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Determination of electrokinetic charge with a particle-charge detector, and its relationship to the total charge

Abstract The main features of polyelectrolyte titrations with end-point indication by means of a particle-charge detector (PCD) were investigated. Because of their well-defined character, the charges of different synthetic polyelectrolytes and of latex samples with different functional groups were measured at different pH and ionic strength. The results show that PCD is a valuable tool for detecting effective or dissociated counterion charge without additional model assumptions. For negatively charged samples with exclusively strong acid functional groups, an excellent agreement was obtained between cation-exchange capacity and the charge measured by PCD over a wide pH range. For samples with additional carboxyl groups, the PCD charge was significantly lower than the total charge calculated from cation-exchange results. It can be concluded that counterion immobilization by a Stern layer-type arrangement is responsible for this effect.

Introduction

Electrokinetic techniques are widely used to characterize the charge distribution around aqueous colloid particles. Electrokinetic effects occur whenever distortion of counterions is caused by movements of charged particles relative to the surrounding solution (Fig. 1). A dipole is formed around each particle and affects the speed of particles in an electric field (electrophoretic mobility) or, for particle movement, forms an electric potential within the suspension (sedimentation potential or streaming potential) [1]. Whereas surface charge determined by titration or exchange techniques measures the amount of total charge, electrokinetic techniques furnish information about the mobile and weakly bound fraction of the counterions [2]. This fraction, which is also called the electrokinetic charge or the effective particle charge, plays an important role in electrostatic interaction among charged particles and hence affects the stability of colloidal suspensions [1]. The interpretation of electrokinetic signals such as electrophoretic mobility or streaming potential remains open to debate. The models applied for the interpretation of electrokinetic data in terms of charge properties require additional parameter estimations and drastic simplifications [3]. Difficulties occur especially for real colloidal dispersions, because they are polydisperse in size, shape, and surface properties. The calculation of surface charge from electrokinetic signals would require special information about the distributions of all particle properties [4].

A relatively new electrokinetic technique is used in the particle-charge detector (PCD 03; Mütec, Germany). This technique is supposed to measure the amount of electrokinetic surface charge directly by combining an electrokinetic probe with titration of a charge-compensating polyelectrolyte. The technique is relatively simple and requires no additional model assumptions. The principle of the electrokinetic experiment is based on the streaming current detector (SCD), first introduced by Gerdes [5]. The PCD technique is widely used in waste-water treatment, in the ceramic or paper industries for controlling coagulant dosage and rheological properties, or for monitoring particle properties in industrial processing [6, 7]. Less is known about the relationship between the charge measured by PCD and the total charge. Weis et al. [8] used the PCD technique to measure the Cu(II) complexation capacity of aquatic humic substances as a result of their change of surface charge, and compared the results with Cu(II) complexation determined by polarography. They found a good relationship between the results from both methods, even though the complexation capacities measured with the PCD were, without exception, lower than those measured by polarography. They explained this difference in terms of the lower pH of the samples measured by use of the PCD. Böckenhoff et al. [9] investigated the charge characteristic of clay–humus fractions from A-horizons of several chernozems as a

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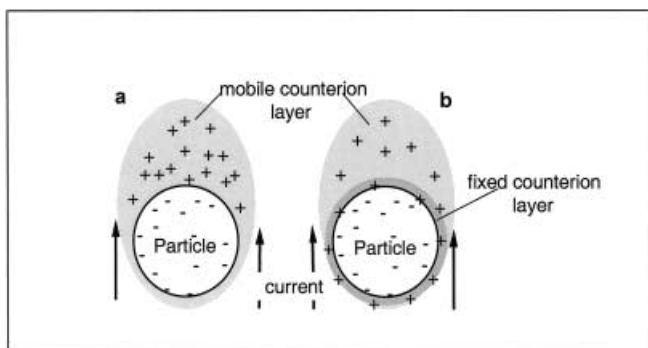e-mail: fischer@ifbk.uni-hannover.de

Fig. 1 Charge partition in the PCD cell for particles without (**a**) and with (**b**) a fixed counterion layer

function of Ca concentration and pH and observed a significant decrease in surface charge whenever there was an increase in Ca concentration and a decrease in pH. The negative particle charges measured with the PCD were significantly lower than had been expected from the cation exchange capacity (CEC), even at low ionic strengths. They explained the difference between the negative PCD charge and the CEC in terms of counterion immobilization and interlayer charges which do not contribute to the electrokinetic effect.

The purpose of this investigation was to determine the main features of PCD measurements and the relationship between the total charge and the electrokinetic surface charge measured by PCD. We performed our investigations on synthetic latex samples and polyelectrolytes, because of the well-defined properties of these materials.

