

C07 - Easy understanding of particle charge and efficient use of it

... explaining the concept of fast and easy particle charge titration offered in the Stabino®

In fine dispersions, where electrostatic repulsion between equally charged particles is responsible for the stability against coagulation or coalescence, the characterization of the ionic particle interface is a must. Total charge and charge density are important parameters to know, when particles are functionalized with ionic end groups. The measurement of the charge is performed in a way to create electrokinetic signals. Depending on the experimental set-up, the result is called electrophoresis, electroacoustic or acoustophoretic zeta potential, and streaming potential as in Stabino®. These names are the most frequently mentioned charge parameters originating from the shearing force acted to the ionic cloud at the double layer of the particle interface (see Fig. 1 below). All of them are measurants which are proportional to the particle interface potential (PIP, also called zeta potential) situated at the shear plane. To create an interface potential, either an electric field as in electrophoresis or electroacoustic setups, or mechanical stress is applied streaming potential and acoustophoretic experiments. By doing this, the outer loosely bound ions from the solution are carried away, leaving the interface potential “open” to be measured.

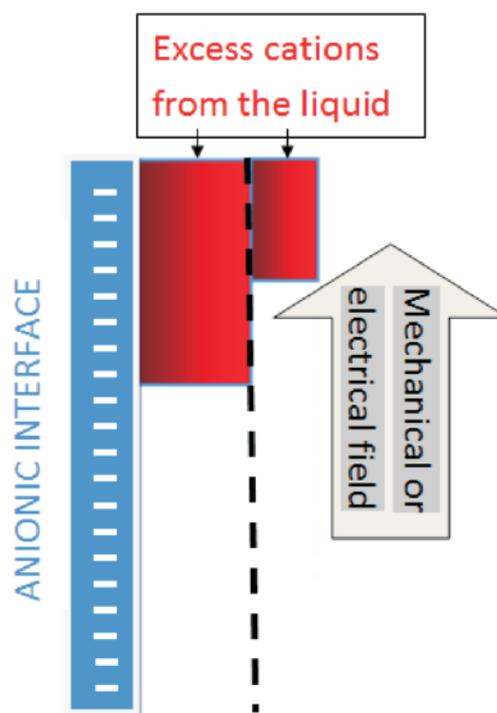


Fig. 1:

The purpose of charge titrations

Depending on the size region, the zeta potential is calculated with Smoluchowski, Henry's and other equations. The size range however, in which calculations can be correctly done, is restricted. In particular, below 100 nm the correct calculation procedures are not yet clearly agreed on. For the formulation practice it is questionable, whether absolute values are necessary at all. In addition, a single point measurement of the PIP does not tell the whole story of a sample. The interface potential is always dependent on the ionic environment. More strictly speaking, a particle interface potential is not defined without its ionic environment.

A tiny change of the pH could make a pigment suspension unstable, although the zeta potential was high before. Therefore, it is useful to look at a titration curve where the PIP is plotted versus the quantity of a substance influencing the potential. This can be the pH, an ionic surfactant or a poly-electrolyte. Having said this, many more useful results can be obtained by charge titrations, one of them being the identification of the stable and unstable regions of a dispersion, another is the dosage of coagulants or catalytic additives causing macromolecular or/and particulate reactions.

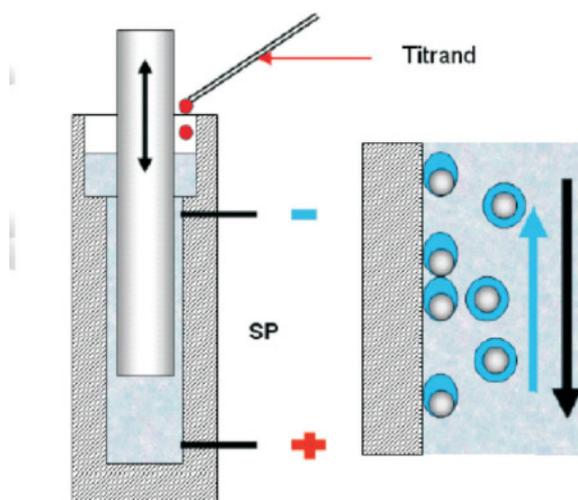


Fig. 2: The principal set-up of a streaming potential SP monitor: Displacement of the ion cloud around the particles sticking to the wall of the PTFE sample container, inducing the SP at the electrode pair.

