

Electrokinetic Characterization of Ceramic Suspensions

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Electrokinetic measurements, such as microelectrophoresis, are often in use for investigating optimal conditions for the preparation of single-component or complex ceramic suspensions, as well as for the control of final ceramic powders. Very often, particularly in the case of aqueous suspensions, the surface electric charge of solid particles and the electrokinetic (zeta) potential is determined by the pH of the dispersing medium. A high, stable electrokinetic potential is in most cases a guarantee for the colloidal stability of the suspension. On the contrary, the so called isoelectric conditions (zero electrophoretic mobility) usually coincide with the agglomeration of particles. One should avoid this, in order to meet the high quality standards of final ceramic bodies. In this work the isoelectric conditions of single oxides: PbO, ZrO₂ and TiO₂, and of complex oxide of general formula PbZr_{0.52}Ti_{0.48}O₃ (PZT) are discussed with respect to the composition (chloride, nitrate, acetate) and the pH of the surrounding medium. The influence of the synthesis temperature and non-stoichiometry of PZT on the electrokinetic data are also discussed.

Key words: electrokinetic characterization; stability of suspensions; suspensions of ceramic oxides; isoelectric points; lead-zirconate-titanate (PZT) complex oxides

Introduction

In the processing of high performance ceramics, one of the critical steps is the preparation of stable suspensions of fine raw powders. In order to meet the high quality standards of final ceramic bodies, one has to avoid the uncontrolled formation of aggregates due to either electrostatic or non-electrostatic interactions between the particles in ceramic suspensions.

Usually, in the multicomponent systems, such as ceramic suspensions, the action of electrical forces between charged particles of equal or opposite polarity is the most critical one for the stability of the dispersion, especially for aqueous systems. The DLVO theory quantifies well the total interaction energy between the particles of equal polarity. According to this theory the repulsive energy component is due to overlapping of the electrical double layers around the approaching particles and the attractive component is due to Van der Waals forces. An energy barrier which prevents the strong association and agglomeration of particles is an important characteristic of the net energy of interaction. In the case of surface charge compensation the energy barrier decreases or even vanishes and, in the absence of any other repulsion mechanism, the particles aggregate in a so called primary minimum¹⁻³.

Since the charge and surface potential of pure oxides are primarily pH dependent it is possible, in some cases, to adjust the pH conditions of the mixture (slurry) in such a way that all the components exhibit the same charge polarity. However, the problem of different charge density and surface potential still remains and may cause the aggregation^{4,5}. Sometimes it is not even possible to obtain the same polarity of all dispersion components by a simple adjustment of the pH. It is due to an excessive span between their isoelectric points. In that case the surface charge and surface potential can be modified by the controlled and selective adsorption of various organic substances (polyelectrolytes, fatty acids, fish oil, etc.) as commonly used in ceramic technology^{6,7}. Adsorption of these compounds can compensate the surface charge of particles, suppressing the electrostatic interactions between the original particles⁸. The DLVO theory revised to include the repulsive energy due to steric effects of the adsorbed polymers accurately quantifies particle-particle interactions in most colloidal dispersions. Thus, either the electrostatic or the steric repulsion controls the stability of the dispersion. The latter becomes important if the adsorbed organic polymers are interacting between the particle surfaces. Both mechanisms are possible, either in aqueous or nonaqueous systems. However, the steric repulsion predominates in the organic dispersion medium, whereas in aqueous systems the electrostatic repulsion controls the dispersion stability⁹.

The present work illustrates the importance of the isoelectric conditions for the colloidal stability of ceramic oxides' suspensions in sodium chloride (NaCl), ammonium acetate

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($\text{CH}_3\text{COONH}_4$) and potassium nitrate (KNO_3) as supporting electrolytes. We assume that the electrophoretic mobility or a calculated electrokinetic (zeta) potential reflects the electrostatic energy barrier between the particles. Specifically, this study deals with complex oxides of formula $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) produced by conventional solid state reaction at $900^\circ\text{C}^{10,11}$ and with single oxides, PbO , ZrO_2 , TiO_2 as commercial raw components. Furthermore, the investigation includes the non-stoichiometric modification of PZT of general formula $\text{Pb}_{1-x}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (x : 0; -0.01; 1.025). In order to investigate the influence of the synthesis temperature, the PZT synthesized at the temperature of 800°C was compared to standard sample produced at 900°C .

