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ORIGINAL CONTRIBUTION

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Residual changes in the surface charge of TiO_2 (anatase) suspensions as a result of exposure to a 44 MHz radiofrequency electric field

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Abstract Potentiometric titrations of TiO_2 (anatase) suspensions in solutions of 10^{-2}, 10^{-3}, and 10^{-4} M NaCl prior to treatment with a radiofrequency (RF) electric field gave values of pH_{pzc} and pH_{iep} of 5.75 ± 0.1 and 5.85 ± 0.1, respectively, within the range of literature values. Surface charge plots versus pH for untreated samples gave curves with a common intersection point, indicating that NaCl acts as an indifferent electrolyte. Identical suspensions of anatase were then exposed for 30 min to an RF electric field with a peak-to-peak, no-load amplitude of 34 V and a frequency of 44 MHz. Portions of the treated suspension were titrated after different time periods following removal of the field (2, 15, 30, and 45 min). At 2 min, the pH_{pzc} had shifted to 6.50 ± 0.1, and at 15, 30 and 45 min, the curves for the three NaCl concentrations were found to lack a common intersection point, an effect which became more pronounced with time. It is proposed that RF treatment results in the formation of a porous gel layer of hydrous titanium dioxide on the surface of the anatase particles that subsequently undergoes a slow ion-exchange reaction involving ions of the supporting electrolyte.

Key words Anatase – radiofrequency electric field – surface charge – hydrous titanium dioxide – ion exchange

Introduction

The behavior of aqueous suspensions of inorganic oxides, such as TiO_2 and others, in electrolyte solutions continues to be a subject of much interest in colloid science because of the technological importance of these materials [1]. According to the two-site dissociation model [1, 2], inorganic oxide surfaces possess a large number of amphoteric hydroxyl groups that can undergo reaction with either H^+ or OH^- to generate positively or negatively charged sites:

$$MOH + OH^- = MO^- + H_2O \qquad (1)$$

$$MOH + H^+ = MOH_2^+ . \qquad (2)$$

For these suspensions, H^+ and OH^- are the potential determining ions, and the surface charge depends on the relative excess of one type of charged site over the other. Because the number and type of charged sites present on an inorganic oxide particle are functions of the suspension pH, surface charge can be determined experimentally by means of careful potentiometric titration [1].

In the case of many metal oxide suspensions, including TiO_2, the magnitude of the titratable surface charge appears anomalously high compared with the measured electrokinetic potential [1]. This seeming inconsistency between surface charge density and zeta potential has been rationalized by a number of hypotheses.

In the porous gel model proposed by Lyklema [3, 4] and others [5–7], the surface of the oxide is assumed to consist of a porous layer that can be penetrated by H^+ and

OH^- ions prior to reaction with amphoteric hydroxyl groups, allowing a high surface charge to develop while, at the same time, maintaining a reasonable separation between charged groups. This model further assumes that penetration of the porous layer by counterions of the supporting indifferent electrolyte can also occur, thereby reducing the net electrical potential of the outer edge of the surface and the zeta potential at the shear plane.

In the site dissociation – site binding model of oxide surfaces [8], ion pairing of the counterions of the supporting electrolyte (say, for example, NaCl) with the surface charges:

$$MO^- + Na^+ = MONa \tag{3}$$

$$MOH_2^+ + Cl^- = MOH_2Cl \tag{4}$$

is used to neutralize a portion of the otherwise large surface charge. Although this treatment somewhat compromises the concept of the "indifferent" electrolyte, the model has been used quite successfully to treat TiO_2 in KNO_3 solutions at several different electrolyte concentrations [1].

In a previous report [9], changes in the zeta potential of TiO_2 (anatase) suspensions were observed when the suspensions at their natural pH in either water or in dilute NaCl solution were exposed to a radiofrequency (RF) electric field with a peak-to-peak amplitude of 34 V and a frequency of 44 MHz. The greatest change in zeta potential was generally observed after approximately 30 min of exposure time, with the effect persisting for periods of up to 90 min following removal of the field. Suspensions of Al_2O_3 and SiO_2 were also treated with the field, but analogous changes in zeta potential were not observed with these oxides.

