

COMPREHENSIVE IONIC CHARGE SENSING FOR MACROMOLECULES AND PARTICLES

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Introduction

Nearly any surface carries ionic charge. If it is sufficiently high, particles repel each other keeping a dispersion stable. Immersed in water, the charge is immediately compensated by surrounding ions, forming an electrostatic double layer. Although it is neutral from outside, the double layer can be peeled off quite easily by physical arrangements such as electrophoresis, ultrasonic vibration, mechanical shearing and others. By applying these techniques, the ionic charge of the interface is measurable as a particle interface potential PIP, indicating dispersion stability or instability. In this contribution, the "streaming potential" sensing is presented as an effective tool to **map the**

electrostatic behavior of polyelectrolytes and particles.

As signal measurement and mixing of titrand solution to the sample is achieved within 5 seconds, one complete titration can be performed within 5 minutes. The method can be applied to polyelectrolyte solutions (size > 0.5 nm) and to dispersions up to 300 μm particle size. To be correct, when going from small to big particles the method changes gradually from streaming to an "inertia potential" sensing.

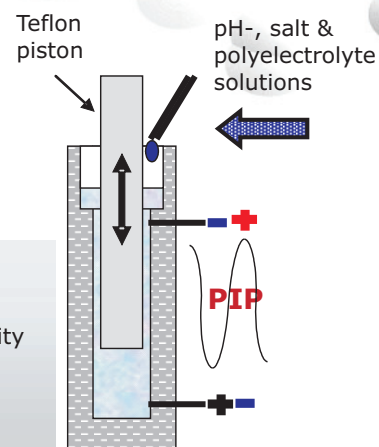
0.1 g is needed as a minimum sample quantity. Concentrations up to 40% are possible, bearing in mind that high viscosity is a limitation. The result correlates to zeta potential in many cases, yet has to be proven for a given sample class.

The method

A fast oscillating flow of the fluid in the gap between the piston and the measurement cylinder is produced by the moving piston. This causes a periodic shearing at the double layer at the particle's / macromolecule's interface leading to an ionic polarization inside the gap. This polarization voltage is proportional to the zeta potential ZP, which is one of the better known candidates of PIP. Macromolecules tend to stick to the wall contributing to a voltage signal proportional to the zeta potential, the velocity of the fluid and some physical constants of the liquid. Big particles deliver an inertia polarization signal. In an inhomogeneous system there is a mixture of both.

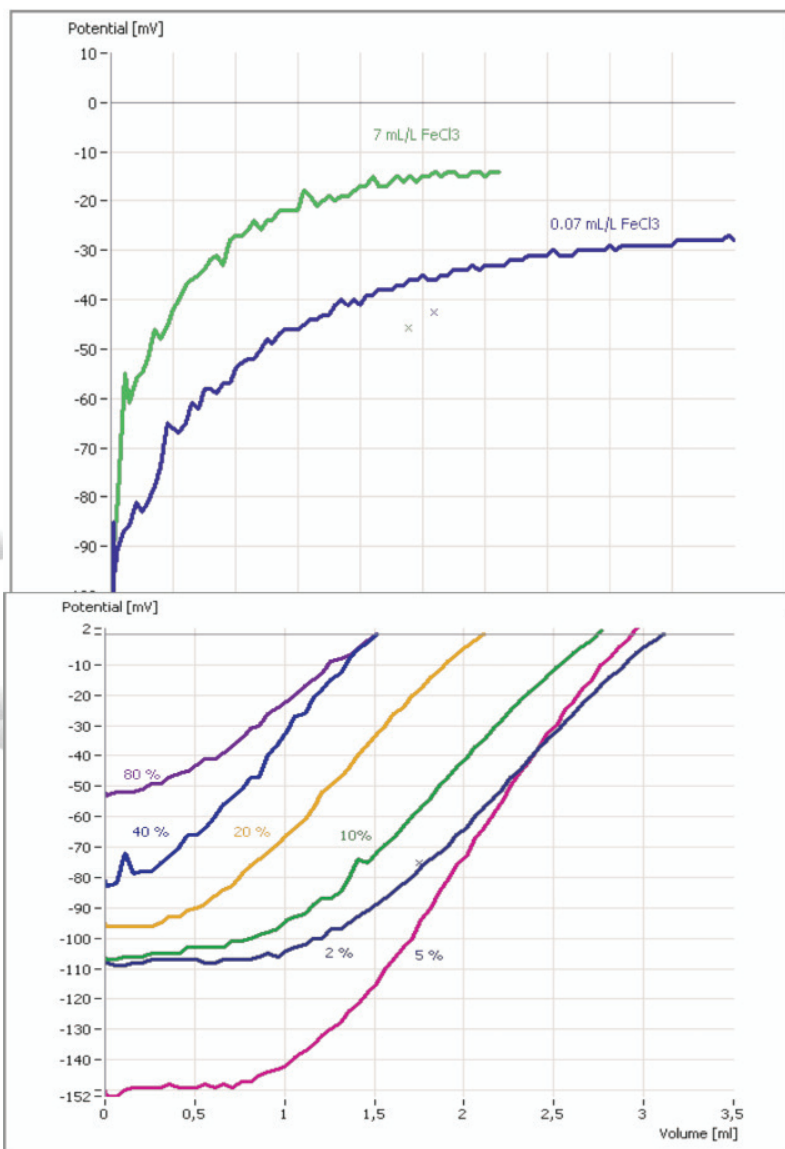
$$PIP = k v_0 \cdot \epsilon \cdot ZP / \eta$$