Experimental

The following chemicals were used for PZT solid state synthesis: PbO (Ventron 99.9% p.a.), TiO_2 (Fluka >99%), and ZrO_2 (Ventron 99% p.a.). These materials were used without further purification or treatment.

Oxide mixtures were prepared according to the formula $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. Typically, 50 g of oxide mixture was homogenized with 25 cm³ of acetone in a 50 cm³ zirconia container (Fritsch Pulverisette 5) loaded up to 30% volume with zirconia balls (diameter 10 mm). The slurries were dried at 100°C . The syntheses were performed in covered alumina crucibles at various temperatures ranging from 800°C to 900°C . The time for synthesis was about two hours. For the present work the sample prepared at 900°C was analyzed. After syntheses the powders (pellets) were crushed in an agate mortar and passed through a 500 μm sieve.

Mineralogical analyses were made with a Phillips 1710 X-ray diffractometer using $\text{Cu K}\alpha$ irradiation. The morphology of the samples was examined by a Leitz AMR 1600T scanning electron microscope.

The measurements of specific surface area were made using a FlowSorb II 2300, Micromeritics, Norcross, Georgia, USA.

The so called neutral or indifferent electrolytes were aqueous solutions of sodium chloride, ammonium acetate, and potassium nitrate. A weighed amount of powder (0.005 to 0.1 g) was dispersed in 100 cm³ of the electrolyte solution and exposed to ultrasound for 5 min. The pH of the suspensions was adjusted either by addition of HCl and NaOH (in the case of sodium chloride solution), with CH_3COOH and NH_4OH (in the case of ammonium acetate) and with KOH and HNO_3 (in the case of potassium nitrate).

An automatic microelectrophoretic instrument, type S3000, from Pen Kem, Bedford Hills, N.Y., USA, combined with an automatic titrator, ABU93 and sample changer, SAC80, from Radiometer, Copenhagen, Denmark, was used for the electrokinetic measurements and titrations.

Zeta potential (ζ) was calculated using Henry's equation¹², assuming $\text{Ka} \gg 1$ where K is the reciprocal of the double layer thickness and a is the particle diameter.

Results

Characteristics of the oxide constituents and PZT

The main characteristics of the oxide constituents, PbO , TiO_2 and ZrO_2 , and of the complex oxide $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) are shown in Table 1. The crystal structure of PZT is a function of the Zr/Ti ratio. The investigated material of formula $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ is characterized by a morphotropic phase boundary, and is typically a mixture of Ti-rich tetragonal and Zr-rich rhombohedral phases¹³, as found also in the present case.

Table 1: Characteristics of Simple and Complex Oxides

Composition	Synthesis temperature (°C)	Crystal structure	Particle size (μm)	Agglomerate size (μm)
PbO		litharge massicot	2	10-25
TiO ₂		anatase	0.2	10-20
ZrO ₂		baddeleyite	0.4	10-15
PTZ ₉₀₀	900	PZT (t,r)	1	10-15
PTZ ₈₀₀	800	PZT (t,r)	1	15
P _{0.025} ZT	900	PTZ (r,t)	1	40-60
P _{1.025} ZT	900	PZT (t,r)	0.5-3	10-20
		PbO massicot		

t-tetragonal, r-rhombohedral

In the PZT sample synthesized under conditions of an excess of PbO , free PbO phase (massicot) was detected by X-ray diffraction. As shown in the next section, electrokinetic measurements on the same sample clearly indicate the presence of unreacted PbO by a significant shift of the isoelectric point in acetate medium.

The particle size (diameter) of the oxide constituents was in the range of 0.2-0.5 μm , whereas the size of the PZT grains was 1 to several μm . The agglomerates present in the final product were typically of 10-15 μm .

