises, the amount of  $\text{NiOH}_2^+$  decreases while the amount of  $\text{NiO}^-$  increases according to reactions 4 and 5, respectively. The acidity constants were used to calculate the PZC of NiO using the relationship

$$\text{PZC} = \frac{1}{2}(\text{pK}_1 + \text{pK}_2) \quad (8)$$

The experimental and calculated PZC values agreed well (Table 3). A good agreement between the PZC values measured from the fast titration and those calculated from the dissociation constants ( $\text{pK}_1$  and  $\text{pK}_2$ ) further validates the method used for the determination of the surface acidity constants. Direct comparison of the acidity constants with the literature is not possible because to our knowledge no previous studies have examined the effects of electrolyte concentration and temperature on NiO acidity constants.

**Thermodynamic Parameters.** van't Hoff<sup>28</sup> derived a thermodynamic equation that relates acidity constants to the temperature of a system. From the linear plots of  $\text{pK}$  ( $\text{pK}_1$  and  $\text{pK}_2$ ) versus  $1/T$ , one can obtain a gradient ( $\Delta H/R$ ) and intercept

**Table 4.** Thermodynamic Parameters Calculated from Dissociation Constants ( $pK_1$  and  $pK_2$ ) for NiO in the Presence of Different Concentrations of  $\text{NaNO}_3$  Solutions

molar concn $\text{NaNO}_3$	$\text{NiOH}_2^+$ (group)		$\text{NiOH}$ (group)	
	$\Delta H_1$ (kJ/mol)	$\Delta S_1$ (J/mol.K)	$\Delta H_2$ (kJ/mol)	$\Delta S_2$ (J/mol.K)
$1 \times 10^{-1}$	27.33	−35.86	14.94	−149.32
$1 \times 10^{-2}$	26.87	−36.15	12.58	−156.30
$1 \times 10^{-3}$	18.54	−60.54	12.54	−155.88

$(-\Delta S/R)$  according to eq 9:

$$pK = -\frac{\Delta S}{R} + \frac{\Delta H}{R} \frac{1}{T} \quad (9)$$

We determined the enthalpies ( $\Delta H$ ) and entropies ( $\Delta S$ ) for the deprotonation of the surface  $\text{NiOH}_2^+$  and  $\text{NiOH}$  groups from the slope and intercept, respectively, of the linear plots (Figure 11). The computed values of both thermodynamic parameters are given in Table 4. As expected, the enthalpy values ( $\Delta H_1$ ) for the deprotonation of surface  $\text{NiOH}_2^+$  are higher than the enthalpy values ( $\Delta H_2$ ) of the  $\text{NiOH}$  groups. The positive enthalpy for proton dissociation may also result from the endothermic contribution from the dissociation of water. The enthalpy values in the current study are comparable with those determined by Morel et al.<sup>43</sup> for alumina and within the range suggested for the proton desorption enthalpies of metal oxides/hydroxides.<sup>1,44</sup> However, the present findings do not agree with the negative  $\Delta H$  values reported<sup>28</sup> for  $\gamma\text{-Al}_2\text{O}_3$ .

Moreover, the negative  $\Delta S$  values for the deprotonation of NiO indicate a loss in entropy, which further illustrates that the potential-determining ions are less hydrated at the solid–liquid interface as compared to the bulk phase. These entropic values are in fair agreement with results reported for  $\text{ZnO}$ .<sup>45</sup> Overall, the thermodynamic parameters show that the positive value of enthalpy is the driving force for the deprotonation of the nickel oxide surface.

