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Characterization of weak polyelectrolytes in aqueous solution - charge and isoelectric point in dependence on the molecule structure

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ABSTRACT

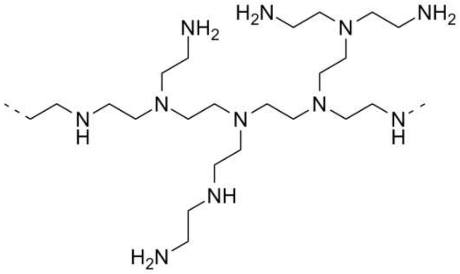
The topic of this work was the characterization of unmodified poly (ethylene imines) (PEI)s in comparison with different oligosaccharide (OS)-PEI-modified dendritic polymers (OM-PEI) using polyelectrolyte titration. It was found that the charge density (CD) as well as the isoelectric points (IEP) was strongly influenced by the details of modification such as the type of oligosaccharide (Lactose or Maltose), its structure and size (Maltose, Maltotriose or Maltoheptaose) and the PEI-OS ratio. Whereas the charge of unmodified PEI is cationic up to pH of about 10, that means IEP of about 10, the IEP decreases with the influence of substituents. Further it is shown that the higher the degree of chemically coupled OS units on the PEI surface, the lower is the charge density. For OM-PEIs the endpoint of titration depended on the speed of titration which is consistent with a relatively slow rate of forming poly-ion complexes between modified PEIs and titrants. For a good reproducibility the titration velocity should be not too high. Therefore a manual titration regime should be preferred instead of an automatic "standard" titration regime with high titration velocity.

Keywords: *poly(ethylene imine), characterization, polyelectrolyte titration, charge density.*

1. INTRODUCTION

Charged polymers, so called polyelectrolytes (PEL), are present almost everywhere in the world. Besides biological systems, which are the most important reservoir of ionic polymers such as proteins or nucleic acids, a multitude of synthetic ionic polymers can be synthesized in the laboratory with a wide variety of properties [1, 2]. So the molecule can be anionic (polyanion) or cationic (polycation), the molecular weights can vary from very low up to extremely high (several millions g/mol) and the charge densities can be adjusted between 0 and 100%. Consequently polyelectrolytes have found important applications in many fields of science and industry because they can combine typical properties of polymers with the ability of electrostatic interactions. For instance, they were used for charge compensation in separation processes [3], for sticky removal [4, 5], as stabilizer for particle dispersions [6, 7], or for surface modification of cellulose or inorganic particles [8].

An exceptional field of application is the formation of complexes with oppositely charged polyelectrolytes or surfactants. It was demonstrated by many authors, that the application relevant properties of complexes can be tuned by the ratio of charges of both components [9-11]. Therefore an exact charge characterization is important for all of the applications mentioned above. But, despite the fact that PEL are widely used, only a few articles were published about details of their charge-characterization. The problem has two aspects: the first is the isoelectric point (IEP). It describes the pH, at which the amount of positive and negative charges is equal. It is very important, especially for so called "weak polyelectrolytes" such as polyethylene imine (PEI), because its charge decreases with increasing pH. Although PEI is not quaternized, it is highly cationic because a large number of its amino groups are protonated even near neutral pH.



Structure 1. Structure of branched PEI.

In contrast, "strong polycations" such as poly-diallyl-dimethyl-ammoniumchloride (PDADMAC) are positively charged, also at high pH. That means, their charge does not depend on pH [7]. The second aspect for characterization is the „charge amount" at certain pH. It can be characterized with polyelectrolyte titration using a dye as an indicator as described by Horn [12] or by the streaming potential. In the latter case the streaming potential of the polyelectrolyte solution is analyzed by a streaming current detector (such as PCD-04) and then an equivalent amount of an oppositely charged "titrant" is added. Highest accuracy and reproducibility is achieved by combining a PCD with an automatic titrator [13]. This procedure works very well and was broadly applied for the characterization of different polyelectrolyte solutions such as PDADMAC, PEI or natural polymers such as starch or chitosan. In most cases, an automatic "standard" titration regime, which is relatively fast, is used. Results can be obtained in several minutes. According to Klix [14], who studied the application of polycations such as PDADMAC with different molecular weights as retention aids, the titration velocity does not have an influence on the detected charge. In contrast, Hubbe and coworkers, who investigated polyampholytes [15], found that increased accuracy of streaming current titrations was achieved when using a longer equilibration time. Whereas an automatic titration took approximately 1 to 2 minutes to complete, they used a slower, manual titration method in which streaming current signals were observed 5 minutes after each addition of titrant was applied. Therefore a typical manual titration took 20 to 40 minutes, but linearity and reproducibility of the results could be improved.

