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Multilaboratory study of the shifts in the IEP of anatase at high ionic strengths

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Abstract

The ζ -potentials of anatase at pH 2–11 in 0.1, 0.3, 0.5, and 1 mol dm⁻³ NaI were studied using the DT 1200 in three laboratories. At [NaI] = 1 mol dm⁻³ the ζ -potentials were positive over the entire pH range. The previously observed tendency of the isoelectric point of anatase to shift to high pH at high ionic strength (M. Kosmulski, J.B. Rosenholm, *J. Phys. Chem.* 100 (1996) 11681) and the salt specificity of this effect were confirmed. The ζ -potentials obtained in different laboratories using DT 1200 are consistent within 3 mV.

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1. Introduction

The isoelectric points (IEP) and points of zero charge (PZC) of metal oxides in the absence of strongly adsorbing species (multivalent ions, surfactants, and polyelectrolytes) are rather insensitive to the nature and concentration of 1–1 electrolytes (alkali nitrates V, chlorates VII, and halides) [1]. In contrast with the PZC, which is constant up to the solubility limit of the salts, the IEP is constant only up to the electrolyte concentration of about 0.1 mol dm⁻³. Above this limit the IEP of anatase shifts to high pH [2]. Since this shift in the IEP is rather surprising (intuitively one would rather expect constant IEP) the electrokinetic behavior of anatase at high ionic strengths needs a careful verification. The problem with high ionic strength electroacoustics is in a high electrolyte signal, namely, the ion vibration current, or ion electroacoustic signal is roughly proportional to the ion concentration. Then the signal from the particles themselves is calculated as a difference between two large and almost equal numbers, and the value and even sign of the calculated ζ -potential is uncertain.

We can recall the following evidence that the observed shifts in the IEP of anatase induced by high electrolyte con-

centration are real (not due to instrument artifacts or erroneous procedure).

1. Some results obtained using classical electrokinetic methods [3] and some studies of colloid stability [4] suggest similar shifts in the IEP of titania and other metal oxides (however, some other results [5] suggest constant IEP of metal oxides up to 1 mol dm⁻³). This kind of evidence has limited significance since classical electrokinetic methods are generally not suitable for measurements at high ionic strengths.
2. In the presence of organic cosolvents, shifts in the IEP of oxides to high pH were observed [6] at relatively low ionic strengths within the normal operation range of classical electrokinetic methods.
3. The shifts in the IEP were confirmed using another sample of anatase [7], for different oxides [8–10], and also by other research groups [11,12] using the same instrument (Acustosizer). Although the assessment of the significance of these results by different authors was not completely consonant [13], basically the same tendency was reported, namely, shifts in the IEP to high pH at high concentrations of certain salts.
4. At low ionic strengths the maximum in the viscosity vs pH curves of concentrated dispersions of anatase matches the IEP. At high ionic strengths the maximum shifts to high pH [14]. A similar result (a shift in the

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maximum in the yield stress to high pH at high concentrations of certain salts) was reported for alumina [15].

Even with the above evidence the shifts in the IEP to high pH induced by a high electrolyte concentration are still a hypothesis rather than a well-established fact, and some independent method to verify these results is greatly desired.

Fortunately DT-1200, a new instrument which is also suitable for measurements at high ionic strengths, became available on the market, but the operation principle and theory are different from those in Acustosizer (CVI (colloid vibration current) is measured rather than ESA (electric sonic amplitude)). We will compare the results obtained by means of both instruments and check the consistency of the results obtained by means of DT-1200 in three different laboratories.

Anatase was selected for this study since its electrokinetic properties at high ionic strengths were studied more extensively than for any other material. The high ionic strength behavior of anatase has been studied in solutions of different salts at different concentrations, temperatures, and solid to liquid ratios. NaI was selected as the salt that induces substantial shifts in the IEP of anatase (and other metal oxides) at relatively low concentrations (compared with other 1–1 salts).

2. Experimental

The details of the preparation of anatase (we used two different lots prepared in the same way) and its characterization are described elsewhere [2]. The other chemicals were reagent grade, water was MilliQ, and all experiments were carried out at 25 °C. All measurements at ionic strengths higher than 0.02 mol dm⁻³ were corrected for the electrolyte background.