k ... Instrument constant
 v_0 ... maximum liquid velocity
 ϵ ... dielectric constant
 η ... Viscosity
 ZP ... zeta potential



Experiments

Repeatability and modern software of the StabiSizer® instrument make optimum use of this particle charge mapping method. Three selected examples discussed here, open a window to look at a wide field of applications.



Optimization of the recycling efficiency for water of a pigment suspension:

Or: The optimum combination of FeCl₃ precipitation and cationic polymer flocculation.

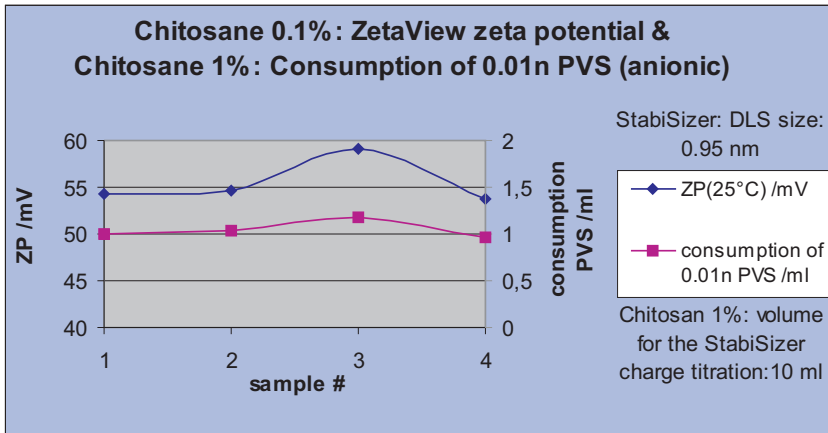
The efficiency of FeCl₃ to bring the PIP near to zero comes to a saturation at a given concentration. The StabiSizer® PIP titration against added volume of FeCl₃ solution at two different concentrations indicating this.

The cationic polymer consumption at various FeCl₃ concentration levels is shown in the [first figure](#). The biggest variation of the cationic polymer consumption is seen between "10%" and "40%" of 7 mL/L ([figure 2](#)). As a result, it does not make sense to operate the recycling above 30% FeCl₃ concentration.

A similar behaviour could be observed using a Turbiscan instrument to follow sedimentation. This is described in the Particle Metrix application note AN-08.