Experimental

Materials

The latex suspensions used in this study were synthesized by the Institut für Angewandte Polymerforschung Teltow (Germany) and were provided as aqueous suspensions. The latex particles are considered to be spherical with exclusively outer surfaces but differing in the kind of functional groups and in diameter. Most relevant properties are shown in Table 1. A solution of sodium polyethylene sulfonate (PES-Na) at a concentration of 10^{-3} mol_C L^{-1} and a solution of 10^{-4} mol_C L^{-1} benzyl(dimethylhexadecyl)ammonium chloride (BDMHAC) were used as reference polyelectrolytes.

Methods

The electrokinetic surface charge was determined by means of a Mütec (Herrsching, Germany) PCD 03 particle-charge detector

Table 1 Characteristics of the latex particles investigated

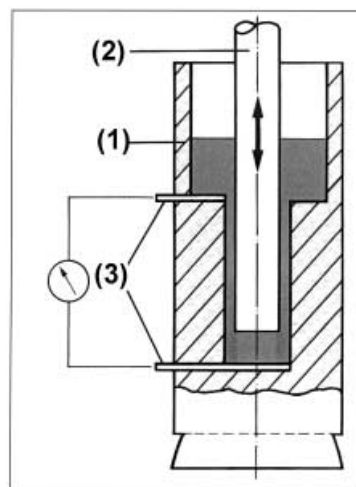| Sample no.	22/II	24/II	283/III	154/III
Diameter (nm)	80±6	120±5	99±3	317±8
Functional groups	Sulfate, sulfonate	Sulfonate	Sulfate, sulfonate	Sulfate, carboxyl
Concentration (g L^{-1})	2.9	1.9	2.4	3.2
Surface area (m^2 g^{-1})	71.2	47.4	57.5	18

Fig. 2 Schematic diagram of the particle-charge detector, PCD: (*1*) PTFE cup; (*2*) oscillating PTFE-piston; (*3*) gold electrodes

(Fig. 2), in combination with a Mettler (Gießen, Germany) Toledo DL 25 automatic titration unit. The principle of charge indication is based on the generation of a streaming potential which is induced by the oscillating movement of a plunger in a PTFE cell. Two gold electrodes placed in the cell record the electrokinetic signal. The negative surface charge is then quantified by titration with a 10^{-3} mol_C L^{-1} solution of a polymeric organic cation (polydiallyl-dimethylammonium chloride, "Poly-Dadmac", molecular weight approximately 10^4–10^5 g). Addition of the titration solution is performed across the point of zero charge, i.e. the point at which the electrokinetic potential is zero. For each measurement of the surface charge we used 10 mL of the suspensions or of the solutions.

The amount of polyelectrolyte required to reverse the sign of the PCD signal was approximated by linear interpolation of the titration curve at the isoelectric point (IEP). The electrokinetic charge (Q_{ek}) of the colloidal system can then be calculated from the amount of required polyelectrolyte by use of the equation:

$$Q_{ek} = \frac{Vc}{w}$$

where V is the volume of titrant added (L), c the charge of the titrant (mol_C L^{-1}), and w the amount of titrated substance (kg).

The total charge of the negatively charged samples was calculated by measuring the cation-exchange capacity (CEC) by extraction with silver thiourea, according to a modification of the method of van Reeuwijk [10]. The CEC of suspended latex particles was determined by adding silver thiourea (5×10^{-4} mol L^{-1}, 10 mL) to latex suspension (10 mL). The CEC of the PES-Na solution was determined by adding silver thiourea (5×10^{-3} mol L^{-1}, 1 mL) to this solution (10 mL); this leads to a complete coagulation of the polymer. After reaction for 1 h in a shaker the flocculated colloids were centrifuged. The concentration of Ag in the supernatant was determined by AAS, and the CEC was calculated by subtracting the amount of Ag in the supernatant from that in the blank.