The specific surface areas were 0.44 m²/g for PbO , 3.4 m²/g for ZrO_2 , 8.4 m²/g for TiO_2 and 0.30 m²/g for PZT synthesized at 900°C .

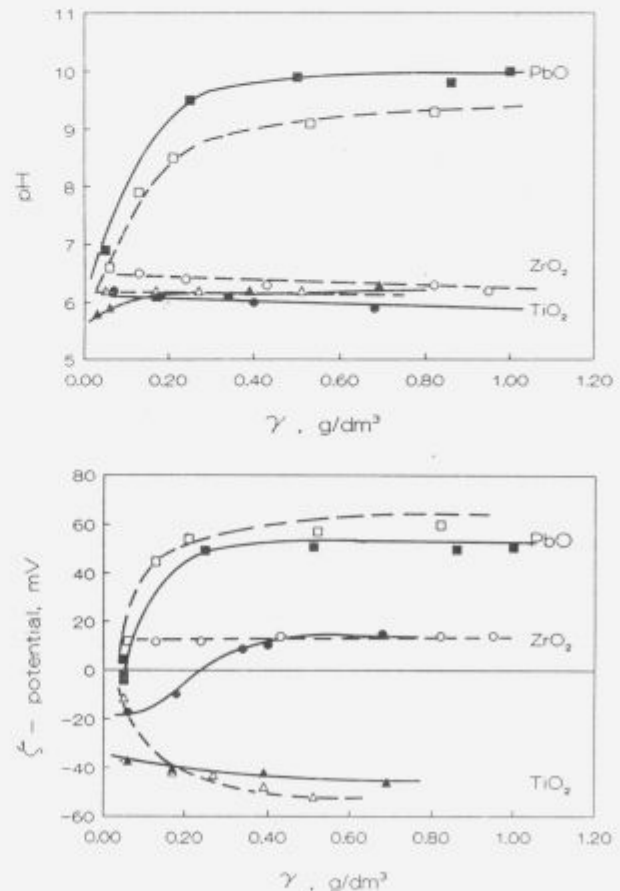


Figure 1: The effect of mass concentration γ on the pH (upper) and zeta potential (lower) of the suspensions: (Filled symbols and full lines denote sodium chloride; open symbols and broken lines denote ammonium acetate: \square , PbO ; \circ , ZrO_2 ; Δ , TiO_2).

Suspension concentration effect

In the microelectrophoretic measurements performed, the effect of the suspension concentration (γ) in the range 0.05-1 g/dm³ was analyzed with respect to the pH and zeta potential. The results are shown in **Figure 1**.

As shown in the upper part of **Figure 1** the pH of the PbO suspension changed from about pH 7 at the lowest concentration of 0.06 g/dm³ to about pH 10 at the concentration 0.5 g/dm³ and higher. The same effect was observed for both sodium chloride and ammonium acetate. The pH of other two oxides, ZrO₂ and TiO₂, did not change significantly over the entire suspension concentration range. In chloride solution, at the highest suspension concentration, the pH values were 6.5 for ZrO₂ and 6.3 for TiO₂. The corresponding values in acetate medium were 6.2 for both oxides. The pH values of PZT suspensions, which are not shown for the sake of clarity of the figure, were constant in both electrolytes, showing pH 6.3 in chloride and pH 6.4 in acetate solution.

The lower part of **Figure 1** shows the change of the zeta potential as an effect of the suspension concentration. A small positive zeta potential at the lowest concentration of PbO raises to high positive zeta potential of about +50 mV at the concentration 0.25 g/dm³ and remaining constant at higher concentrations.

