

## Isoelectric Points of Metal Oxides at High Ionic Strengths

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High ionic strengths induce a shift in the isoelectric point (IEP) of rutile to pH values substantially higher than its pristine IEP. When a critical concentration of electrolyte is exceeded ( $0.6 \text{ mol dm}^{-3}$  for rutile and  $0.35 \text{ mol dm}^{-3}$  for hematite), there is no IEP at all and the electrokinetic potential is positive even at very high pH values. Similar shifts in the IEP have been observed for anatase, alumina, indium oxide, and niobium oxide. The critical NaI concentration is low for the oxides of metals whose valence is odd, and it is high (or it does not exist) for the oxides of elements whose valence is even. There is no simple correlation between the critical NaI concentration and the pristine IEP. The above results regarding the shifts in the IEP of oxides at high NaI concentrations must not be generalized for other 1–1 salts; e.g., cesium nitrate induces a substantial shift in the IEP of silica and no shift in the IEP of alumina while the opposite is true for NaI.

### Introduction

High ionic strength dispersed systems occur in diverse fields of practical importance ranging from ceramics to nuclear waste management. The knowledge of electrokinetic properties of metal oxides in such systems would be much desired, e.g., in view of the correlation between the electrokinetic potential and the colloid stability and rheology. Until recently a tacit assumption was often made that the pristine isoelectric point (IEP) determined in solutions of inert electrolyte at low ionic strengths is also valid at higher ionic strengths. Classical electrokinetic methods fail to produce reliable  $\zeta$  potentials at very high ionic strengths, so assessment of this hypothesis was rather difficult. The minimum in parabolas representing the stability of alumina dispersions as a function of pH slightly shifts to high pH at a high ionic strength,<sup>1</sup> and this suggests a shift in the IEP. However, the pH effect on the stability at high ionic strengths is rather insignificant; thus the minimum observed in  $1 \text{ mol dm}^{-3}$  electrolyte was very shallow.

The recently introduced electroacoustic method is suitable for electrokinetic measurements at high ionic strengths.<sup>2</sup> The direct experiments showed that the isoelectric points of anatase, zirconia, and alumina shift to pH values substantially higher than their pristine IEP at high concentrations of certain 1:1 electrolytes, and it was suggested that other materials behave similarly.<sup>3</sup> Very recently the existence of the shift in the IEP of alumina at high ionic strengths was confirmed using another sample ( $\alpha$ -alumina), and similar results were observed for indium and niobium oxides.<sup>4</sup>

The shifts in the IEP discussed above indicate that “inert” electrolytes behave indifferently only at low concentrations, and at concentrations exceeding  $0.1 \text{ mol dm}^{-3}$  small alkali metal cations tend to specifically adsorb on metal oxides. The driving force for specific adsorption in these systems has not been unequivocally identified. The interactions in solution certainly play a significant role.<sup>2,5,6</sup> The shift in the IEP is salt specific,

and combination of a large anion with a small cation gives the most significant shift. The ability of particular salts to induce a shift in the IEP of anatase is correlated with Marcus’ structure-breaking and -making scale of anions and cations,<sup>7</sup> and NaI (structure-making cation and structure-breaking anion) shifted the IEP to greater degree than any other salt studied. Johnson et al.<sup>5</sup> studied the effect of alkali metal nitrates and potassium halides on the IEP of alumina at high ionic strengths, and the  $\zeta$  potentials in NaI solutions were not examined. However, the observed salt specificity followed the same trends as described previously.<sup>2</sup> Johnson et al.<sup>5</sup> claim that the shifts in the IEP are only cation specific while the nature of the anion does not play any significant role. The absence of anion effect was indeed experimentally found, but only for different salts of potassium, which is a nondifferentiating cation.<sup>2</sup> Had Johnson et al.<sup>5</sup> studied a series of lithium or sodium salts, then they would probably have observed some anion specificity.