While a number of existing theories [9] could account for instantaneous changes in interfacial polarization observed when TiO_2 suspensions were exposed to the RF field (i.e., dispersion of conductivity and dielectric constant), these effects were not likely to persist following removal of the RF field. Of the several possible mechanisms which were considered in the previous study [9], those involving RF-induced changes associated with the solid TiO_2 particles were thought most likely. Although a search of the literature did not reveal any similar observations of persistent RF-induced effects with titania suspensions, previous chemical studies of the electrophoretic mobility and surface charge of titania suspensions [10, 11] have shown that these parameters are very sensitive to changes in surface crystallinity, hydration state, and specific adsorption of cations and anions. In a study of the electrokinetic behavior of titanium dioxide, Furlong and Parfitt [11] discuss some of the factors that can alter the isoelectric point of suspensions. These factors include surface phase transitions from anatase to rutile, surface dehydration and dehydroxylation, and an increase in surface impurities due to impurity migration from the bulk.

Because zeta potential is a parameter characterizing the solid–liquid interface at some distance from the solid surface (i.e., at the shear plane), it cannot be used to unambiguously characterize the state of the surface [12]. To avoid the ambiguities and extrapolations required to interpret changes at the surface in terms of zeta potential, direct determination of surface charge of RF-treated anatase suspensions was undertaken.

In this paper we report the results of potentiometric titrations conducted on TiO_2 (anatase) suspensions exposed to an RF field for 30 min – the exposure period previously shown to have the greatest effect on the zeta potential [9]. To check for residual variations in surface charge, the titration with NaOH solution was performed several times for each treated sample, following different time periods after removal of the field.

Experimental

Materials

The same TiO_2 (anatase, Titandioxid P-25) powder (Degussa, Teterboro, NJ) was employed in this study as was used in the previous zeta potential determinations [9]. Purity of the powder was better than 99.5%, and the impurities present were Al_2O_3 ($< 0.3\%$), SiO_2 ($< 0.2\%$), and Fe_2O_3 ($< 0.01\%$). The specific surface area of the sample, as given by the manufacturer [13], was 50 ± 15 m^2/g, and the average primary particle size (diameter) was 30 nm.

To make surface charge measurements, 1000 cm^3 of stock suspensions were prepared using 1 g $TiO_2/100$ cm^3 of liquid, deionized water, and NaCl (Mallinckrodt, Inc., St. Louis, Missouri) as the supporting electrolyte (10^{-2}, 10^{-3}, and 10^{-4} M). The initial pH of each of the three suspensions was adjusted to between 3.5 and 4.0 with a pH meter using hydrochloric acid (Mallinckrodt), and all suspensions were allowed to age for a minimum of 24 h prior to use. A solution of 0.10 M NaOH (Mallinckrodt, analytical reagent grade) was used as the titrant.

Methods

Potentiometric titrations of the oxide suspensions were conducted in the usual manner [1], where a known mass of solid oxide was suspended in a known volume of electrolyte and titrated by addition of different volumes of NaOH. Along with the suspension, an identical volume of electrolyte solution without the solid oxide was also titrated with NaOH. A plot of pH versus volume of added base was prepared for the suspension and for the corresponding sample of electrolyte solution without the oxide. The volume of NaOH taken up by the oxide surface at a given pH was determined from the difference in volume of added base for the suspension and for the pure electrolyte at the given pH. Relative surface charge (σ_0), in C/cm^2, was calculated at each pH according to the equation:

$$\sigma_0 = \frac{FNV}{1000\,mA}\,, \qquad (5)$$

where F is Faraday's constant in C/equivalent, N is the concentration of the titrant in equivalents/L, V is the titrant volume difference in cm^3 between the suspension and the pure electrolyte for a given pH, m is the mass of oxide in g, and A is the surface area per unit mass in cm^2/g. Plots of relative surface charge versus pH were then prepared to determine the common intersection point for different electrolyte concentrations. Absolute surface charge was determined by translating the vertical axis of the surface charge versus pH plots so that zero surface charge corresponded to the common intersection point for the different electrolyte concentrations titrated. The pH of the common intersection point was taken as the point of zero charge (pH$_{\rm pzc}$).

Potentiometric titrations were performed first on untreated samples and then on samples exposed to the RF field for 30 min. The radiofrequency generator and sample treatment cell have been described previously [9]. A 50-cm^3 sample of the suspension was used for each titration, and all samples originated from the same stock suspensions. Titrations were performed using an automatic titrator.