Measuring streaming current potential

By moving a piston up and down in a cylindrical container, the liquid in the gap between the cylinder and the piston is flowing down and up. Due to the shearing force at the interface of immobilized particles, the ionic cloud of the particles is displaced as shown above. The immobilization is either achieved by the adhesion of macromolecules or small particles to the walls or due to inertia of bigger particles. In the quiet section of the sample bottom, there is no such ion displacement. Therefore, an oscillatory signal between the bottom and a higher section of the measurement cylinder can be picked up.

The charge cloud of the small particles in the suspension stays more or less symmetric and does therefore not significantly contribute to the potential.

The phase of the alternating SP signal is related to the polarity of the particle charge. Depending on the application, a polyelectrolyte, a pH or salt titration is executed. The titration together with streaming current potential monitoring determines the cationic / anionic demand as well as the isoelectric point. Whether the zero point of charge is important or the maximum of the titration curve, the objective of the study dictates the strategy. In recycling processes, where the separation of dispersions should be achieved, the user wants to know the amount of additive which is needed to reach a zero potential.

In the other case, when a dispersion should be stabilized by changing the electric surface charge, the charge titration is used to determine the dosage which is necessary to bring the sample into a flat region far away from zero. This can be achieved by setting the pH to the corresponding value.

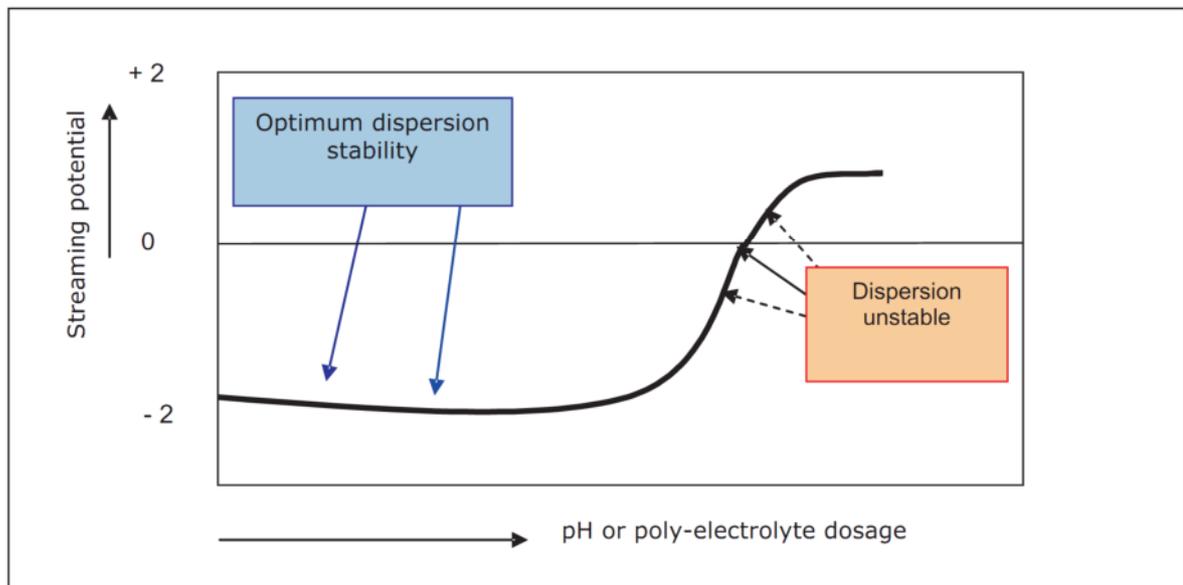


Fig. 3: Typical titration curve: pH- or poly-electrolyte titration to find the point where the particle charge is zero, or where the dispersion / emulsion is stable

Or, in another example, where particles are going to be coated with a polyelectrolyte, the polyelectrolyte titration curve delivers the optimum dosage of coating material, whereas the height of the potential signifies the repulsion strength.

