**Application Note – Colloid Analysis**

C08 - Ionic Charge Mapping of Macromolecular Solutions and Dispersions

Introduction

Nearly any surface carries ionic charge. When it is sufficiently high particles repel each other keeping a dispersion stable. If it is low, the particles of the dispersion may coagulate. Immersed in water, the surface 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. In particular with dispersions, electrophoresis, ultrasonic vibration and mechanical shearing reveal the charged character of the double layer. By applying these techniques, the ionic charge of the interface is measurable as a particle interface potential PIP. In this contribution, the "streaming potential" sensing is presented as an effective tool to map the electrostatic behavior of polyelectrolytes and particles against external ionic parameters such as pH, conductivity or polyelectrolyte concentration.

The Charge Titration Method

The movement of the piston in the Teflon® measurement cylinder causes a fast oscillating flow of the sample fluid which is kept in the small gap between the piston and the cylinder. As a consequence, shearing at the double layer at the particle / macromolecule interface leads to a polarization of the ionic clouds. This oscillating polarization voltage signal is proportional to the velocity difference between the particle and the fluid. The measured voltage is known as "streaming potential" and proportional to the particle interface potential PIP. Macromolecules and nanoparticles tend to stick to the wall, whereas big particles stay in suspension but - due to inertia - are retarded related to the fluid velocity. In an inhomogeneous system there is a mixture of both phenomena.
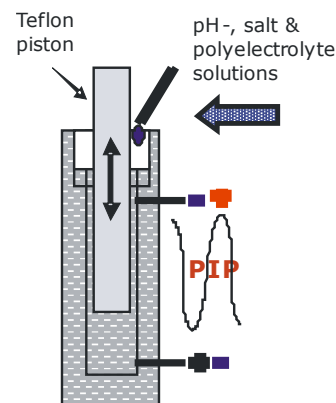
$$PIP = k\ v_0.\varepsilon.ZP/\eta$$
k ... Instrument constant
v_0 ... maximum liquid velocity
ε ... dielectric constant
η ... Viscosity
ZP ... zeta potential

As the measurement of the PIP itself and the mixing of any titrant solution into the sample is achieved within 5 seconds, one complete titration can be performed within 5 minutes. **Mapping of the ionic interface behavior** against external ionic conditions is becoming very quick. In addition, no physical parameter entry is necessary. The method can be applied to polyelectrolyte solutions (size > 0.5 nm) and to dispersions from nanometer size up to 300 µm particle size.

0.01 g in 10 ml 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. In dispersion stability formulation and in nanoparticle design, the measurement of the electrostatic potential of involved species is often important. Reactions can happen between charged macromolecules, between polyelectrolytes and particles, between pH determining ions and particles, between particles and walls.

individual particle processing
size – concentration – zeta potential
> 20 nm size distribution
10^4 to 10^{12} particles/mL concentration
zeta potential stability parameter
patented image sharpness stability