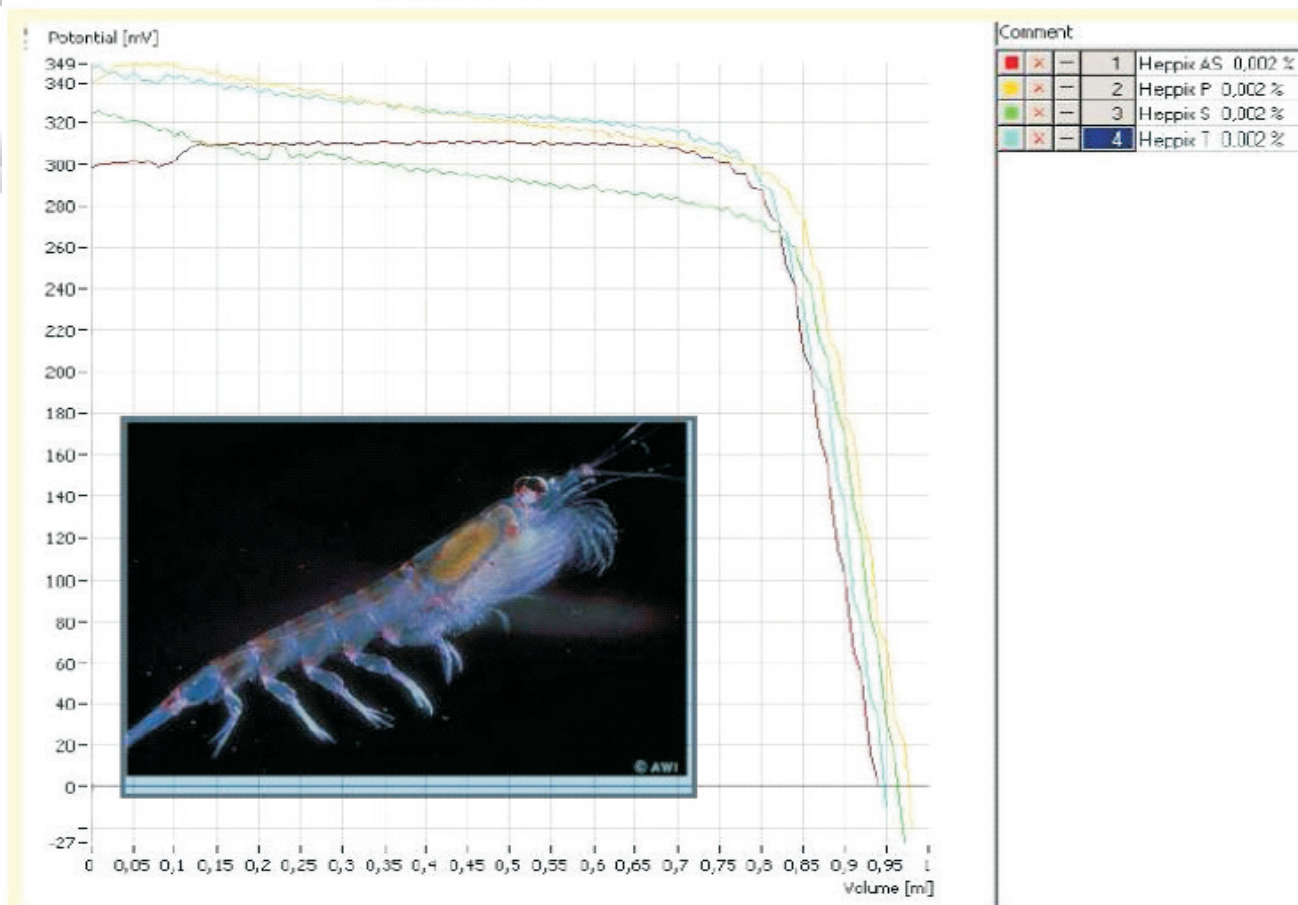
Total charge of 4 cationic Chitosan polymer solutions and correlation to zeta potential

The anionic polymer consumption of 1% Chitosane measured with the StabiSizer® is compared with the electrophoresis zeta potential determined with the ZetaView® ([figure 3 and 4](#)). The size of the Chitosane macromolecules is 0.96 nm and was found with the Nanotracc ® DLS analyzer.