Results and discussion

Determination of the surface charge from titration curves

The reproducibility of the titration is apparent from Fig. 3, which shows eight curves for titration of Poly-DADMAC (10^{-4} mol_C L^{-1}, 10 mL) against PES-Na solution (10^{-3} mol_C L^{-1}). Each curve starts at positive poten-
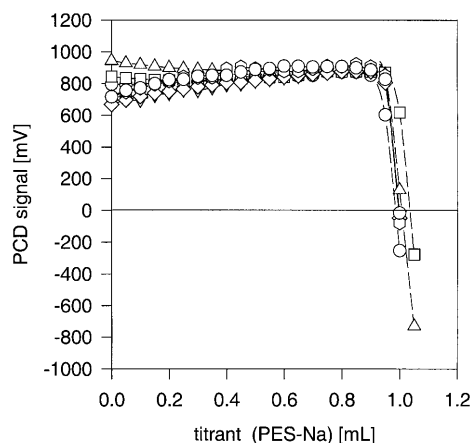
Fig. 3 PCD titration of Poly-DADMAC (10^{-4} mol$_C$ L^{-1}, 10 mL) against PES-Na (10^{-3} mol$_C$ L^{-1})

tials, owing to the electrokinetic effect of poly-DADMAC cations. During addition of increasing amounts of PES-Na the titration curves form a quasi plateau followed by a steep decrease of the signal across the isoelectric point (IEP), which marks the end of the titration.

Interpretation of both the initial PCD signal and the shape of the titration curve is not simple. Several investigations have been conducted to correlate the electrokinetic signal from the SCD or PCD with those obtained by other electrokinetic techniques. Although satisfactory linear (statistic) correlations have been found, the calculation of a zeta potential from the signal is highly dependent on the type of model selected [5, 6, 11, 12, 13]. Besides the general criticism of deducing zeta potentials from electrokinetic signals [3], the principal mechanism of the generation of the PCD signal is still poorly understood [6]. Most investigators assume that the signal is generated by the distortion of counterions from colloids that are immobilized on the piston and on the surface of the sample cell, which physically leads to a streaming potential. In contrast, Müller [6] reported that for larger particles adsorption on PTFE walls is unlikely. He assumed that the polarization is the result of the different velocities of the solid particle and the mobile counterions in the oscillating current. This mechanism would physically be the same as for a sedimentation potential. If, however, the mechanism of signal generation is not known with certainty, a model that relates the PCD-signal to the zeta potential is not useful. The PCD signal itself is, moreover, poorly reproducible. The signal is highly affected by unstable streaming conditions, because of variation of the distance between piston and cell. Also, even small impurities in the cell and on the piston have considerable effects on the PCD signal.

More reliable information is obtained if only the sign of PCD signal is used. For the polyelectrolyte titration in the PCD, the point at which the sign of signal gets reversed is of sole interest. This point can be interpreted as the isoelectric point (IEP) of the solution or suspension, when the charge of the sample is balanced by counterions. The amount of titrated polyelectrolyte can be accurately

calculated by linear interpolation at the IEP. The reproducibility of the amount of titrated agent is usually satisfactory. From other experiments not reported in this study we also found that the deviation from the average is usually less than 3 %, although the reproducibility can decrease markedly at increasing particle size. For particles coarser than 20 µm, sedimentation can occur during the titration and sufficient mixing is not guaranteed.

Measurable colloidal systems

The upper limit of the particle size for which the charge can be measured in the PCD is given by the distance between the piston and the wall of the cell which, in the probe commonly used, is approximately 900 µm. As mentioned above, for particles coarser than 20 µm particle sedimentation during the titration can affect the reproducibility of the results. For colloidal-sized fractions and organic molecules the lower limit of particle or molecule size that contributes to the electrokinetic effect is of more interest. For this reason, the charge of 10^{-4} mol$_C$ L^{-1} benzyldimethylhexadecylammonium (BDMHAC) solution with a molecular weight of only 414.1 g mol^{-1} was measured. This molecule was selected because its low molecular weight and its ammonium group, with the expectation that the counterions would nearly be fully dissociated at neutral pH. Figure 4 shows the curve for titration of the positively charged BDMHAC with 10^{-3} mol$_C$ L^{-1} PES-Na solution. Like the poly-DADMAC molecules, the much smaller BDMHAC molecules produce a sufficient electrokinetic signal. At the IEP nearly 100% of the default molecule charge (10^{-4} mol$_C$ L) was neutralized by PES-Na.

Effect of pH on the charge of the polyelectrolytes

If poly-DADMAC and PES-Na are used as titration agents for studying counterion effects on charged colloids, their charge measured in the PCD should be broadly indepen-
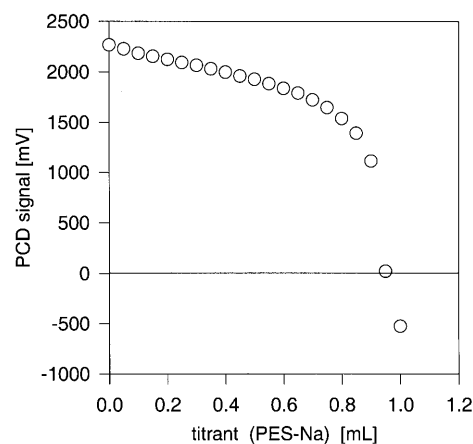