## CONCLUSIONS

The NiO PZC values determined by potentiometric titration, mass titration, and salt addition are 8.25, 8.53, and 8.45, respectively, at 303 K. The slight differences in the PZC values diminish at higher temperatures, and the nice agreement indicates the validity of all the experimental methods tested here. The resemblance between the PZC and IEP reveals that no specific adsorption of the electrolyte occurs at the  $\text{pH}_{\text{PZC}}$  of NiO. The downward shift in the PZC values with the increase in Cd ion concentration indicates its specific adsorption onto the NiO surface. The decrease in the intrinsic acidity constants ( $pK_1$  and  $pK_2$ ) and PZC values as temperature increases suggests that the relative affinity of the potential-determining ions ( $\text{H}^+$  and  $\text{OH}^-$ ) for the NiO surface varies with temperature. The negative values of entropy ( $\Delta S$ ) suggest that the potential-determining ions are relatively less hydrated at the interfacial region than the in bulk phase. Overall, the thermodynamic parameters show that the positive value of enthalpy is the driving force for the deprotonation of the nickel oxide surface.

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## REFERENCES

- (1) Anderson, M. A.; Rubin, A. J. *Adsorption of Inorganic at Solid Liquid Interfaces*; Ann Arbor Science Publishers: Ann Arbor, MI, 1981; Chapter 1.
- (2) Sposito, G. On Points of Zero Charge. *Environ. Sci. Technol.* **1998**, *32*, 2815.
- (3) Schoonen, M. A. A. Calculation of the Point of Zero Charge of Metal-Oxides Between 0 and 350 °C. *Geochim. Cosmochim. Acta* **1994**, *58*, 2845.
- (4) Bourikas, K.; Kordulis, C.; Lycourghiotis, A. Differential Potentiometric Titration: Development of a Methodology for Determining the Point of Zero Charge of Metal (Hydr)Oxides by One Titration Curve. *Environ. Sci. Technol.* **2005**, *39*, 4100.
- (5) Parks, G. A. The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems. *Chem. Rev.* **1965**, *65*, 177.
- (6) Mahmood, T.; Saddique, M. T.; Naeem, A.; Mustafa, S.; Dilara, B. Cation Exchange Removal of Zn from Aqueous Solution by NiO. *J. Non Cryst. Solids* **2011**, *357*, 1016.
- (7) Kosmulski, M. pH-Dependent Surface Charging and Points of Zero Charge III. Update. *J. Colloid Interface Sci.* **2006**, *298*, 730.
- (8) Naeem, A.; Westerhoff, P.; Mustafa, S. Vanadium Removal by Metal (Hydr)Oxide Adsorbents. *Water Res.* **2007**, *41*, 1596.
- (9) Mustafa, S.; Naeem, A.; Hamid, A. Effect of Temperature and Solvent Composition on the PZC of  $\text{Fe}_2\text{O}_3$ . *Phys. Chem.* **2003**, *14*, 1.
- (10) Mustafa, S.; Tasleem, S.; Naeem, A. Solvent Effect on the Electrophoretic Mobility and Adsorption of Cu on Iron Oxide. *Colloids Surf. A* **2008**, *330*, 8.
- (11) Sen, T. K.; Sarzali, M. V. Removal of Cadmium Metal Ion ( $\text{Cd}^{2+}$ ) from its Aqueous Solution by Aluminum Oxide ( $\text{Al}_2\text{O}_3$ ): A Kinetic and Equilibrium Study. *Chem. Eng. J.* **2008**, *142*, 256.
- (12) Schiendler, P. W.; Leichti, P.; Westall, J. C. Adsorption of Copper, Cadmium and Lead from Aqueous Solution to the Kaolinite Water Interface. *Neth. J. Agric. Sci.* **1987**, *35*, 219.
- (13) Wieland, E.; Stumm, W. Dissolution Kinetics of Kaolinite in Acidic Aqueous-Solutions at 25-degrees-C. *Geochim. Cosmochim. Acta* **1992**, *56*, 3339.
- (14) Kriaa, A.; Hamdi, N.; Srasra, A. Proton Adsorption and Acid-Base Properties of Tunisian Illite in Aqueous Solution. *J. Struct. Chem.* **2009**, *50*, 273.
- (15) Noh, J. S.; Schwarz, J. A. Estimation of the Point of Zero Charge of Simple Oxides by Mass Titration. *J. Colloid Interface Sci.* **1989**, *130*, 157.
- (16) Tertre, E.; Castet, S.; Berger, G.; Loubet, M.; Giffaut, E. Surface Chemistry of Kaolinite and Na-Montmorillonite in Aqueous Electrolyte Solutions at 25 and 60 °C: Experimental and Modeling Study. *Geochim. Cosmochim. Acta* **2006**, *70*, 4579.
- (17) Mustafa, S.; Shahida, P.; Naeem, A.; Dilara, B. Sorption Studies of Divalent Metal Ions on ZnO. *Langmuir* **2002**, *18*, 2254.
- (18) Janusz, W. Cadmium-Oxide Aqueous NaCl or  $\text{NaClO}_4$  Solution System. *J. Colloid Interface Sci.* **1991**, *145*, 119.
- (19) Tewari, P. H.; Campbell, A. B. Temperature-Dependence of Point of Zero Charge of Cobalt and Nickel Oxides and Hydroxides. *J. Colloid Interface Sci.* **1976**, *55*, 531.
- (20) Feng, J. T. J.; Lin, J. Y.; Evans, D. G.; Duan, X.; Li, D. Q. Enhanced Metal Dispersion and Hydrodechlorination Properties of Ni/ $\text{Al}_2\text{O}_3$  Catalyst Delivered from Layered Double Hydroxides. *J. Catal.* **2009**, *266*, 351.
- (21) Dongare, M. K.; Malshe, K.; Gopinath, C. S.; Murvani, I. K.; Kemnitz, E. Oxidation Activity and O-18-Isotope Exchange Behavior of Nickel Oxide-Stabilized Cubic Zirconia. *J. Catal.* **2004**, *222*, 80.