The goal of the present study is to check the validity of the discussed above allegation that the IEP of metal oxides is shifted to high pH at high ionic strengths, i.e., whether this type of behavior (so far confirmed only for a few materials) can be considered as a general rule. Moreover, we are interested in how the critical electrolyte concentration necessary to reverse the sign of the electrokinetic potential to positive over the entire range depends on the nature of the adsorbent. Insensitivity of the critical concentration to the nature of the adsorbent (the results obtained with anatase and zirconia suggest it) would support a hypothesis that the interactions in solution are responsible for the observed effect.

NaI was selected for this study as the salt, which induced reversal of sign of the  $\zeta$  potential of anatase at lower concentrations than any other salt. This concentration was not too far beyond the standard operating range of the instrument. There is no direct evidence (indirect evidence for zirconia and alumina was discussed above) that NaI is the most effective “IEP shifter” for all metal oxides. That is, no experimental work was undertaken to compare NaI with other salts in terms of the shifts in the IEP of materials other than anatase. In view of published results on the subject of electrokinetics at high ionic strengths, a similar study with salts other than NaI would probably require

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ionic strengths over  $1 \text{ mol dm}^{-3}$ . Rowlands et al.<sup>8</sup> recommend a special calibration of the instrument for very high ionic strengths up to  $3 \text{ mol dm}^{-3}$ . On the other hand, with moderately high ionic strengths (up to about  $0.5 \text{ mol dm}^{-3}$ ) the standard calibration procedure still gives reasonable results.

We selected rutile and hematite as the adsorbents. The physical and chemical properties of these materials including surface charging and electrokinetic properties are well documented in the literature.<sup>9</sup> We also use our recent results<sup>4</sup> obtained with aluminum, indium, and niobium oxides in the present analysis.

### Experimental Section

The electrokinetic potential and particle size were determined using an Acustosizer (Colloidal Dynamics) with the 1.13 software version. All measurements at ionic strengths greater than  $0.02 \text{ mol dm}^{-3}$  were corrected for the electrolyte background. The titrations were carried out without any protection of the samples from the atmospheric  $\text{CO}_2$ .

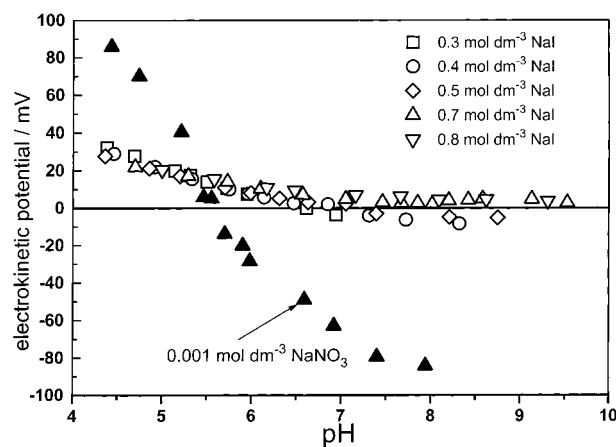
Reagent grade rutile from Aldrich was purified following the procedure described elsewhere.<sup>10</sup> Such material can be easily obtained in kilogram amounts, and the electroacoustic measurements were carried out at 13% rutile mass fraction. The pristine IEP corresponds to the "recommended" value.<sup>9</sup> The particles are about  $1 \mu\text{m}$  in diameter, and the dispersions are rather unstable even at low ionic strengths and far from IEP.

Hematite was synthesized using the method described by Matijevic,<sup>11</sup> and then carefully washed using NaOH and  $\text{HNO}_3$  to remove any trace of chloride and other possible impurities. Only acidic dispersions ( $\text{pH} < 3$ ) were allowed to contact with glass. The BET surface area is  $34.55 \text{ m}^2/\text{g}$ , and the structure has been confirmed by X-ray diffraction. The production and especially washing of this material is very tedious since the dispersions are rather stable, and we had to find a compromise between a good signal-to-noise ratio in electroacoustic experiments (which require high solid concentration), and reasonable time used for hematite preparation. The electroacoustic measurements were run at 1.2% hematite mass fraction, which is at the lower limit of the range recommended for such experiments. Unfortunately, commercially available hematites show their IEP substantially below the "recommended" pristine value,<sup>9</sup> and even washing of these materials does not shift the IEP to the pristine value. This indicates presence of strongly adsorbed ions on the surface. Therefore, commercial hematites are not suitable for the present study. In contrast, the synthetic hematite had an IEP close to the "recommended" pristine value.<sup>9</sup>