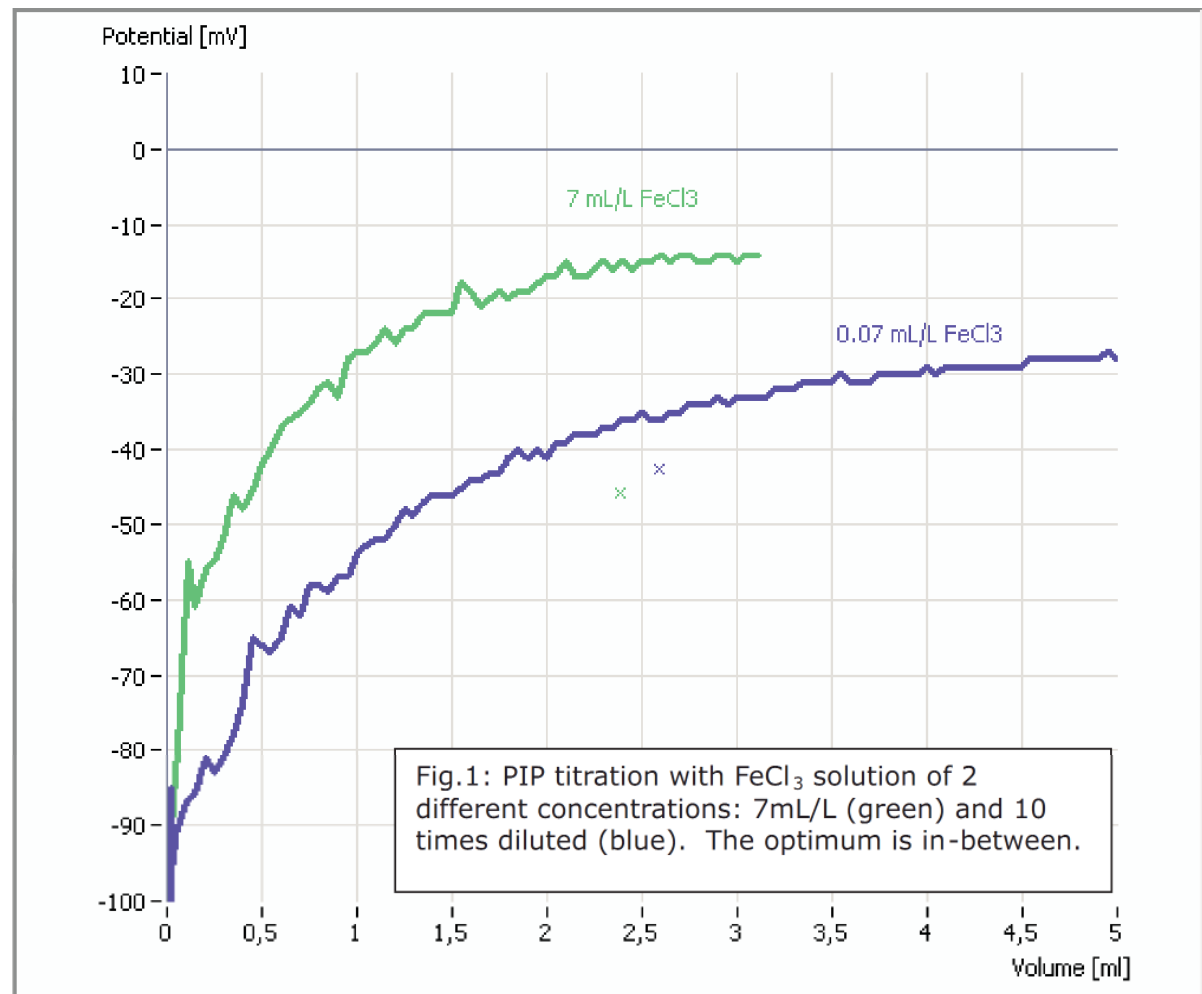**Particle Metrix.**
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Particle Metrix designed the Stabino® instrument to offer maximum comfort for charge titration and mapping work. As the following examples demonstrate, the applications are widely spread.

Experiments

Optimization of the water recycling efficiency in a pigment suspension:
Or: The optimum combination of $FeCl_3$ precipitation and cationic polymer flocculation

Fig.1: PIP titration with $FeCl_3$ solution of 2 different concentrations: 7mL/L (green) and 10 times diluted (blue). The optimum is in-between.

The efficiency of a $FeCl_3$ solution as a flocculant for an anionic pigment suspension is very good up to a certain concentration. From then on, commensurately much $FeCl_3$ is consumed to bring the PIP of the suspension to the flocculation point near zero mV. (Fig. 1). The Stabino® titration curves versus consumption of $FeCl_3$ solution [mL] at two different concentrations indicate this. Therefore the flocculation process is continued in a more efficient way by adding cationic polyelectrolytes to the suspension, until the zero point of charge is reached.

The cationic polymer addition after treatment with FeCl3 shows its biggest influence between "10%" and "40%" (Fig. 2). "100%" corresponds to the 7mL/L iron chloride concentration which the operator used to apply. As a result of these titrations, the optimum efficiency of the flocculation process is at "30%". Consequently, it does not make sense to operate the recycling above that point.