Because residual variations in the zeta potential of TiO$_2$ suspensions treated by the RF field had been shown to vary in a time-dependent fashion [9], the treated samples were titrated at several different times (2, 15, 30 and 45 min) following removal of the RF field. In order to complete each titration in about 10 min, the titrator was preset to add 50-μL portions of the titrant (0.10 M NaOH) automatically after the drift became less than 1 mV/min. (This corresponded to a change of less than 0.017 pH unit/min). Using this mode of titrant addition, the time required to titrate any particular sample over a pH range from 4 to 10.5 pH units was approximately 6–12 min. Therefore, any adsorption–desorption equilibria taking place on the TiO$_2$ surface during the time required for the titration should be considered as fast.

To determine how equilibration time affected the experimentally measured values of surface charge (and especially the pH corresponding to the point of zero charge), a second set of titration experiments was conducted in which a constant delay period of 120 s (60 s in case of 10^{-3} M NaCl) was introduced prior to the addition of each 50-μL portion of titrant. Using a constant delay period of 120 s, the longest time required to titrate any particular sample over a pH range from 4 to 10.5 pH units occurred for suspensions in 10^{-2} M NaCl and was equal to approximately 44 min.

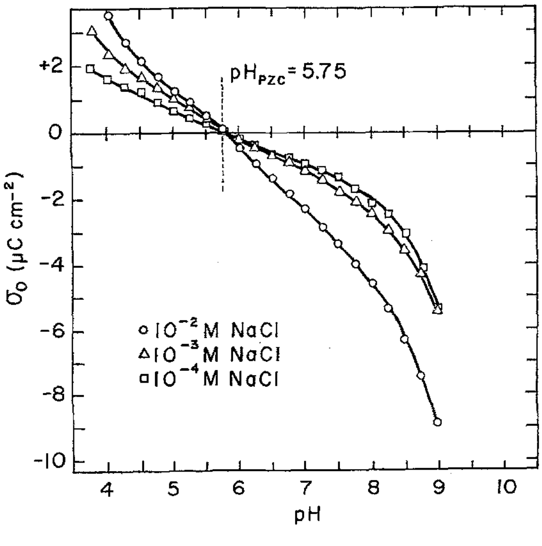
The pH of the isoelectric point of the TiO$_2$ suspensions (given as 6.6 pH units by the manufacturer) was also verified by conducting zeta potential measurements on the titanium dioxide suspensions (0.01 g/100 cm^3) in 10^{-4} and 10^{-3} M NaCl solutions as a function of the pH of the suspensions. The procedure and apparatus employed for the zeta potential determinations have been described previously [9].

The manufacturer's value (50 m^2/g) for the specific surface area of TiO$_2$ was used in calculating the surface charge [13]. Zeta potentials were corrected for temperature and also multiplied by the factor 0.699 to correct for size, as described previously [9].

Results

Surface charge (σ_0) and the pH corresponding to the point of zero charge (pH$_{\rm pzc}$) for the untreated TiO$_2$ suspensions are shown in Fig. 1. Both the experimentally determined

Fig. 1 Surface charge (σ_0) of TiO$_2$ suspensions (1 g/100 cm^3) in 10^{-2}, 10^{-3} and 10^{-4} M NaCl solution as a function of suspension pH. Titration performed automatically using a constant delay period of 120 s (60 s for 10^{-3} M NaCl) following the addition of each 50-μL aliquot of 0.1 M NaOH to allow for sample equilibration. pH$_{\rm pzc}$ = pH corresponding to the point of zero charge



pH_{pzc} (5.75 ± 0.1) and the values of the surface charge are within the range of values reported in the literature [14]. The presence of a common intersection point shows that NaCl behaves as an indifferent supporting electrolyte.