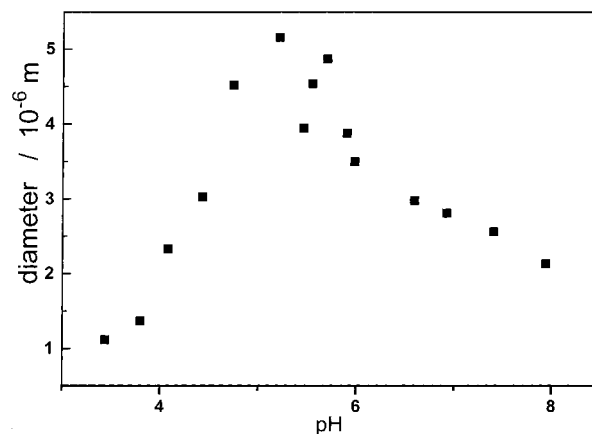
The other chemicals were of reagent grade, water was MilliQ, and the experiments were carried out at  $25^\circ\text{C}$ .

### Results and Discussion

The IEP of rutile in  $10^{-3} \text{ mol dm}^{-3} \text{ NaNO}_3$  at  $\text{pH} 5.7$  (Figure 1) corresponds to the pristine value recommended in the literature.<sup>9</sup> The acid and base titrations (only base titration is shown) produce the same IEP. The effect of NaI on the electrokinetic potential of rutile is similar to the results previously reported for anatase.<sup>2</sup> NaI induces a shift in the IEP to higher pH values ( $5.7$  in absence of NaI,  $6.5$  in  $0.3 \text{ mol dm}^{-3}$  NaI,  $7$  in  $0.4 \text{ mol dm}^{-3}$  NaI, and  $7.3$  in  $0.5 \text{ mol dm}^{-3}$  NaI), and when the critical NaI concentration (in this case about  $0.6 \text{ mol dm}^{-3}$ ) is exceeded, the sign of the  $\zeta$  potential is positive up to  $\text{pH} > 9$ , and probably also at much higher pH. This critical value is in good agreement with the critical NaI concentration found for anatase. Both rutile and anatase are forms of  $\text{TiO}_2$ , so this match is not surprising. However, the surface properties often differ from one crystalline form to another.