Fig. 2: Consumption of cationic polymer solution after precipitation with FeCl$_3$ (2% to 80% of 0.7mL/L)
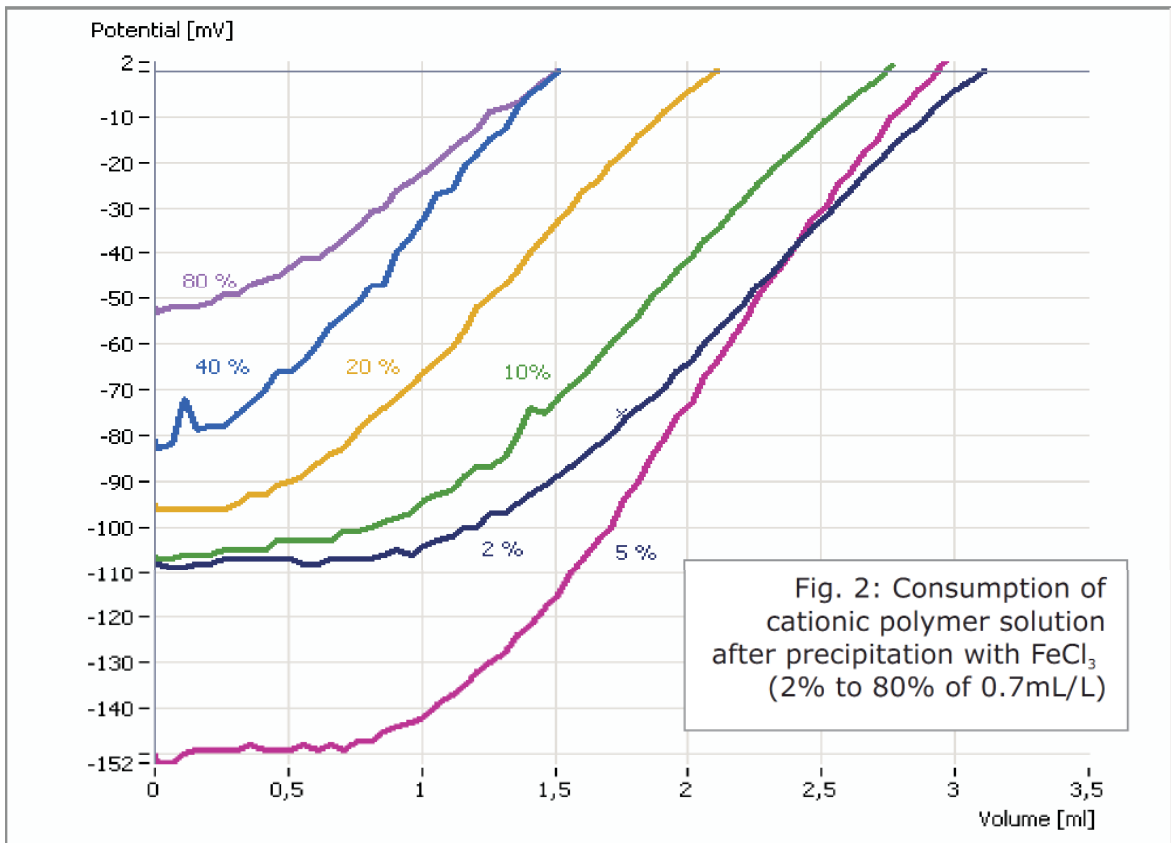
The flocculation and subsequent precipitation of pigment flocks were simulated using a Turbiscan instrument (Fig. 3). Up to about 3 mL/L FeCl$_3$ concentration, the sedimentation is rapidly rising. From then on, the sedimentation efficiency does not grow any more (red curve). For comparison, the cationic demand result from figure 2 is plotted in blue showing a bend at the same concentration as the Turbiscan curve, as expected.