The versatile streaming potential of Stabino®

Looking at the size range where the SP method can be applied, makes it obvious that SP is the most general method: 0.3 nm sized macromolecular solutions can be measured as well as particle suspensions and emulsions up to 300 µm. The allowed conductivity ranges from near zero up to 50 mS/cm, whereby the sample concentration can be 0.01 or 10 vol% and more. The upper limit for the viscosity is 300 mPas. At this viscosity, the efficiency for mixing titrand solutions into the sample becomes very questionable. Besides the concentration of the sample and the titrands, no sample parameters are needed. Last but not least, if zeta potential is important to know, in many applications the streaming potential can be calibrated to zeta potential by a simple multiplication with a constant factor.

The efficiency of the streaming potential for charge titrations

The fact that mixing, homogenizing and signal measurement is made in one device, make the titrations with Stabino® most effective. Before going into the detail of titrations, it should be mentioned, that 5 to 15 minutes is the typical duration for one titration.

Instrumental arrangement for the charge titration

In the principle set-up of the PARTICLE METRIX Stabino® - shown in Fig. 4 - for simplicity reasons and by restricting to problem solving - two titrators are integrated in the instrument. These are dedicated to charge titrations. The sensing signal is the interface potential. The sample volume is 10 mL. The titration method is available as an SOP and is programmed for a defined end point. Kinetic studies are also possible.

By titration of the sample with a charge standard, the specific charge of the sample per gram or the specific charge density (Coulomb per m²) can be evaluated, provided the volume concentration and the specific surface area of the dispersion are known. Practical limits are high viscosity, strong sedimentation or clogging in the sample cell limiting the upper size to approximately 300 µm.