The DT-1200 characterizes the ζ -potential by means of a specially designed probe that uses ultrasound as a driving force for generating an electroacoustic effect [16]. One of the advantages of using ultrasound rather than electric field as a driving force is related to eliminating the possible contribution of various magnetic effects, which might be induced by high frequency electric fields. This probe looks like a stainless steel cylinder 3 cm in diameter and 10 cm long. Piezo-electric crystal inside of the probe converts an electric pulse generated by electronics into an acoustic pulse of the same frequency. In default it is one frequency of 3 MHz. There is an option to change this frequency or to use multiple frequencies. The acoustic pulse launches into the sample through the plastic rod with acoustic impedance close to the value of the sample. This minimizes reflection on the probe–sample interface and enhances intensity of the sound in the sample. This rod is covered with a thin gold layer that performs the function of a sensing electrode. The stainless steel cylinder is a reference electrode placed outside the sound field. An ultrasound pulse generates electric current

between two electrodes due to the motion of either ions or particles, or both. Electronics measures this current by accumulating a response from the number of pulses in order to gain a high signal-to-noise ratio. This number is automatically adjustable depending on the signal level. For low signals at high ionic strength it goes to the millions. The instrument software has an option to calibrate a probe for a given liquid that would be considered as a reference for the further measurement of colloids with this liquid as the dispersion medium. For more details, see Section 8.6, “Colloids with High Ionic Strength–Electroacoustic Background” of the book by Dukhin and Goetz [16].

The measured colloid vibration current yields information about particle surface properties, ζ -potential in particular. In order to calculate this parameter from CVI, the software uses modern electroacoustic theory, which is described in Chapter 5 of Ref. [16]. This theory takes into account particle inertia and particles' hydrodynamic interaction using the Kuvabara cell model and the coupled phase acoustic model. Electrodynamic interaction and surface conductivity effects are taken into account with the Shilov–Zharkikh cell model. Particles are modeled as spheres. There is no superposition assumptions involved in derivations, as the “coupled phase model” makes it possible to relate microscopic and macroscopic parameters of concentrated polydisperse colloid with no superposition assumption. For details, see Chapter 5 of Ref. [16]. This theory has been experimentally verified with several colloids, as described in Chapter 6 of the same book.

The experimental setups (e.g., the size and shape of the vessels) were somewhat different in the three laboratories. One of two identical vessels was filled with electrolyte solution, e.g., 0.3 mol dm⁻³ NaI, and the other with a suspension of anatase 10% by mass in the same solution. A few experiments were also conducted at variable solid loads, and they produced similar results. No attempt was made to insulate the dispersion from the atmospheric CO₂. The particle size of 0.3 μ m, which corresponds to the result obtained by TEM, was pre-assumed in the calculation of ζ from CVI. The DT-1200 produced a somewhat higher size from the acoustic attenuation measurement, namely, median particle diameter of 0.35 and mean diameter of 0.53 μ m (standard deviation 0.41) in the anatase dispersion at pH 2.68 at a low ionic strength.

The experimental protocol, specially designed for measurements at high electrolyte concentration, was the same in all three laboratories. After the pre-equilibration, the ζ -probe was put in the vessel without anatase and the background signal was collected. This signal was saved as a calibration constant and used as the reference null in measurements with dispersion. Then the probe was put in the vessel with the dispersion and a pH-titration was carried out. Every three to five data points the probe was withdrawn, washed from the leftovers of the dispersion, wiped with soft tissue, and put in the vessel with the background electrolyte to update the background signal, and then the probe was put

back into the vessel with the dispersion and the titration was continued. A few series of data points were collected without changing the pH to test the stability of the signal. In most instances the ζ -potential of the same dispersion measured against new background was consistent within 1 mV (typical shifts of about ± 0.3 mV), but a few background updates resulted in a shift in the measured ζ -potential by 1–2 mV.

3. Results and discussion

A typical set of the electrokinetic curves (obtained in one laboratory, with one lot of anatase) is shown in Fig. 1. The pristine IEP at pH 6.2 (0.01 mol dm⁻³ NaNO₃, no background correction) was slightly higher than most IEP of other samples of anatase reported in the literature [1], and the electrokinetic curve is nearly symmetrical with respect to the IEP. Acid and base titration produce the same IEP (no hysteresis loop). An increase in the NaI concentration above 0.1 mol dm⁻³ produces the following effects. The absolute value of ζ decreases, and the decrease is more pronounced on the negative branch. Thus, the electrokinetic curves become unsymmetrical with respect to the pristine IEP. At pH > 7 and at high ionic strengths the electrokinetic curves reach a plateau; i.e., an increase in the pH does not induce more negative ζ . The values of the ζ -potential at the plateau ζ_{\min} are summarized in Table 1. The results obtained in different laboratories and with different lots of anatase are consistent within 3 mV. The observed “selective” depression of negative ζ -potentials (typical for specific adsorption of cations) is in line with the results obtained previously [2], and the numerical values of the ζ -potential at the plateau are relatively consistent with the results obtained using the Acustosizer. Figure 1 also confirms the shift in the IEP to high pH at high ionic strength, and with 1 mol dm⁻³ NaI