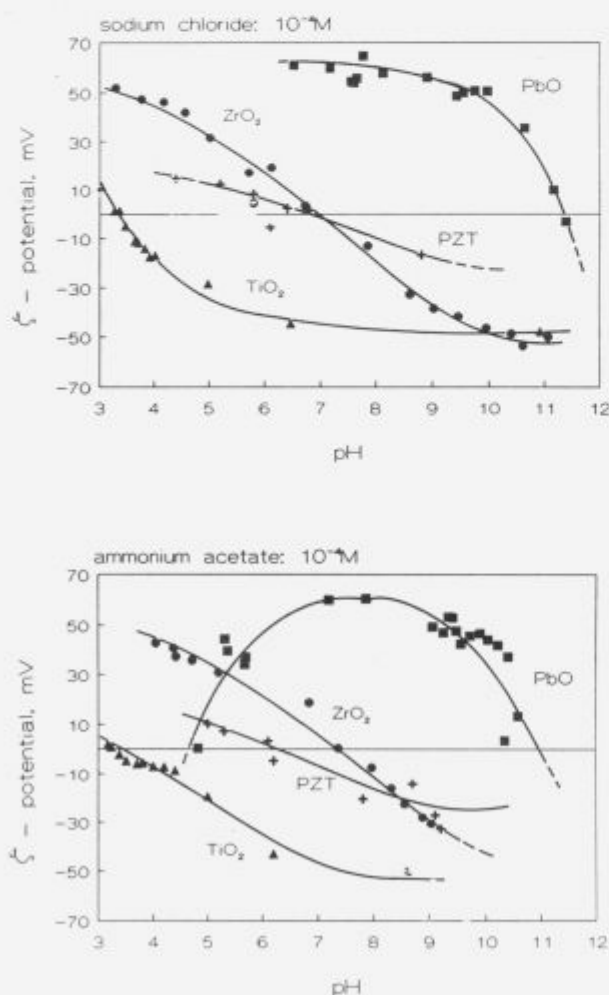


Figure 2: Zeta potential of suspensions in 10⁻⁴ mol/dm³ sodium chloride (upper) and ammonium acetate (lower) for PbO (■), ZrO₂ (●), TiO₂ (▲) and PZT (+)

The zeta potential of ZrO₂ depends significantly on the suspension concentration, changing from negative to positive values with an intersection point at 0.25 g/dm³. The zeta potential of TiO₂ at the low suspension concentration changes from small to higher negative values and reaching at the suspension concentration of 0.25 g/dm³ about -40 mV in chloride and -50 mV in acetate medium. Generally, the zeta potential was constant for all compounds at the concentrations higher than approximately 0.25 g/dm³. These, stable values of zeta potential are +50 to +60 mV for PbO, +16±1 mV for ZrO₂ and -40 to -50 mV for TiO₂. For PbO and TiO₂ the lower values are for the chloride and higher for the acetate solution.

Isoelectric conditions

Figure 2a and 2b show the zeta potential data for PbO, ZrO₂ and TiO₂ and for the complex oxide (PZT) in the pH range 3-12 in 10⁻⁴ M chloride and acetate solutions. The isoelectric points were at pH 6.8 for ZrO₂ and at pH 3.5 for TiO₂ in both electrolytes. The isoelectric point of PZT at pH 6.6±0.2 roughly coincides with one for ZrO₂. In ammonium acetate there is a shift of the isoelectric point to pH 6.3.

The electrokinetic data for PbO are quite different compared to the other two oxides. One can observe a pH region of stable, highly positively charged PbO between pH 6 and pH 10 in 10⁻⁴ mol/dm³ NaCl and between pH 7 and 9 in acetate medium. The results for PbO in these two electrolytes indicate the isoelectric point between pH 10.6 and 11.2. At higher pH values negative

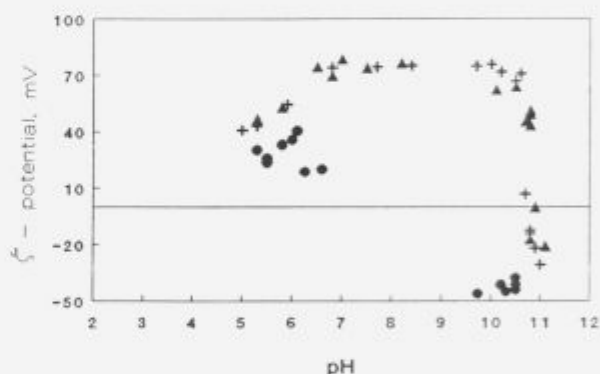


Figure 3: Zeta potential of PbO as a function of pH of the suspensions in sodium chloride at various electrolyte concentrations: +, 10⁻⁴ mol/dm³; ▲, 10⁻³ mol/dm³; ●, 10⁻² mol/dm³