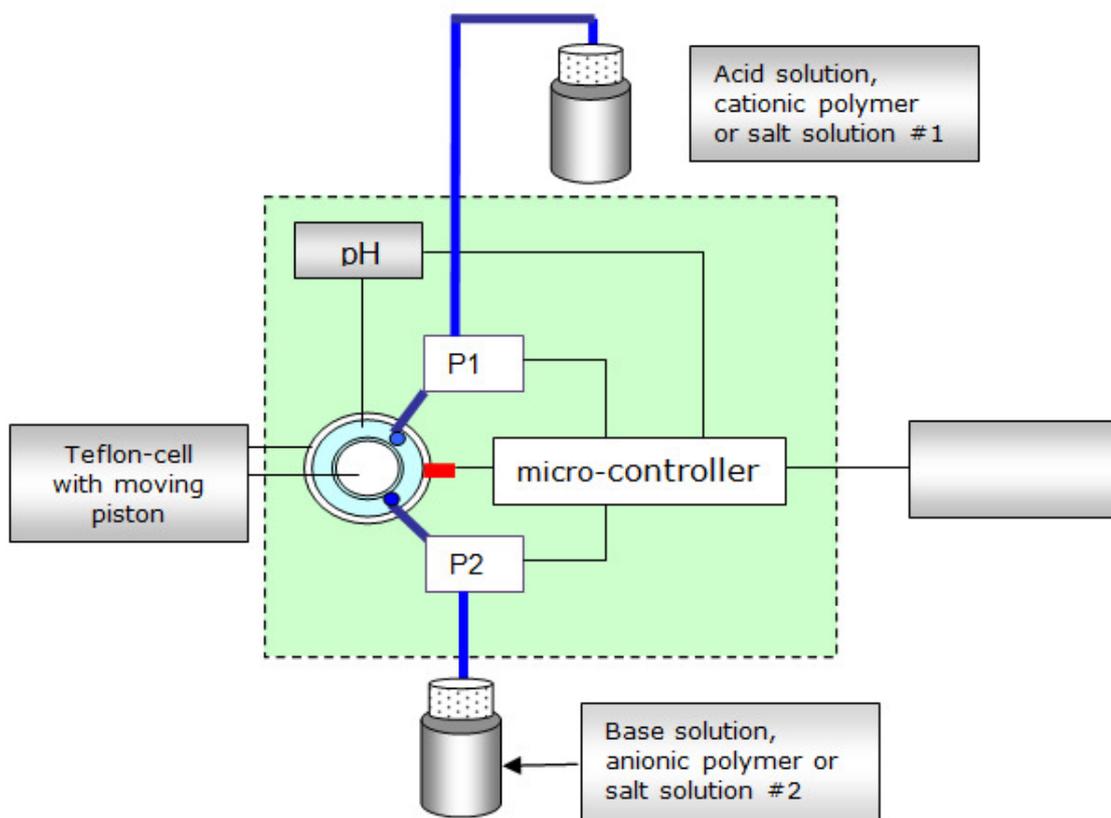
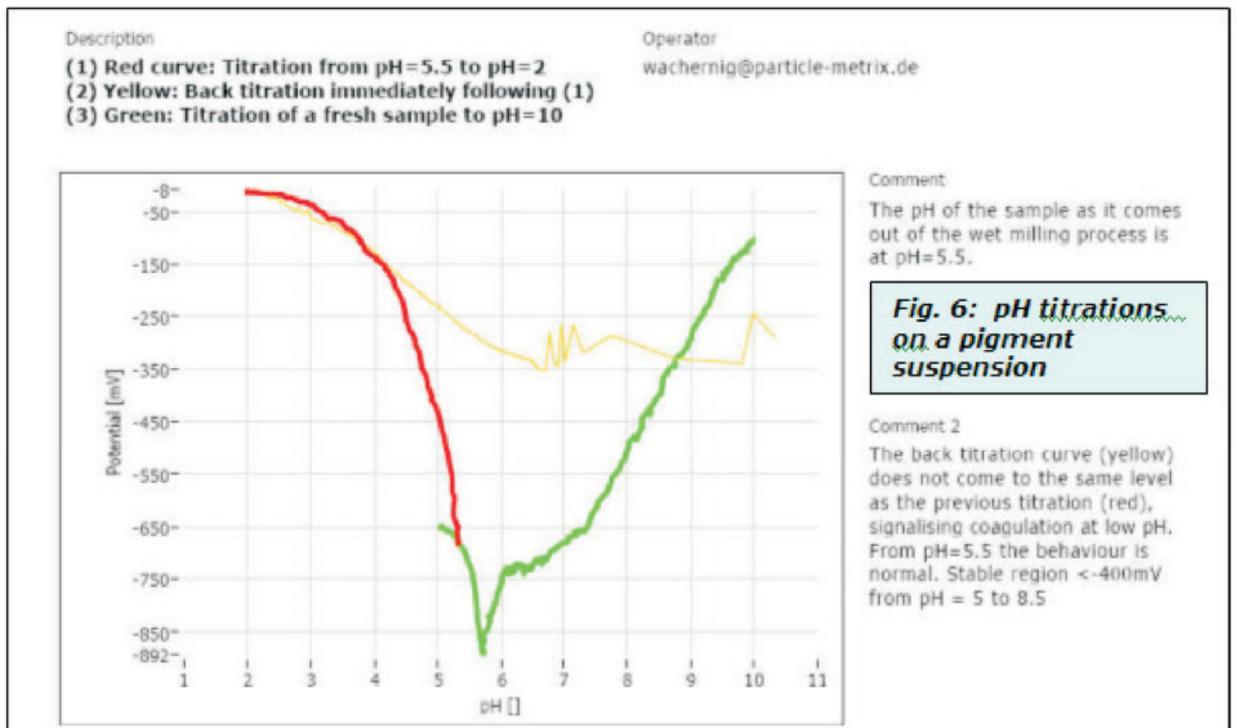
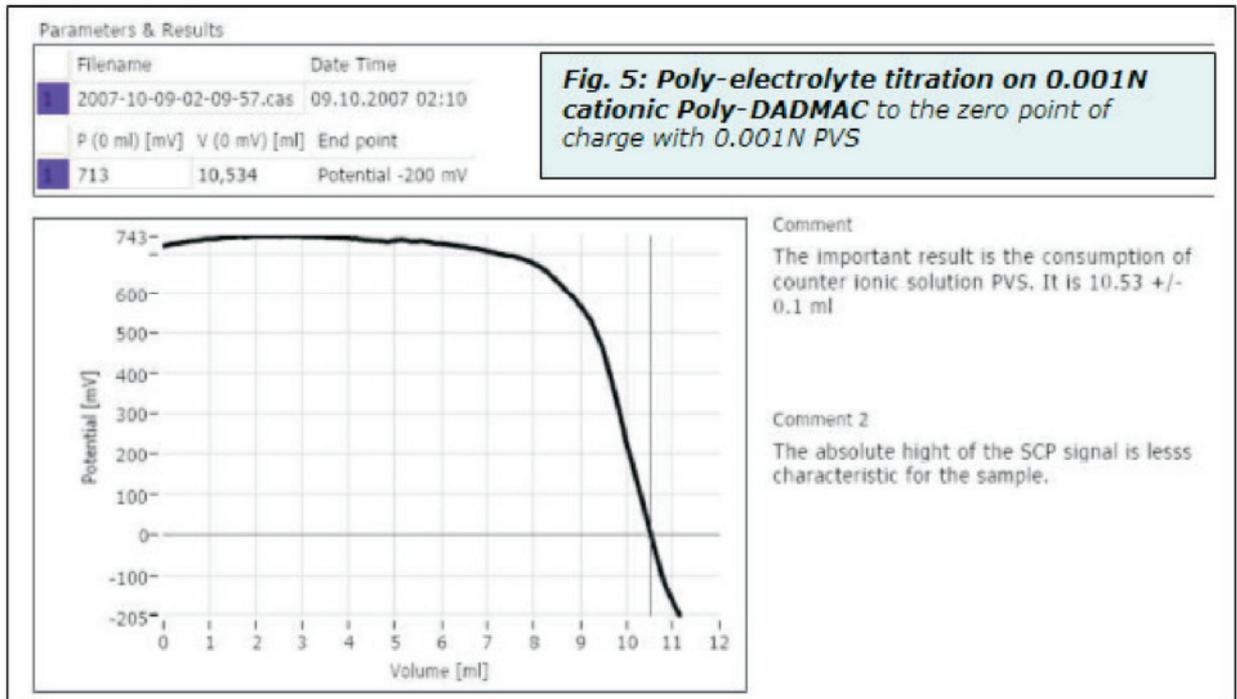