Fig. 4 PCD-Titration of benzyldimethylhexadecylammonium chloride (10^{-4} mol$_C$ L^{-1}, 10 mL) against PES-Na (10^{-3} mol$_C$ L^{-1})

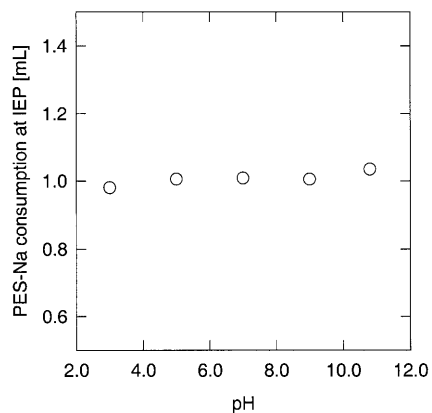**Fig. 5** PCD-Titration of poly-DADMAC (10^{-4} mol_C L^{-1}, 10 mL) against PES-Na (10^{-3} mol_C L^{-1}) at different pH

dent of pH and from changes in ionic strength. Therefore, 10 mL 10^{-4} mol_C L^{-1} Poly-DADMAC were titrated with 10^{-3} mol_C L^{-1} PES-Na at different pH values. As shown in Fig. 5, the amount of PES-Na required to neutralize the charge of poly-DADMAC, is not significantly affected by pH between pH 3 and pH 10. Changes in the sodium and chloride concentration, which necessarily occurred if NaOH or HCl was added, will, therefore, not affect the electrokinetic charge of these polyelectrolytes either. Accordingly, Müller [6] reported that for both polyelectrolytes no effect on the titrated charge was measured over a wide pH range and for ionic strengths <1 mol L^{-1}. He explained this result by the strongly acidic and strongly basic character of the functional groups of poly-DADMAC and PES-Na, respectively.

PCD charge and total charge of PES-Na

Assuming that electrokinetic effects result from the replacement of dissociated counterions, the relationship between total charge and PCD charge represents the extent of dissociation. For PES-Na in a completely dissociated state the PCD charge should be identical with the total charge determined by exchange with silver thiourea ($AgTU_{ads}$). Table 2 shows the specific charge of a 10^{-3} mol_C L^{-1} PES-Na solution obtained both from PCD titrations and from measurement of adsorption of silver thiourea. Results from both methods were in good agreement with regard to the amount of charge detected – the default charge value of -10^{-3} mol_C L^{-1} for PES-Na solution found with the PCD was almost exactly the same as that calculated from the amount of adsorbed AgTU (-0.99×10^{-3} mol_C L^{-1}). The good agreement between total charge and PCD charge, and the independence of the titration from the pH value support the idea of completely dissociated counterions of PES-Na over a wide pH range.

Although the titration of Poly-DADMAC against PES-Na gives reasonable results, the mechanism of charge compensation in the PCD is still poorly understood. It seems rather unlikely that the charges of poly-DADMAC

Table 2 Negative charge of different latex samples determined by PCD titration (poly-DADMAC) and by silver thiourea exchange

Sample No.	22/II	24/II	283/III	154/III
Functional groups	Sulfate, sulfonate	Sulfonate	Sulfate, sulfonate	Sulfate, carboxyl
Surface area (m^2 g^{-1})	71.2	47.4	57.5	18
PCD_{tit} ($mmol_C$ kg^{-1})	66.8	48.7	105.5	24.5
$AgTU_{ads}$ ($mmol_C$ kg^{-1})	68.0	48.4	106.8	40.0

and PES-Na are neutralized by a site-by-site interaction. Lagaly et al. [7] assumed that the charge compensation in the PCD is the effect of complexes with only statistically balanced positively and negatively charged sites. The dispersing forces of the water current in the PCD cell, which have an effect on the relatively large molecules, polyanions, and polycations, might also separately produce oppositional electrokinetic signals that overlay each other.