**Figure 1.** Electrokinetic potential of rutile as a function of pH and NaI concentration.

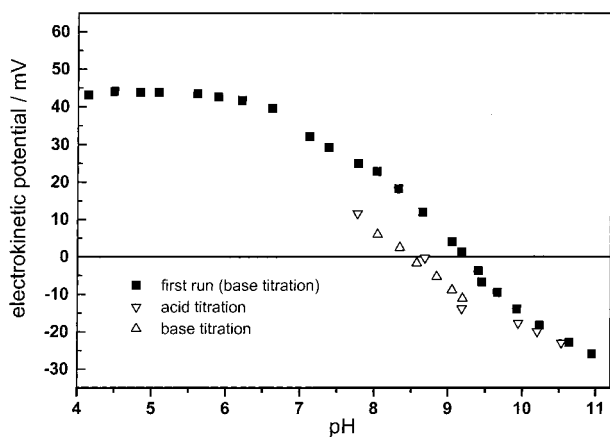


**Figure 2.** Particle size of rutile in  $10^{-3} \text{ mol dm}^{-3} \text{ NaNO}_3$  as a function of pH.

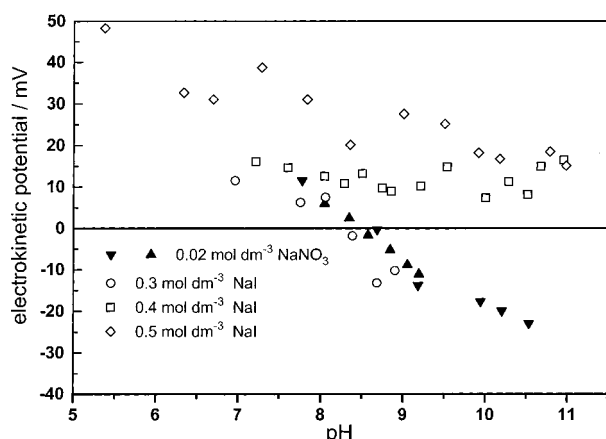
The particle size of rutile in  $10^{-3} \text{ mol dm}^{-3} \text{ NaNO}_3$  shown in Figure 2 exhibits a maximum at the IEP, and the size obtained at  $\text{pH} < 4$  reflects the diameter of primary particles.

The particle diameter of hematite in  $2 \times 10^{-2} \text{ mol dm}^{-3} \text{ NaNO}_3$  was about  $100 \text{ nm}$  over the pH range  $2$ – $6.5$ , and this corresponds to the size of primary particles. Two measurements at  $\text{pH} \approx 9.5$  resulted in a particle size of about  $600 \text{ nm}$ , and the other attempts to determine the particle size of hematite at  $\text{pH} > 6.5$  were not successful (too low particle concentration; cf. Experimental Section).

The electrokinetic behavior of hematite in  $2 \times 10^{-2} \text{ mol dm}^{-3} \text{ NaNO}_3$  is presented in Figure 3. The first titration was started at acidic pH, and it resulted in the IEP at  $\text{pH} 9.2$ . This value is rather high compared with other values of IEP reported in the literature for hematite.<sup>9</sup> To our best knowledge, the only electroacoustic IEP reported for synthetic hematite was at  $\text{pH} 8.3$ ,<sup>12</sup> while the other available values were obtained using classical electrokinetic methods. Analysis of the effect of the choice of the experimental method on the PZC/IEP of alumina indicates that the electroacoustic method produced substantially higher IEP than other methods, and the present result confirms this trend. However, back-titration with acid produced the IEP at  $\text{pH} 8.7$ , which is substantially lower than the original IEP. The next base and acid titrations produced the IEP at the same pH; i.e., no hysteresis loop was observed. One way to explain this discrepancy is that the IEP at  $\text{pH} 9.2$  is the pristine value and the shift in the IEP from  $\text{pH} 9.2$  to  $8.7$  is due to some kind of surface contamination. For example, the shift in the IEP of hematite to low pH (determined by means of microelectro-