Fig. 4: Basic set-up of Stabino® with two integrated dosing pumps and 2 reservoirs for the automatic titration. The sample cylinder has one notch for a pH probe and one for a 180° DLS size probe of an optional NANO-flex instrument (not shown).

In figure 5 and 6 below, typical titration curves are shown, figure 5 presenting a polyelectrolyte titration with another polyelectrolyte solution and figure 6 pH titrations on a blue pigment.



Stabino® – an invitation to LEARN charge analysis AND to USE it daily

In general, to enter the subject of zeta potential, charge analysis and titration, is more difficult than the subject of size analysis. There are many influences to the particle interface potential. To understand them, physical and chemical knowledge is required. The quickest and simplest way to see all these interdependences is by making titration experiments realized in the Stabino®. It does neither require optical data nor shape parameters or viscosity. Due to the presence of two dedicated dosing pumps, the titration method selection is simple. In particular, there is little need in rinsing tubes and bottle handling.

As the only method the SP based charge titration allows the charge characterization of macromolecular solutions. In many applications, the polyelectrolyte additives used in coating, in functionalizing the surface and in recycling processes can therefore be characterized with the same method as the particles, which these additives are anticipated to react with.

All this offers a “learning by seeing” opportunity. It is the most efficient entry to the subject ionic particle charge potential.



The optional 180° back-scattering DLS sensor delivers size distributions from 0.3 nm to 6.5 µm, together with specific surface area information, which can be used to calculate the charge per surface area. With the size probe coagulation can be attributed to specific ionic conditions.

The flexibility and the capability to show the **FULL IONIC CHARACTER** of an interface is an invitation to enter the subject of particle charge characterization with Stabino® ... **AND** to use it every day!