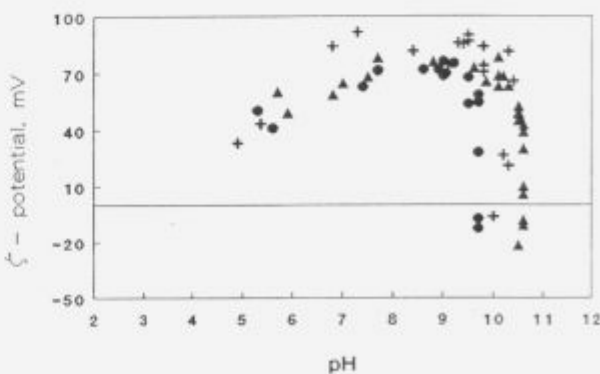


Figure 4: Zeta potential of PbO as a function of pH of the suspensions in ammonium acetate at various electrolyte concentrations: +, 10⁻⁴ mol/dm³; ▲, 10⁻³ mol/dm³; ●, 10⁻² mol/dm³

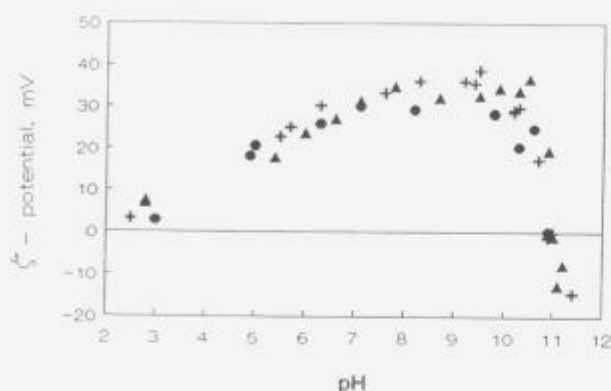


Figure 5: Zeta potential of PbO as a function of pH of the suspension in potassium nitrate at various electrolyte concentrations: +, 10^{-4} mol/dm³; \blacktriangle , 10^{-3} mol/dm³; \bullet , 10^{-2} mol/dm³

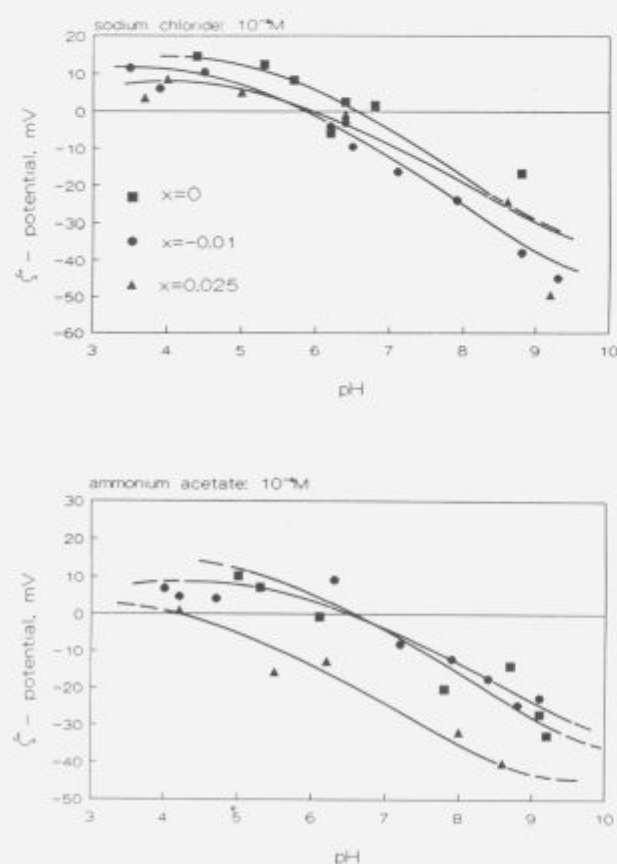
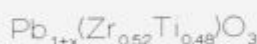