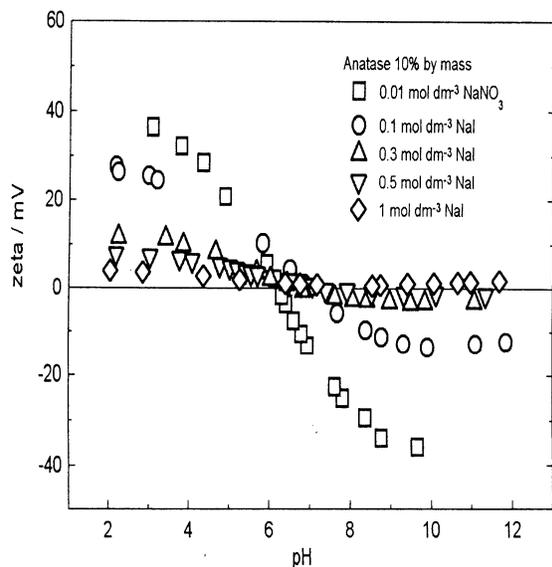


Fig. 1. Electrokinetic potential of anatase at different NaI concentrations.

Table 1

The most negative ζ -potentials of anatase at different NaI concentration observed in different laboratories

[NaI]/mol dm ⁻³	ζ_{\min} /mV (Acustosizer [2])	ζ_{\min} /mV (DT-1200)
0.1		-16; -13; -13; -12
0.3	-7.4	-5; -3.3; -3.9; -3.4
0.5	-0.3	0.3; -1.5; -1.3
1	5.7	1; 0.7; 2.1; 0.4

there is no IEP at all and the electrokinetic potentials are always positive. However, the positive ζ -potentials at high pH in 1 mol dm⁻³ NaI (Table 1) observed in the present study were lower than the results obtained using the Acustosizer. The presence of 0.3 and 0.5 mol dm⁻³ NaI induced shifts in the IEP, but the significance of the numerical values of the corresponding IEP is limited. This is because ζ -potentials in the range from -2 to +2 mV are obtained over a broad pH range around the apparent IEP (Fig. 1); thus a small error in the ζ -potential might have produced a large error in the IEP. For instance a mixture of positive and negative ζ_{\min} was obtained in experiments performed in different laboratories with 0.5 mol dm⁻³ NaI (Table 1). This result is in a qualitative agreement with the critical concentration (electrolyte concentration that reverses the sign of the ζ -potential of anatase to positive over the entire pH range) of 0.53 mol dm⁻³ reported in the previous study for NaI [2].

Anatase shows rather sharp IEP in concentrated KCl solutions (in contrast with NaI) as demonstrated by means of the Acustosizer [2]. The IEP of anatase in 0.5 mol dm⁻³ KCl at pH 7.6 obtained in the previous study is close to that obtained in the present study by means of DT-1200 (pH 8). Thus, although a systematic study of the salt-specificity was not carried out, two examples of NaI and KCl confirm the salt-specificity effects found by means of the Acustosizer [2]. Namely, certain salts induce sign reversal of the ζ -potential of metal oxides to positive over the entire pH range at relatively low concentrations (e.g., about 0.5 mol dm⁻³ for anatase–NaI system) while for other salts (e.g., KCl) negative ζ -potentials can be always obtained at a sufficiently high pH.

4. Conclusions

1. DT-1200 is suitable for electrokinetic measurements at high ionic strengths.
2. DT-1200 and Acustosizer produce qualitatively consistent ζ -potentials at high ionic strengths.
3. An increase in the ionic strength induces a shift in the IEP of anatase to high pH. This effect is salt specific. When the critical concentration of salt (0.5 mol dm⁻³ for NaI) is exceeded the ζ -potentials are positive up to pH 11 and probably there is no IEP at all.

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