The role of functional groups

As mentioned above, the type of functional group plays an important role in the relationship between the charge measured by the PCD and the total charge represented by the exchange capacity. Latex samples with different kinds of negatively charged functional groups were therefore used to evaluate the respective effects on the PCD charge. For latex samples with negative charge exclusively from strongly acid sulfate and sulfonate groups, the charge titrated with the PCD is in a good agreement with the amount of adsorbed equivalents of AgTU. Effects from different surface areas or from different charge densities were not detected. In contrast, for latex particles with partly carboxyl groups, the amount of adsorbed equivalents of AgTU (40.0 mol_C kg^{-3}) is significantly higher than is measured by the PCD titration (24.5 mol_C kg^{-3}). This difference is probably the effect of immobilization of cations in a sense of Stern layer adsorption which influences the PCD charge.
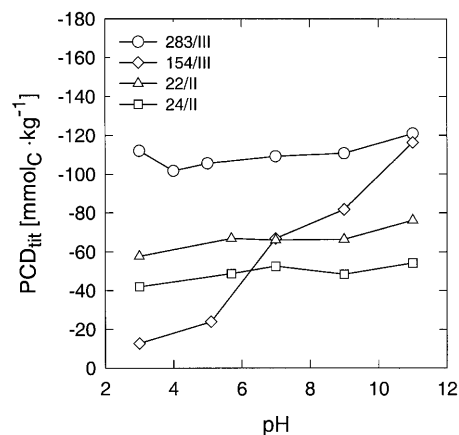

Fig. 6 Influence of pH on the electrokinetic surface charge of different latex particles with sulfate and sulfonate groups (283/III, 22/II, 24/II) and with additional carboxyl groups (154/III)

Differences between latex samples with and without carboxyl functional groups also occur in the pH dependence of the PCD charge (Fig. 6). The charges of latex particles with sulfonate groups and latex with sulfate and sulfonate groups, measured by the PCD, are nearly pH-independent, whereas the charge of latex with carboxyl groups increased from 12.7 $mmol_C$ kg^{-1} to 116.3 $mmol_C$ kg^{-1} when the pH was increased from 3 to 11.

The effect of pH on the particle charge of latex with carboxyl groups is probably not only the result of protonation and deprotonation of functional groups, but probably also an effect of a change in the amount of sodium associated with the surface, because of variation of the sodium concentration.

Conclusions

The particle-charge detector (PCD) is a valuable tool for detecting the charge of colloidal-sized particles. The electrokinetic signal should not be interpreted quantitatively in the sense of a zeta potential, because of its strong dependence on model assumptions and experimental conditions. As long as the PCD signal is only used in combination with polyelectrolyte titration to detect the sign of particle charge and to indicate the point of zero charge, it produces reasonable results. Polyelectrolytes used for charge titration should have functional groups with strong acid or strong base character, to provide nearly completely dissociated counterions. The good agreement between the titrated PCD charge of negatively charged colloids and the cation exchange capacity, for systems with strong acid functional groups, demonstrates that the PCD technique is capable of accurately detecting the dissociated charge. Differences between total charge and PCD charge are indicative of the presence of an immobile counterion layer, such as a Stern layer. PCD charge measurements are, therefore, an excellent tool for investigating interactions of ions with charged surfaces and the structure of electrolyte interfacial regions.

References

1. Hunter R (1993) Introduction to Modern Colloid Science. Oxford Science
2. James RO, Parks GA (1982) Characterization of Aqueous Colloids by their Electrical Double-Layer and Intrinsic Surface Chemical Properties. In EJ Matijewic (ed.) Surface and Colloid Science, Vol. 12. Plenum Press, New York, 119–216
3. Harsh JB, Xu S (1990) Adv Soil Sci 14:131–165
4. Dukhin AS, van de Ven TGM (1994) J Colloid Interface Sci 165: 9–18
5. Gerdes WF (1966) A New Instrument – The Streaming Current Detector. 12th National Analysis Instrument Symposium, Houston, TX, USA
6. Müller HM (1996) Zetapotential in der Laborpraxis. Wissenschaftliche Verlagsgesellschaft mbH Stuttgart
7. Lagaly GO, Schulz R, Ziemehl (1997) Dispersionen und Emulsionen: Eine Einführung in die Kolloidik feinverteilter Stoffe einschließlich der Tonminerale. Darmstadt: Steinkopff
8. Weis M, Valera FS, Frimmel FH (1989) Z Wasser-Abwasser-Forsch 22:253–257
9. Böckenhoff K, Gall S, Fischer WR (1997) Z Pflanzenernähr Bodenk 160:341–346
10. van Reeuwijk LP (1993) Procedures for Soil Analysis. 4th edn. ISRIC Wageningen
11. Dentel SK, Kingery KM (1989) Water Sci Technol 21:443–453
12. Barron W, Murray BS, Scales PJ, Healy TW, Dixon DR, Pascoe M (1994) Colloids Surfaces 88:129–139
13. Walker AW, Kerby JT, Dentel SK (1996) J Colloid Interface Sci 182:71–81