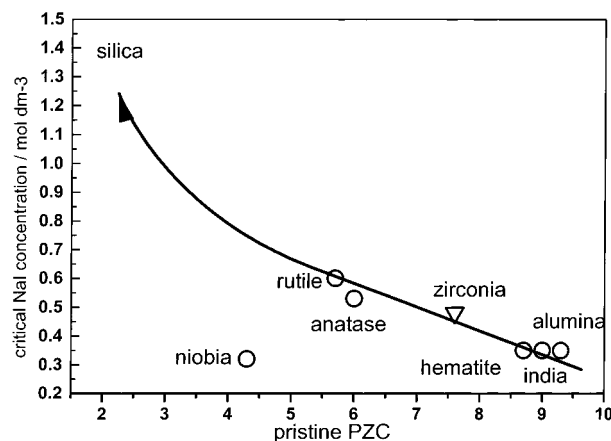


**Figure 3.** Electrokinetic potential of hematite in  $2 \times 10^{-2}$  mol dm $^{-3}$  NaNO $_3$ .



**Figure 4.** Electrokinetic potential of hematite as a function of pH and NaI concentration.

phoresis) as the effect of storage in glass at neutral and basic pH is well-known.<sup>9</sup> This hypothesis is, however, rather unlikely in view of high solid-to-liquid ratio in our experiment. Probably the high initial value was rather due to some “memory effect” caused by storage of hematite in strongly acidic solution before the measurements, and pH 8.7 is the actual pristine value. Therefore, in Figure 4 (showing the NaI effect on the electrokinetic potential of hematite) the IEP at pH 8.7 was used as the reference point. In contrast with rutile and anatase, 0.3 mol dm $^{-3}$  NaI did not induce a shift in the IEP of hematite to higher pH, and even the IEP appeared to shift slightly to lower pH. However, with 0.4 mol dm $^{-3}$  NaI the sign of the electrokinetic potential of hematite was reversed to positive over the entire pH range. Thus, the critical NaI concentration for hematite is substantially lower than that for titania. The available information on the critical NaI concentration for different materials and the correlation between this critical concentration and the pristine point of zero charge (PZC) are presented in Figure 5. Six data points (circles) represent actual measurements with NaI. The triangle represents the critical concentration for the zirconia–NaBr system.<sup>2</sup> For anatase the critical concentration of NaI was slightly lower than that of NaBr $^{2-}$ , and (in view of the similarity between Ti and Zr on the one hand and between Br and I on the other) we can speculate that a similar relationship is valid also for zirconia. With the exception of one data point representing niobium(V) oxide the shift in the IEP to high pH at high concentration of NaI appears to be more pronounced for oxides whose pristine IEP falls at high pH. The hyperbola with the arrow in Figure 5 represents extrapolation of available



**Figure 5.** Critical NaI concentrations (inducing reversal of sign of  $\zeta$  potential to positive over the entire pH range) for different oxides. The symbols are explained in the text.

results (ignoring the data point corresponding to niobia) to low pH. This extrapolation leads to a very high critical NaI concentration for silica (very low IEP if any). This is in qualitative agreement with the experimentally found<sup>13</sup> absence of NaI effect on the IEP of silica.

Interestingly, for all oxides of odd-valent metals the critical NaI concentration is below 0.4 mol dm $^{-3}$ , and for all oxides of even-valent elements the critical NaI concentration is above 0.4 mol dm $^{-3}$  or it does not exist at all.

The relationship presented in Figure 5 is not necessarily valid for salts other than NaI. Systematic studies of salt specificity were carried out for anatase<sup>2</sup> and alumina,<sup>5</sup> and to less extent for silica (ref 13 and references therein). It appears from these fragmentary results that the trend shown for NaI in Figure 5 is opposite the trend in the effects of cesium salts on the IEP of oxides. Johnson et al.<sup>5</sup> observed no substantial effect of CsNO $_3$  on the IEP of alumina at concentrations up to 1 mol dm $^{-3}$ . With anatase<sup>2</sup> 0.1 mol dm $^{-3}$  CsI induced a shift in the IEP by a fraction of one pH unit, and the IEP of silica was shifted to pH as high as 5 in 0.1 mol dm $^{-3}$  solutions of cesium salts.<sup>9</sup> Apparently the effect of the nature of oxide on the specific adsorption of Na is dramatic: from the absence of any shift in the IEP for silica to the sign reversal to positive over the entire pH range at NaI concentration as low as 0.4 mol dm $^{-3}$  for hematite. In contrast, the specific adsorption of cesium on oxides is less sensitive to the nature of the adsorbent.

The above analysis neglects the anion specificity, which was observed for anatase and zirconia,<sup>2</sup> but apparently it is less significant for silica<sup>9,13</sup> and alumina.<sup>5</sup> The present results are in qualitative agreement with the cation effects on the surface charge density of oxides, which are observed at low ionic strengths.<sup>9</sup> That is, the surface charge of metal oxides at constant pH and ionic strength decreases in the series from Li to Cs while the opposite order is observed with silica. However, the cation specificity at low ionic strengths was only observed for negatively charged surfaces (above the pristine PZC), while below the pristine PZC the surface charge density is anion dependent (no cation specificity). Apparently the deficit of water in high ionic strength systems and thus incomplete hydration of cations (as compared with dilute solutions) is responsible for their specific adsorption also below the pristine IEP.<sup>2</sup>

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