Figure 6: Influence of the stoichiometry of PZT on the zeta potential in 10^{-4} mol/dm³ sodium chloride (upper) and ammonium acetate (lower): \blacksquare , PZT; \bullet , $\text{P}_{0.99}\text{ZT}$; \blacktriangle , $\text{P}_{1.025}\text{ZT}$

zeta potential and further on an agglomeration was observed. Another, low-pH isoelectric point was at pH 4.5 in acetate medium. At higher electrolyte concentration in such a low pH region either precipitation (in the case of chloride) or dissolution (in the case of acetate) occurs.

Due to peculiar behaviour of PbO the electrophoretic measurements have been extended to three electrolytes (chloride, acetate, nitrate) and three concentrations (10^{-2} , 10^{-3} and 10^{-4} M). The results are shown in **Figures 3-5**. In 10^{-4} and 10^{-3} M sodium chloride solutions, in the pH region 7 to 9, the constant high positive values of zeta potential are persisting. In 10^{-2} M electrolyte fast agglomeration occurs making the measurements hardly reproducible. For all three electrolytes one can observe high positive constant values of zeta potential between pH 7 and 9. At the same time the system maintains colloidal stability during 48 hours. At higher pH values, a steep decrease of zeta potential occurs between pH 10 and 11. At pH<7 there is a slow decrease of zeta potential in the nitrate medium, while in the other two electrolytes the abrupt changes occur, accompanied by either precipitation (in chloride) or by dissolution (in acetate). For all three electrolytes the high-pH isoelectric point is at 10.5 ± 0.2 . Only in the case of acetate the isoelectric points appear in the range of pH 9.6-10.3.

The specific reactivity of acetate with PbO was used to detect the free PbO phase in nonstoichiometric PZT, where an excess of PbO was added to the reaction mixture. In **Figure 6** the zeta potential data are shown for stoichiometric PZT of the formula $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and compared with those for non-stoichiometric PZT, either with a PbO deficiency as in $\text{Pb}_{0.99}(\text{Zr}, \text{Ti})\text{O}_3$ or with an excess of PbO in $\text{Pb}_{1.025}(\text{Zr}, \text{Ti})\text{O}_3$. In sodium chloride medium there is a common isoelectric point for all three samples, whereas in acetate medium it was shown that an excess of PbO caused a shift from $\text{pH}_{\text{iep}} 6.3$ to $\text{pH}_{\text{iep}} 4.7$, which reflects a strong interaction of acetate ions with PbO.

Furthermore, the shift of the isoelectric point from about pH 6.5 to 3.5 was detected in the case of PZT synthesized at 800°C instead of 900°C . This results are shown in **Figure 7**.

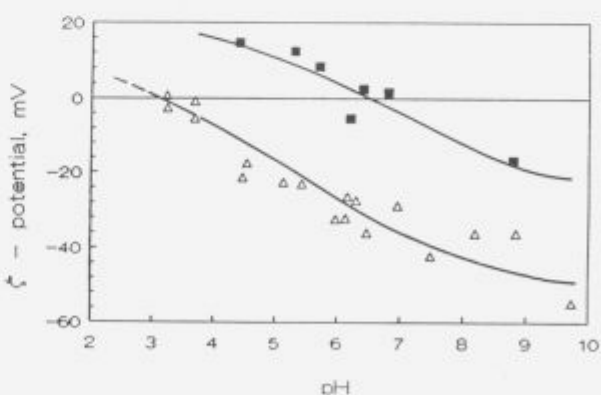


Figure 7: Influence of the synthesis temperature of PZT on the zeta potential in 10^{-4} mol/dm³ sodium chloride: Δ , 800°C ; \blacksquare , 900°C

Interpretation of the data and discussion

Suspension concentration

For the most oxide/aqueous solution systems the generation of surface charge is due to amphoteric surface reactions generally described by equations (1) and (2).



where $\equiv\text{S-OH}$ are the surface hydroxyl groups.