Figure 2 shows a plot of zeta potential for the TiO_2 suspensions in 10^{-3} and 10^{-4} M NaCl as a function of pH. (Zeta potentials at 10^{-2} M NaCl could not be determined, as our suspensions were not sufficiently stable at these elevated electrolyte concentrations for the time periods required to make the measurements.) From Fig. 2, it can be seen that the experimentally determined pH at the isoelectric point of the sample ($pH_{iep} = 5.85 \pm 0.1$) is comparable to the value of pH_{pzc} (Fig. 1) and also to pH_{iep} values reported in the literature [8]. The value $pH_{iep} = 5.85 \pm 0.1$ is, however, lower than the $pH_{iep} = 6.6$ specified in the manufacturer's literature for this product [13]. (A measured value of $pH_{iep} = 6.4 \pm 0.1$ could be obtained if the determination was made immediately following preparation of the suspension, i.e., the suspension was not allowed to age.) The agreement between pH_{pzc} (5.75 ± 0.1) in Fig. 1 and pH_{iep} (5.85 ± 0.1) in Fig. 2 for these TiO_2 suspensions also shows that NaCl behaves as an indifferent supporting electrolyte with the untreated samples. Moreover, since the pH_{iep} determination was conducted using a much lower percentage of solid in the dispersion (0.01 g/100 cm^3) than the pH_{pzc} determination (1 g/100 cm^3), an agreement between these two parameters also suggests that the influence of any trace impurities present in either the water or the TiO_2 solid phase is minimal [14].

The titration procedure which produced the results shown in Fig. 1 introduced a constant pause of 120 s (60 s in the case of 10^{-3} M NaCl) between the addition of each 50-μL aliquot of titrant to allow for sample equilibration. Using this procedure, up to 44 min were required to complete each titration. Previous observations [9] had indicated that the properties of the treated TiO_2 suspensions are time dependent and change rather quickly after removal of the RF field. Therefore, a shorter titration time was necessary if the surface charge was to be determined on a time scale which was meaningful in comparison to that of the changes which were taking place.

To determine if pauses of 60–120 s were really necessary, titrations of the untreated TiO_2 suspensions were repeated by presetting the titrator to add 50-μL aliquots of titrant only after the drift had become less than 0.017 pH units/min (1 mV/min). Using this variable pause procedure, titration time was reduced to 6–12 min. (It is worth mentioning that the difference in titration time for both procedures is less for lower pH values, i.e., below pH 9.) Using the variable pause procedure, the measured pH_{pzc} was found to be 5.85 ± 0.1, which is equal, within

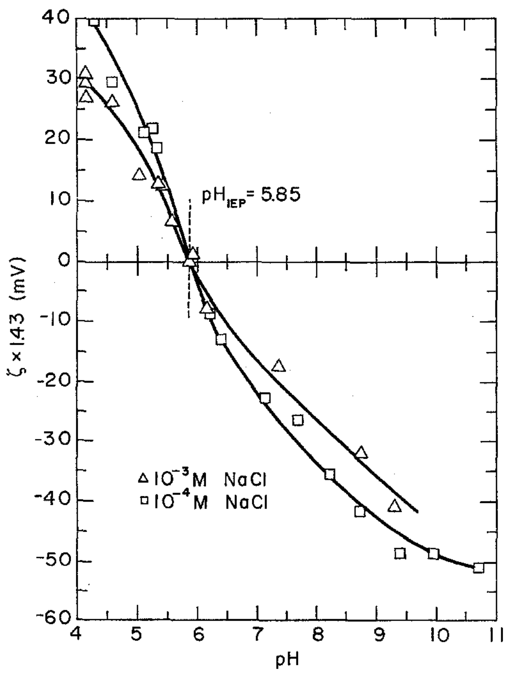


Fig. 2 Measured zeta potentials (ζ) of untreated TiO_2 suspensions (0.01 g/100 cm^3) in 10^{-3} and 10^{-4} M NaCl solution as a function of suspension pH. pH_{iep} = pH corresponding to the isoelectric point

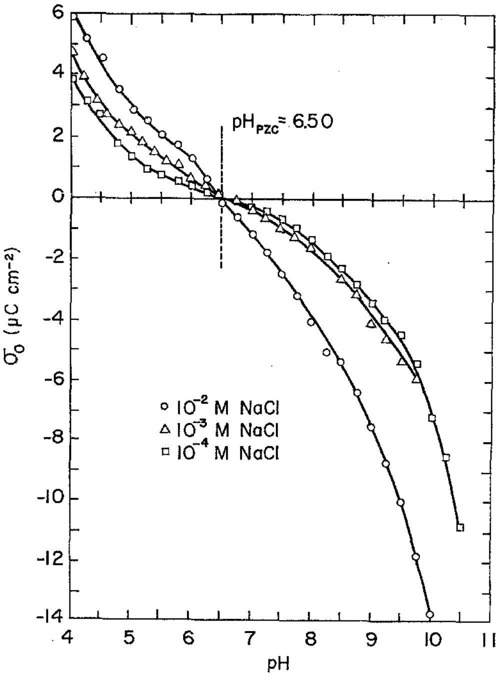


Fig. 3 Surface charge (σ_0) as a function of suspension pH for TiO_2 suspensions (1 g/100 cm^3) in 10^{-2} (2–9 min), 10^{-3} (2–8 min) and 10^{-4} (2–9 min) M NaCl solution. Suspensions were treated by the RF field for 30 min, and times in parentheses indicate the beginning and end of each titration relative to removal of the RF field