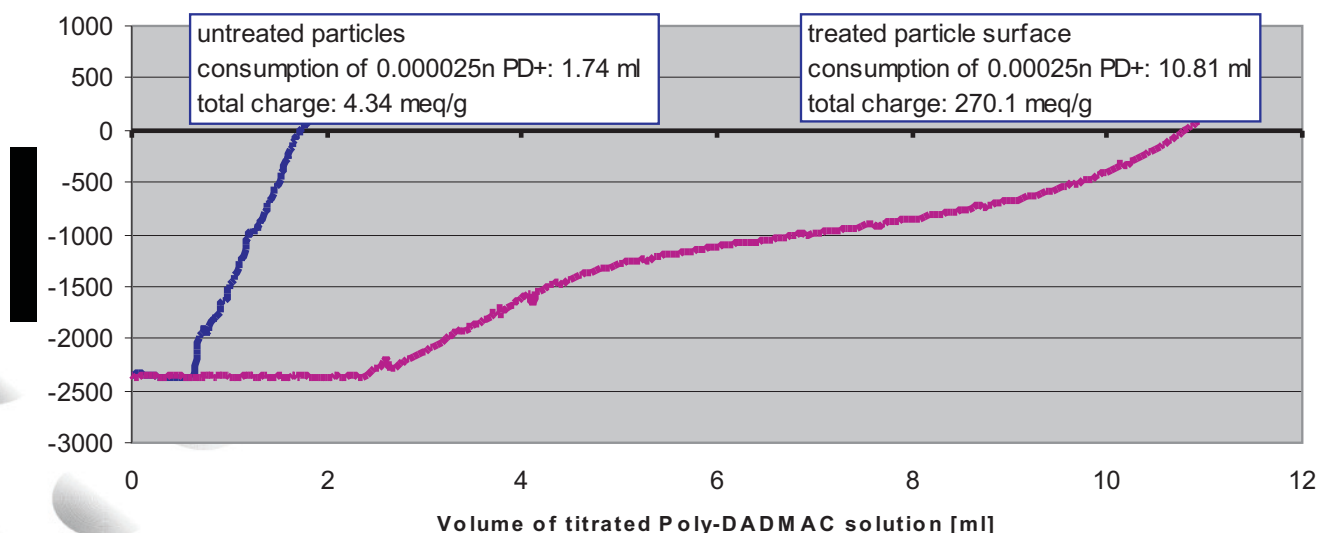
Although the lower size limit of ZetaView® is at 80 nm size, the measurement on a few Chitosane agglomerates could deliver very reasonable zeta potential results. The correlation of the StabiSizer® polyelectrolyte consumption (titration curves below) to zeta potential is interesting for those used to “think” in zeta potential. No other method could deliver an indication of zeta potential.

To measure ionic charge of macromolecules and nano-particles < 5 nm size in general is a unique feature of the method. An example of PIP versus pH titration on proteins is given in the application note AN-08.



The last example demonstrates the capability of using this principle to measure the dispersability of particles. This is strongly connected with the amount of functional ionic end groups at the particle interface. The amount of end groups per gram sample can be easily determined with a polyelectrolyte titration (figure 5). The following example on anionic CNT carbon nano tubes demonstrates this:

10 ml of dispersion 0.1% @ pH=10
titrated with cationic Poly-DADMAC, StabiSizer PMX 200C



The untreated sample (blue) consumes much less calibrated cationic Poly-DADMAC than the modified one (red). The density of COOH charge at the treated CNT interface was 270 meq/g sample.

Resumee

The PIP titration is a versatile tool to map the ionic behaviour of macromolecular solutions and particle dispersions in various ways.

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Literature: Particle Matrix Application Note AN-08, issued at the ACS Colloid & Surface Science Symposium, June 14-19, 2009 @ Columbia University, New York, NY.