In the case of high mass concentration (more than 30 g/dm³) and in absence of any specific adsorption of foreign ions, the inherent pH would be identical to the isoelectric point¹⁴. In present work the suspension concentrations are 10 to 100 times lower. Therefore, in some cases the suspension concentration was not sufficient to establish an equilibrium. That is in the case of ZrO₂ where its inherent pH is only slightly lower than the isoelectric point. Therefore a reversal of charge occurs on each minute change in the suspension, including the mass concentration, which might influence the equilibrium, as shown in **Figure 1**.

The results for ZrO₂ and TiO₂ can be simply explained considering the amphoteric equilibria. For example, if the inherent pH values for ZrO₂ and TiO₂ are at pH 6.5 and 6.2 in chloride solution and their isoelectric points (as found by this work) are at pH 6.8 and pH 3.5, then the expected electrokinetic result would give small positive zeta potential for ZrO₂ and comparatively high negative zeta potential for TiO₂. Indeed, it was observed in the region of constant pH of the suspension at mass concentration >0.25 g/dm³ (**Figure 1**).

Low isoelectric point for TiO₂ at pH 3.5 was not often found by other authors. However, there is a literature evidence of the isoelectric point of TiO₂ at the pH 2¹⁵. It obviously depends on the technological process of production.

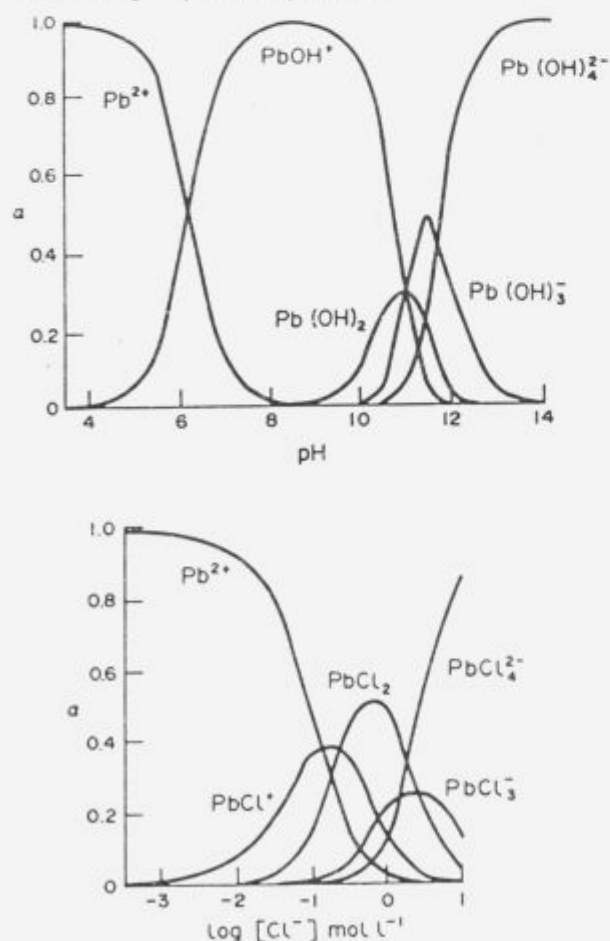


Figure 8: Distribution diagram for lead hydroxy and lead chloro species (Redrawn from reference 17)