experimental error, to the value determined using the constant delay period of 120 or 60 s (Fig. 1). The differences in surface charge determined by the two procedures are also within 1 $\mu C/cm^2$ for corresponding pH values and NaCl concentrations. Thus, it can be concluded that simple adsorption/desorption equilibria of H^+/OH^- ions are reasonably fast in these systems, and that changes in the surface charge of TiO_2 after exposure to RF electric fields can be determined on a meaningful time scale.

Titanium dioxide suspensions were treated with the RF field for 30 min, and then several 50 cm^3 portions of each treated suspension were titrated after different time periods following removal of the field. Figures 3–6 show the results obtained for titrations run after various times following removal of the RF field. In Fig. 3 (2 min after removal of the RF field) the curves for the three NaCl concentrations still yield a common intersection point, although the pH_{pzc} has shifted to a more basic value. The most notable feature observed in the remaining curves is the lack of a common intersection point – a divergence which becomes more pronounced as the time following removal of the RF field increases. Since the curves in Figs. 4–6 no longer have a common intersection point, the choice of $\sigma_0 = 0$ is completely arbitrary, and the intersection points for 10^{-3} and 10^{-2} M NaCl were selected simply for the purpose of defining reference points for each system.

Discussion

It is clear from Figs. 1–2 that in the absence of exposure to the RF field, these anatase suspensions behave quite normally. The potential determining ions are H^+ and OH^-, the point of zero charge is determined solely by the amphoteric hydroxyl groups on the surface and the supporting electrolyte (NaCl) is involved with the surface only in a non-specific manner.

Figures 3–6 demonstrate that the behavior of the suspensions following exposure to the RF field is quite different. At 2 min following removal of the field, treatment has shifted the pH_{pzc} to more basic values (Fig. 3), indicating a relative increase in negative charge on the surface. At 15, 30 and 45 min following removal of the RF field, plots of surface charge versus pH for different concentrations of NaCl no longer yield a common intersection point – a situation which becomes more pronounced with time following removal of the RF field.

Fig. 4 Relative surface charge (σ_0) of TiO_2 suspensions (1 g/100 cm^3) in 10^{-2} (15–24 min), 10^{-3} (15–22 min) and 10^{-4} (12.5–18 min) M NaCl solution. Suspensions were treated by the RF field for 30 min, and times in parentheses indicate the beginning and end of each titration relative to removal of the RF field. The intersection of the 10^{-2} and 10^{-3} M NaCl curves was selected as a reference point in defining $\sigma_0 = 0$

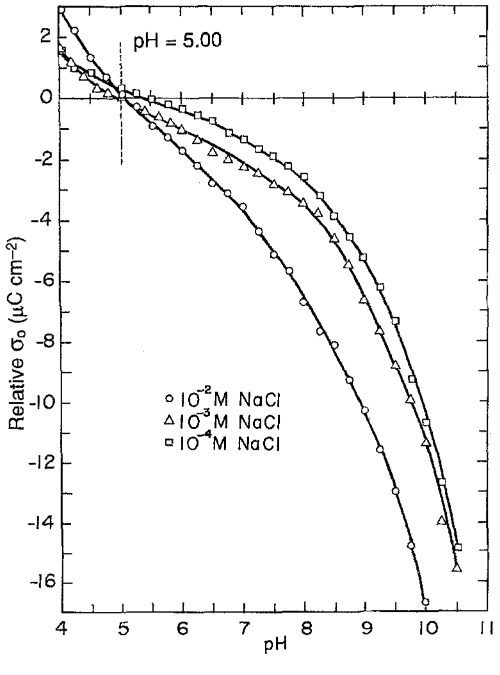
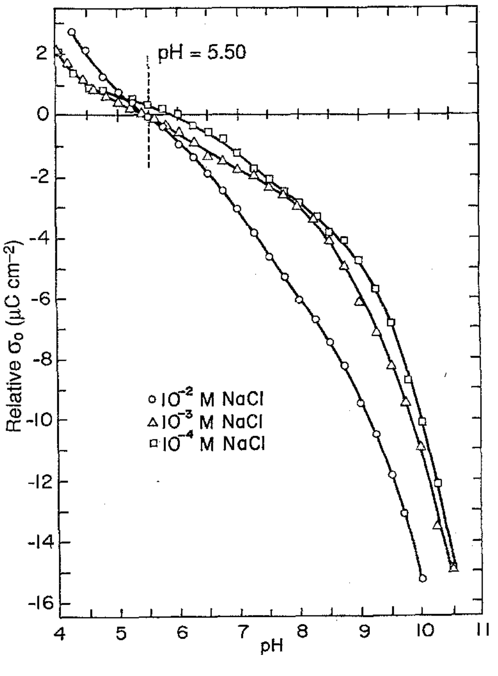