Fig. 3: result of the cationic polymer consumption and the sedimentation number of the Turbiscan versus FeCl$_3$ concentration
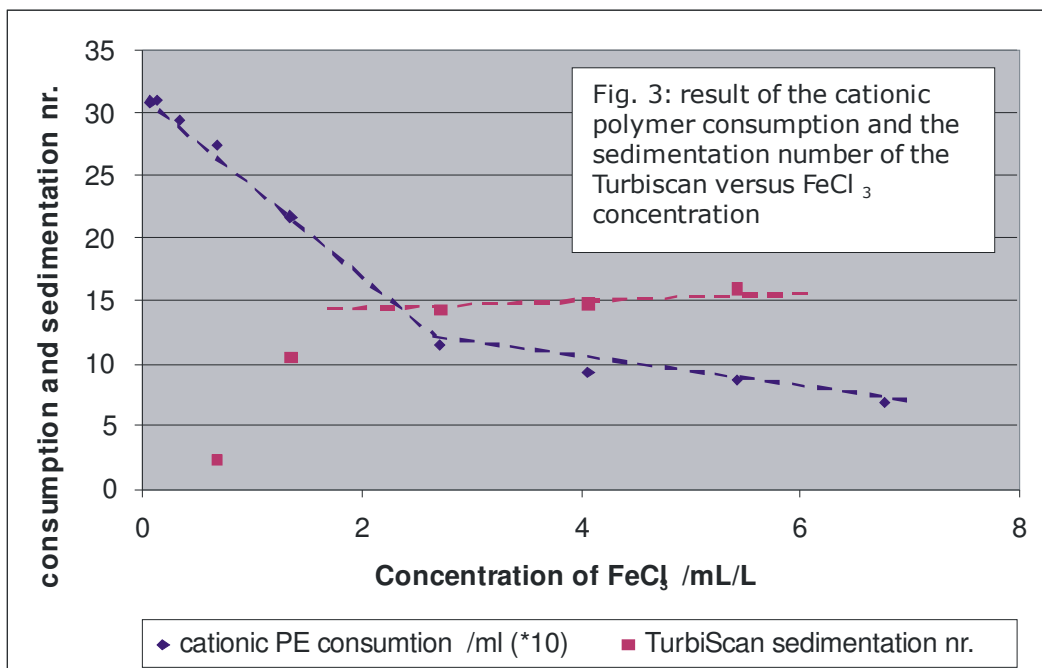
Total charge of cationic Chitosan polymer and correlation to zeta potential

By titrating a cationic Chitosan solution with the calibrated anionic polyelectrolyte PVS(*) solution, the total ionic charge at the Chitosan interface can be determined in meq per gram sample. The size of the Chitosan macromolecules was determined with the Stabino® DLS method(***) to be 0.96 nm. The curves in figure 4 show the polyelectrolyte (PVS-) titrations on cationic Chitosan.
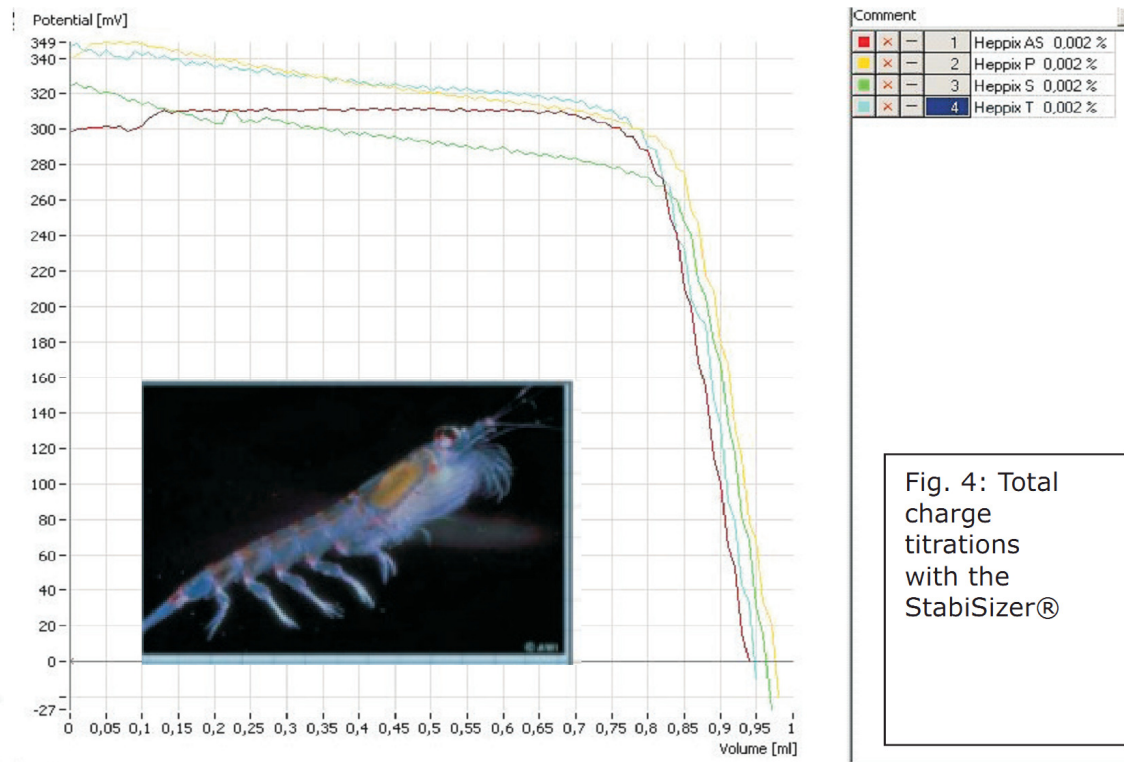