- (22) Naeem, A.; Saddique, M. T.; Mustafa, S.; Tasleem, S. Removal of  $\text{Co}^{2+}$  Ions from Aqueous Solution by Cation Exchange Sorption onto NiO. *J. Hazard. Mater.* **2009**, 172, 124.
- (23) Mahmood, T.; Saddique, M. T.; Naeem, A.; Mustafa, S.; Dilara, B.; Raza, Z. A. Cation Exchange Removal of Cd from Aqueous Solution by NiO. *J. Hazard. Mater.* **2011**, 185, 824.
- (24) Naeem, A.; Saddique, M. T.; Mustafa, S.; Kim, Y.; Dilara, B. Cation Exchange Removal of Pb from Aqueous Solution by Sorption onto NiO. *J. Hazard. Mater.* **2009**, 168, 364.
- (25) Mahmood, T.; Saddique, M. T.; Naeem, A.; Mustafa, S. Kinetic and Thermodynamic Study of Cu(II), Co(II) and Zn(II) Adsorption from Aqueous Solution by NiO. *J. Chem. Eng.* **2011**, 171, 935.
- (26) Tan, W. F.; Lu, S. J.; Liu, F.; Feng, X. H.; He, J. Z.; Koopal, L. K. Determination of the Point of Zero Charge of Manganese Oxides with Different Methods Including an Improved Salt Titration Method. *Soil Sci.* **2008**, 173, 277.
- (27) Bourikas, K.; Vakros, J.; Kordulis, C.; Lycourghiotis, A. Experimental and Theoretical Establishment of a New Technique for Determining the Point of Zero Charge (PZC) of Metal (Hydr)Oxides. *J. Phys. Chem. B* **2003**, 107, 9441.
- (28) Mustafa, S.; Dilara, B.; Neelofer, Z.; Naeem, A.; Tasleem, S. Temperature Effect on the Surface Charge Properties of  $\gamma\text{-Al}_2\text{O}_3$ . *J. Colloid Interface Sci.* **1998**, 204, 284.
- (29) Wang, Y. P.; Zhu, J. W.; Yang, X. J.; Lu, L. D.; Wang, X. The Catalytic Effect of NiO on Thermal Decomposition of Nitrocellulose. *Thermochim. Acta* **2005**, 437, 106.
- (30) Ismail, H. M. Effects of the Preparation Procedure and Additives on Surface Texture of Nickel and Cobalt Oxides as Final Decomposition Products of Nickel and Cobalt Oxysalts. *Colloids Surf. A* **1996**, 110, 159.
- (31) Coudun, C.; Grillon, F.; Hocheplied, J. F. Surfactant Effects on pH-Controlled Synthesis of Nickel Hydroxides. *Colloids Surf. A* **2006**, 280, 23.
- (32) Hernandez, N.; Moreno, R.; Sanchez-Herencia, A. J.; Fierro, J. L. G. Surface Behavior of Nickel Powders in Aqueous Suspensions. *J. Phys. Chem. B* **2005**, 109, 4470.
- (33) Ludwig, C.; Casey, W. H. On the Mechanisms of Dissolution of Bunsenite  $[\text{NiO(s)}]$  and Other Simple Oxide Minerals. *J. Colloid Interface Sci.* **1996**, 178, 176.