Fig. 5 Relative surface charge (σ_0) of TiO_2 suspensions (1 g/100 cm^3) in 10^{-2} (30–40 min), 10^{-3} (30–39 min) and 10^{-4} (30–35 min) M NaCl solution. Suspensions were treated by the RF field for 30 min, and times in parentheses indicate the beginning and end of each titration relative to removal of the RF field. The intersection of the 10^{-2} and 10^{-3} M NaCl curves was selected as a reference point in defining $\sigma_0 = 0$



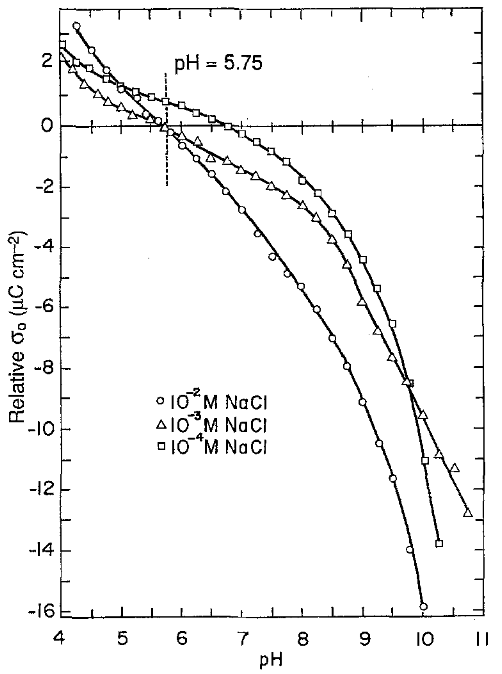


Fig. 6 Relative surface charge (σ_0) of TiO_2 suspensions (1 g/100 cm^3) in 10^{-2} (45–55 min), 10^{-3} (45–53 min) and 10^{-4} (45–51 min) M NaCl solution. Suspensions were treated by the RF field for 30 min, and times in parentheses indicate the beginning and end of each titration relative to removal of the RF field. The intersection of the 10^{-2} and 10^{-3} M NaCl curves was selected as a reference point in defining $\sigma_0 = 0$

The clear implication of these observations is that RF treatment of the suspensions alters the surface of the anatase particles so as to allow some form of specific interaction between the electrolyte and the surface that was not possible prior to RF treatment. In addition, whatever the nature of the RF-induced surface alteration, the specific interaction of the ions of electrolyte with the surface is a slow process that persists for a period of at least 45 min following removal of the RF field. While it is not possible to rule out unequivocally mechanisms involving surface phase transitions or the migration of bulk impurities to the surface during RF treatment, alteration of the hydration state of the surface could be involved in the explanation of the RF-induced effect since the frequency of the RF field employed in this study (44 MHz) corresponds to the maximum dielectric loss expected for bound water ([15] and Fig. 2, ref. [16]).

Under this hypothesis, the residual variations in zeta potential reported previously [9] for these same suspensions could be due to the RF-induced formation of a porous surface layer of hydrous titanium dioxide on the particles. When produced commercially by chemical means, hydrous titanium dioxide is a white amorphous material with the general formula $TiO_{(2-x)}(OH)_{2x} \cdot yH_2O$ where $x < 1$ [17]. It is a well-known inorganic cation exchange material [17], and its ion-exchange properties have been studied extensively, particularly in nuclear engineering for the decontamination of highly radioactive solutions [18–24]. The material is thought to be a macromolecular gel formed by the polymerization of hydrolyzed species such as $(-TiO-)_n^{2n+}$ which produces a cross-linked network structure that is more or less porous [21]. Thermogravimetric studies on hydrous titanium dioxide have shown that it contains a variable amount of water, most of which is interstitial [21].