Fig. 4: Total charge titrations with the StabiSizer®

For interest, the result of the above total charge measurement (consumption [mL]) of the 4 different samples was plotted together with the zeta potential of the same samples.
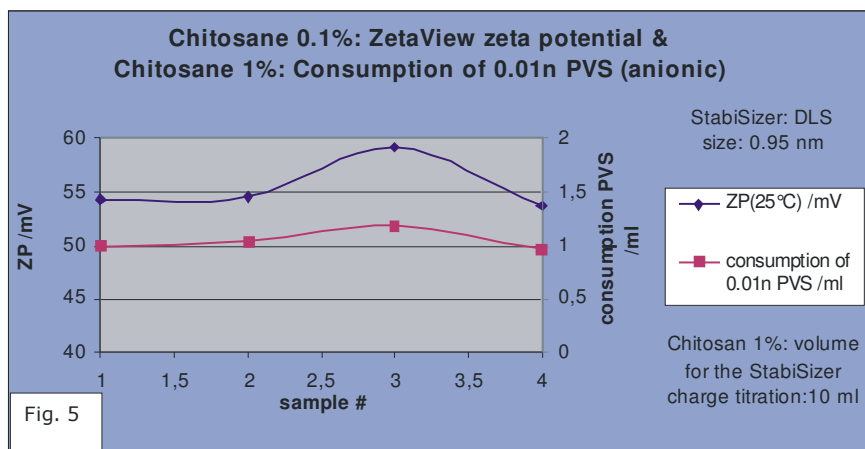