If other species are included in surface charge formation as probably in the case of the PbO/electrolyte interface, then a simple interpretation such as surface amphoteric ionization is not sufficient. In that case a large number of hydrolytic processes and a variety of ionic equilibria determine the species in the solution¹⁶. Each of those species could be adsorbed at the solid surface depending on the pH and the composition and concentration of the electrolyte. **Figure 8**¹⁷ shows the distribution of lead species in aqueous solutions. It is clear that in the pH range 7-9 where our results showed a constant, highly positive zeta potential, the dominating species are the PbOH⁺ ions. These species are possibly adsorbed at the surface and they determine the overall surface charge and zeta potential. At higher pH the dominating species are Pb(OH)₂, which could precipitate giving a new solid phase, Pb(OH)₂. Raising the pH, the negative species, such as Pb(OH)₃⁻ dominate and determine the overall charge. On the other side, at pH <7, the Pb²⁺ species dominate, lowering slowly the zeta potential due to double layer compression until either precipitation (in chloride) or dissolution (in acetate) begins. The isoelectric point for PbO at the pH 10.6 ± 0.2, found in our work, coincides excellent with the pH of the transition from positive, over neutral, to negative lead hydroxo species, as shown in **Figure 8**. If other foreign ions are present such as Cl⁻, Ac⁻ or NO₃⁻, one may expect even more complicate distribution of species. However, the nitrate medium seems to be indifferent toward PbO compared to the other two electrolytes.

From the results in **Figure 1** - **Figure 8** we may conclude that in the pH range 7-9 established by oxide powders suspended in aqueous solutions, PbO particles are highly positively charged, in contrast to TiO₂ and ZrO₂, which are negatively charged. In such a case the electrostatic repulsion barrier between PbO and TiO₂ and ZrO₂ particles is absent and strong interaction between them can be expected. It should be tested practically whether such interactions lead to unfavorable hard agglomeration or to formation of relatively stable suspensions of microaggregates between PbO particles and TiO₂ or ZrO₂ particles.

For PZT the surface charge in NaCl solutions is probably determined by zirconia, as one can conclude from the common isoelectric points for PZT and ZrO₂. In ammonium acetate there is a slight shift in the isoelectric point of PZT from pH 6.8 to pH 6.3, which is probably due to the strong affinity of acetate ions for the lead oxide components in PZT. For the same reason a significant shift in the isoelectric point of PZT synthesized under conditions of excess PbO was observed. This could serve as a quick qualitative analysis of free PbO phase in PZT, which may have significant practical implications. For that purpose the systematic analyses of the isoelectric points of PZT samples having different percentage of free PbO would be necessary.

The isoelectric point for PZT sample synthesized at 800°C found at the pH 3.5 indicates some difference between the samples synthesized at 800°C and 900°C or higher (**Figure 7**). It is possible that the process of mixed crystal phases formation is not completed at the lower temperature. It seems that the Ti-rich phase determine the surface charge and the zeta potential in this case. However, at present, this is a speculation rather than proved finding.

Conclusion

Electrokinetic results suggest that commercial raw materials TiO₂ and ZrO₂ used in this work behave as typical acidic and amphoteric oxides having isoelectric points at pH 3.5 and pH 6.8.

Lead oxide, PbO, positively charged at electrolyte concentration lower than 10⁻¹ M within the limited pH range of about 7-9, behaves as a reactive constituent which practically deter-

mines the overall behavior of the suspension. Due to solubility of PbO and hydrolysis of Pb^{2+} a number of hydroxo species can be formed. In chloride and acetate media several additional species are possible. Small pH changes, particularly between pH 9 and 10 (PbO suspension inherent pH), and the presence of foreign ions, such as chloride or acetate, is the reason for poor stability of lead-based oxide aqueous suspensions. In practice, either the additives are used to improve the colloidal stability or, instead of aqueous, the non-aqueous medium is applied. However, such a solution is not always convenient, either for the reason of economy, or ecology or the quality of the final product.

Lead oxide showed particularly strong interaction with acetate. This effect was used to determine the free PbO phase in PZT.

The isoelectric point analysis showed the difference between the samples synthesized at 800°C and 900°C. This is ascribed to a non-completed mixed phases structuring, where Ti-rich phase determine the zeta potential. This preliminary conclusion has to be proved to be valid.

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