- (34) Naklicki, M. L.; Rao, S. R.; Gomez, M.; Finch, J. A. Flotation and Surface Analysis of the Nickel(II) Oxide/Amyl Xanthate System. *Int. J. Miner. Process.* **2002**, 65, 73.
- (35) Moon, J. W.; Lee, H. L.; Kim, J. D.; Kim, G. D.; Lee, D. A.; Lee, H. W. Preparation of  $\text{ZrO}_2$ -Coated NiO Powder Using Surface-Induced Coating. *Mater. Lett.* **1999**, 38, 214.
- (36) Rao, S. R.; Finch, J. A. Base Metal Oxide Flotation Using Long Chain Xanthates. *Int. J. Mineral Process.* **2003**, 69, 251.
- (37) Mustafa, S.; Tasleem, S.; Naeem, A. Surface Charge Properties of  $\text{Fe}_2\text{O}_3$  in Aqueous and Alcoholic Mixed Solvents. *J. Colloid Interface Sci.* **2004**, 275, 523.
- (38) Zarzycki, P.; Szabelski, P.; Charnas, R. A Monte Carlo Simulation of the Heterogeneous Adsorption of Hydrogen Ions on Metal Oxides: Effect of Inert Electrolyte. *Appl. Surf. Sci.* **2005**, 252, 752.
- (39) Jablonski, J.; Janusz, W.; Reszka, M.; Sprycha, R.; Szczypa, J. Mechanism of Adsorption of Selected Monovalent and Divalent Inorganic Ions at the Alumina/Electrolyte Interface. *Pol. J. Chem.* **2000**, 74, 1399.
- (40) Mustafa, S.; Dilara, B.; Nargis, K.; Naeem, A.; Shahida, P. Surface Properties of the Mixed Oxides of Iron and Silica. *J. Colloid Interface Sci.* **2002**, 205, 273.
- (41) Chibowski, S.; Janusz, W. Specific Adsorption of Zn(II) and Cd(II) Ions at the  $\alpha\text{-Fe}_2\text{O}_3$ /Electrolyte Interface Structure of Electrical Double Layer. *Appl. Surf. Sci.* **2002**, 196, 343.
- (42) Tewari, P. H.; McLean, A. W. Temperature Dependence of Point of Zero Charge of Alumina and Magnetite. *J. Colloid Interface Sci.* **1972**, 40, 267.
- (43) Morel, J. P.; Marmier, N.; Hurel, C.; Desrosiers, N. M. Effect of Temperature on the Acid-Base Properties of the Alumina Surface: Microcalorimetry and Acid-Base Titration Experiments. *J. Colloid Interface Sci.* **2006**, 298, 773.
- (44) Davis, J. A.; James, R. O.; Leckie, J. O. Surface Ionization and Complexation at Oxide-Water Interface 1. Computation of Electrical Double-Layer Properties in Simple Electrolytes. *J. Colloid Interface Sci.* **1978**, 63, 480.
- (45) Mustafa, S.; Parveen, S.; Ahmad, A.; Dilara, B. Temperature Effect on the Surface Properties of  $\text{ZnO(am)}$ . *Adsorpt. Sci. Technol.* **1997**, 15, 789.