Fig. 5: The electrophoresis zeta potential was measured with the ZetaView® particle tracking analyzer.
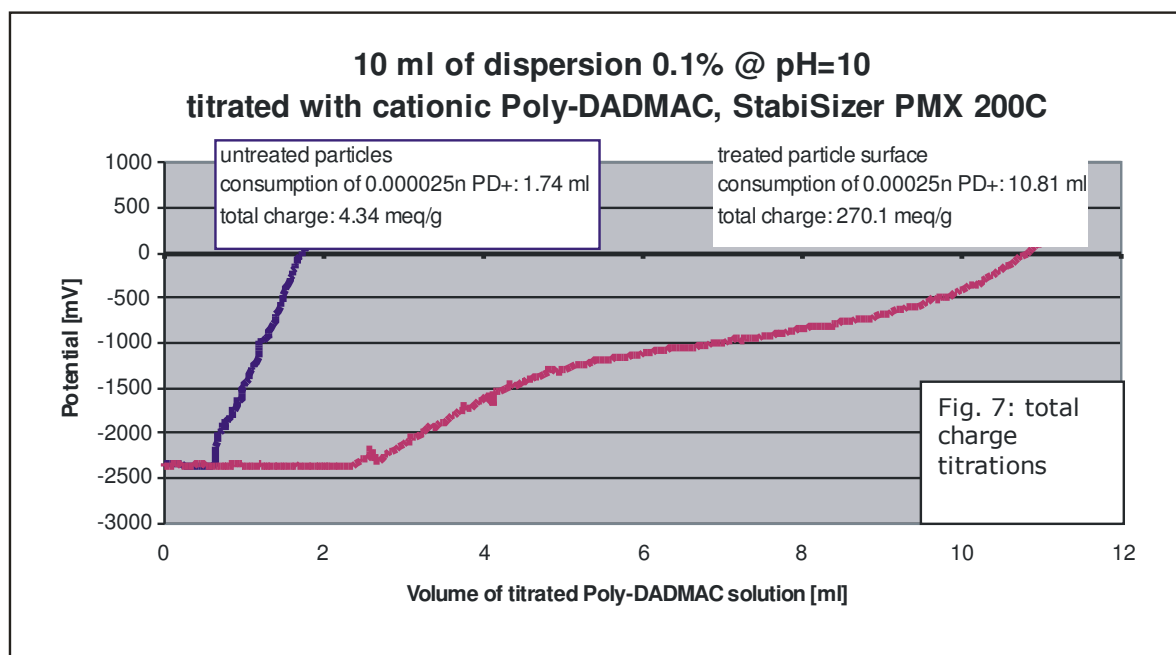
Although the lower size limit of that particular ZetaView® was at 80 nm size, the measurement on a few Chitosan agglomerates could deliver very reasonable zeta potential results. The Stabino® total charge was well correlating to zeta potential, which is an interesting result for those who are used to "think" in zeta potential.

The Stabino® PIP method is also proven as a powerful tool to measure the **ionic charge characteristics of nanoparticles**. The following example shows a pH titration of nm **protein** dispersions delivering information on the solubility of the proteins.