Inoue and Tsuji [22–24] have studied the cation exchange behavior of hydrous titanium dioxide in depth and have determined that the material possesses four distinct exchange sites [22] with $pK_1 = 6.7 \pm 0.1$, $pK_2 = 10.3 \pm 0.2$, $pK_3 = 12.3 \pm 0.2$, and $pK_4 = 13.2 \pm 0.2$. These workers have shown that the most acidic site differs from the others by accounting for more than half of the total exchange capacity of the material and by having a faster rate of exchange. On the basis of ion-exchange capacity considerations and other data from infrared spectra and x-ray diffraction, Inoue and Tsuji [24] have concluded that the unit structure for the exchanger must contain 4 hydroxyl groups per 8 atoms of titanium. At 623 °C, the material begins to crystallize, forming a mixture of anatase and brookite [24].

If the RF treatment targets primarily the Ti-OH_2^+ groups on the surface – promoting the loss of H^+ as observed previously during the first 10 min of RF treatment (Fig. 4, ref. [9]) – the formation of Ti-OH (the reverse of Eq. 2) could occur. The formation of a layer of amorphous hydrous titanium dioxide on the surface of the crystalline anatase might lead to ion exchange reactions between the bulk electrolyte and the surface layer. Since the process would involve the diffusion of ions into the gel layer, equilibrium would require relatively long periods of time. The involvement of hydrogen ions [9] strongly suggests that the specific interaction of the supporting electrolyte is a cation exchange process involving the sodium rather than chloride ions:

$$\{TiOH\} + Na^+ = \{TiONa\} + H^+ , \qquad (6)$$

where the braces indicate the solid phase.

Studies with hydrous titanium dioxide prepared chemically have shown that it acts as a cation-exchange material, and that ion exchange between the solution and the solid phase is a slow process that requires more than 2 days to reach equilibrium [24]. The pronounced lack of a common intersection point in Figs. 4–6, an effect which appears to become more pronounced with time, can be understood in terms of this long equilibration time.

Conclusions

Untreated suspensions of TiO_2 in NaCl supporting electrolyte had a pH_{pzc} and pH_{iep} of 5.75 ± 0.1 and 5.85 ± 0.1, respectively, well within the range of values reported in the literature [14]. Prior to treatment with an RF electric field, plots of surface charge versus pH for supporting electrolyte concentrations of 10^{-2}, 10^{-3}, and 10^{-4} M displayed a common intersection point, indicating that NaCl behaves as an indifferent electrolyte. Agreement between pH_{pcz} and pH_{iep} supports the behavior of NaCl as an indifferent electrolyte and also suggests that the influence of any trace impurities present in any part of the system was minimal.

After exposure of these anatase suspensions for 30 min to an RF electric field with a no-load amplitude of 34 V and a frequency of 44 MHz, plots of surface charge versus pH for suspensions in 10^{-2}, 10^{-3}, and 10^{-4} M NaCl showed that significant changes had occurred. At 2 min following removal of the field, the pH_{pzc} had shifted to 6.50 ± 0.1. At periods of 15, 30 and 45 min following removal of the field, the curves for the three NaCl concentrations no longer exhibited a common intersection point, indicating that ions of the electrolyte were interacting with the surface in site-specific ways that were non-coulombic in nature. Since the interaction appeared to become more pronounced with time following removal of the RF field, the interaction of the electrolyte with the surface appears to be slow.

One hypothesis consistent with these observations and those reported previously [9] is the formation of a porous gel layer of hydrous titanium dioxide on the surface of the particles as a result of exposure to the RF field. Since hydrous titanium dioxide is a well-known cation exchange material [17–24], formation of a gel layer of this material on the surface of the anatase particles would create a non-equilibrium situation, making possible the exchange of hydrogen and sodium ions on the surface of the particles. Slow diffusion of ions in and out of the newly created gel layer could explain why the effect persists long after removal of the RF field and produces the residual changes in zeta potential observed previously when these suspensions were treated by the same RF electric field.

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