Fig. 6: pH charge titration of proteins of 1 nm (red) and 5 nm (blue) protein dispersions
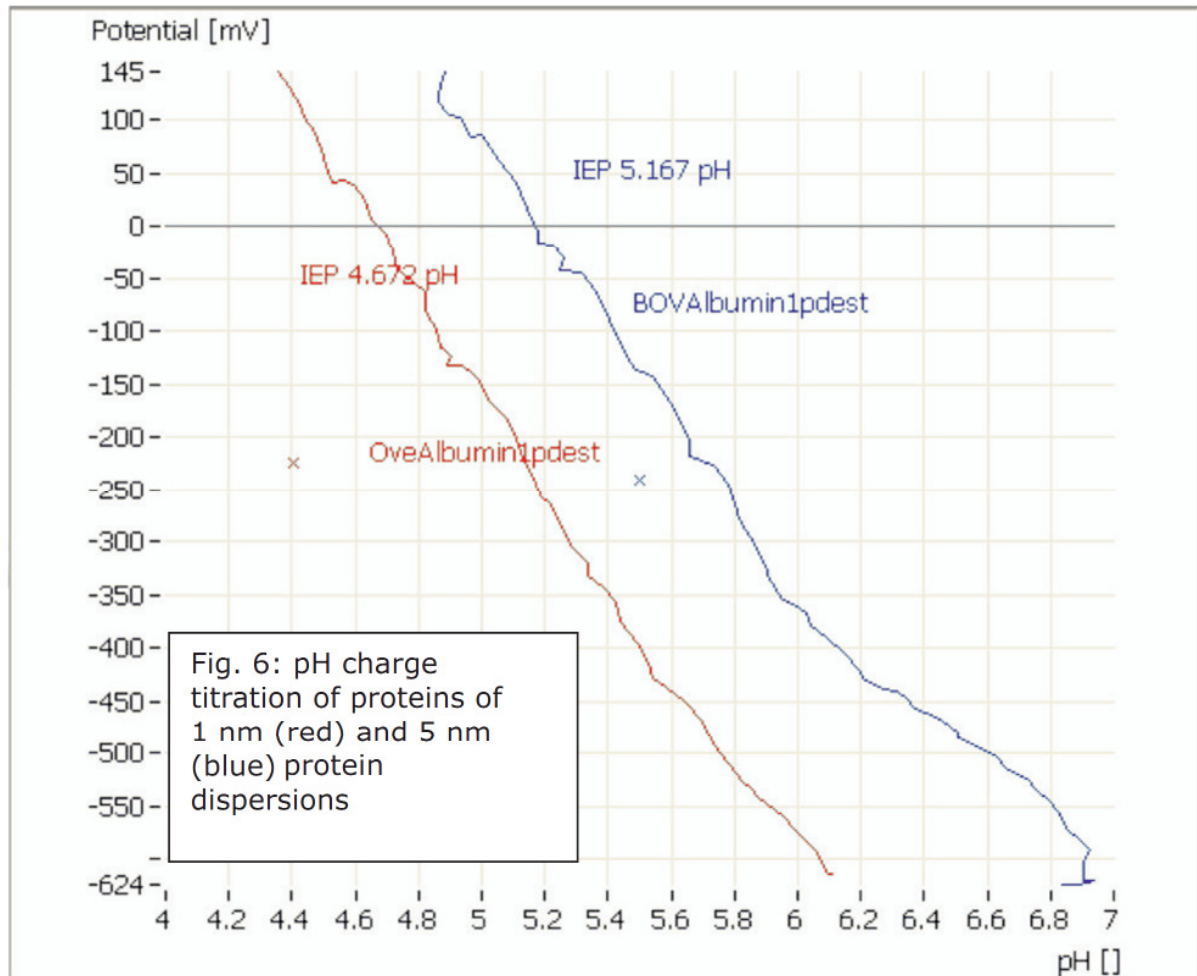
The last example demonstrates the capability of using the streaming potential principle to measure the dispersability of particles. This is strongly connected with the amount of functional ionic end groups at the particle interface. The amount of end groups per gram sample can be easily determined with a polyelectrolyte titration to the zero point of charge. The example on CNTs in figure 7 demonstrates this:

The untreated sample had nearly no polyelectrolyte (cationic poly-DADMAC**) consumption. It was also difficult to disperse. Fortunately the moving piston keeps the sample in a homogeneous and mixed state. The other sample was modified to carry $COOH^-$ end groups at the interface. By titration with cationic Poly-DADMAC the amount of anionic end groups could be determined, as charges compensate each other 1 by one. As 1 molar of poly-DADMAC solution is carrying 1 molar elementary charges, the total charge could be determined in meq per gram sample.

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

untreated particles
consumption of 0.000025n PD+: 1.74 ml
total charge: 4.34 meq/g

treated particle surface
consumption of 0.00025n PD+: 10.81 ml
total charge: 270.1 meq/g

Fig. 7: total charge titrations

The streaming potential titration is a versatile tool to map the ionic behavior of macromolecular solutions and particle dispersions. The moving piston keeps the samples in a homogeneous state allowing even big particles of several 100 µm size to be analyzed. As the measurement of the streaming potential is not sensible on convection, it is immediate. Therefore the speed of the titration is only limited by the rise time of the pH signal and the mixing speed for the titrant. No circulation with an external sample preparation container is necessary. All these points contribute to the fact that one titration can be performed within 5 minutes. In formulation work, this speed helps doing screening experiments.

(*)   PVS = Potassium polyvinyl sulfonate salt
(**)   Poly-DADMAC = poly (diallyldimethylammonium chloride)
(***)   Stabino® DLS method is based on the Nanotrac®, produced by Microtrac, Inc.

Hanno Wachernig, Wachernig@particle-metrix.de

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For more information contact:

analytikLtd (UK and Ireland Distributor)
Barn B, 2 Cygnus Business Park, Middle Watch, Swavesey, Cambridge, CB24 4AA
T: +44 (0)870 991 4044 F: +44 (0)870 135 2488 E: info@analytik.co.uk **www.analytik.co.uk**