As already mentioned, an exact charge determination is important, not only in classic fields such as paper industry, but also in new fields of polyelectrolyte application such as biology or medicine [7]. For instance, Müller and Torger [16] investigated the application of PEI and its complexes with poly-acrylic-acid (PAC) or other polyanions. The complex nanoparticles were found to release a model drug compound. Höbel, Loos and Appelhans [17] described that polycationic nonviral polymers are widely employed as delivery platforms of plasmid DNA. Among those poly (ethylene imines) took a prominent position due to their high efficiency. However, their biodistribution profiles upon systematic delivery and their toxicity pose limitations which can be addressed by the introduction of PEI modifications using polysaccharides as described [18]. The authors systematically synthesized a set of lactose, maltose-, maltotriose-or maltoheptaose-modified PEIs for complex formation with DNA. Therefore charge characterization using polyelectrolyte titration was necessary. Usually, the charge should be independent from the titration parameters and a “standard procedure” was used. But, the molecules` structure, which is highly branched, as well as their size should have a big influence on the velocity of complex formation during the titration. Compared with other molecules, having lower molecular weight, their charge titration should be influenced by the type of oligosaccharide too. Therefore the topic of this work was to characterize the isoelectric point and charge density of different oligosaccharide-modified dendritic polymers (OM-PEIs) and to compare these results with commercial (unmodified) PEI of different suppliers. Further, the influence of titration parameters such as titration velocity was studied.

2. EXPERIMENTAL SECTION

2.1. Materials. PEI: The poly(ethylene imine) type G 100 for dendrimer modification was supplied by BASF as a clear colorless liquid (50%) with a molar mass of about 5000 g/mol. The PEI molecule is branched. For comparison, poly (ethylene imine) P with a molar mass M_w of 750 000 g/mol was characterized too.

PEIs, modified with different polysaccharides (Lactose, Maltose) were synthesized by Appelhans as described [18]. The structure of such molecules can be influenced by the conditions of synthesis. So called “disubstituted polymers” are formed in the presence of an excess of oligosaccharides. They are characterized by a dense shell of the oligosaccharides whereas “monosubstituted” PEIs were obtained by adding a smaller amount of the oligosaccharides.

For charge characterization the following influences were varied:

-Type of polysaccharide: Lactose compared with Maltose

-Polysaccharide structure: The size of the substituents was enlarged with increasing number of OS-units: Maltose (Disaccharide) < Maltotriose (Trisaccharide) <Maltoheptaose (seven saccharide-units)

-The ratio between PEI- and OS-units was varied between 0.2 (low), 0.4-0.5 (medium) or high (up to 1:10).

2.2. Methods. For an exact charge characterization the streaming current detector PCD 04 is combined with an automatic titrator. Different titration regimes, for instance “dynamic” or “static” (with different, but constant rates of polymer addition), are possible. In most cases the “dynamic” mode was used. But, in some cases, to test the influence of different titration velocities (from 0.01 to 0.26 ml/min), the “static mode” was applied.

2.3. Determination of the isoelectric point. The isoelectric point (IEP) describes the pH at which the number of positive charges is equal to the number of negative charges. It can be measured by determining the streaming potential in dependence on pH. Different **volumes** (between 0.05 ml und 2.50 ml) of PEI or of the OM-PEIs in 15 ml solution with pH = 10 (0.1 M sodium hydroxide) were titrated automatically with hydrochloric acid (0.1 mol/l), up to pH of 3. Alternatively, a solution with pH 3 (with hydrochloric acid (0.1M) was titrated with NaOH (0.1M) to pH of 10.

2.4. Determination of the specific charge density. The streaming potential of the polyelectrolyte solutions at certain pH (positive or negative) is analyzed by the streaming current detector and then an equivalent amount of an oppositely charged “titrant” is added. A “standard” poly-diallyl-dimethyl-ammoniumchloride (PDADMAC; 0.001 mol/l) is used for polyanions and polyethylenesulfonic acid (PES; 0.001 mol/l) for the titration of polycations. Both standards have a low molecular weight (<10 000 g/mol) and are strong PELs. For comparing equal samples, for instance from different flocculation processes, the term “cationic or anionic demand” [eq/l] can be used [13]. But for an exact characterization the mass of the polymer should be included in the calculation to obtain the so-called specific charge density (q), calculated by the following formula:

$q= V*c/m$

V: consumed titrant volume (l)

c: Titrant concentration [eq/l]

m: mass or active substance [g]

By multiplying the specific charge density in eq/g by the Faraday’s constant F = 96485 C/eq, the total charge in C/g will be obtained.

2.5. Influence of polymer concentration on specific charge density. In one experiment the influence of polymer concentration in the measuring cell on the detected specific charge density (q) was tested. Different volumes (0.15 ml, 0.30 ml, 0.50 ml, 1.00 ml or 1.50 ml) of the PEI-stock solution were diluted with Millipore water (the total volume in the measuring cell is up to 15 ml). The pH was kept constant for all samples. Because all polymers were positively charged at this pH, PES-standard solution (0.001 mol/l) was used for titration.

2.6. Influence of kinetic effects on the specific charge density. In the next part of experiments the influence of the velocity of polymer addition on detected charge density was investigated with disubstituted PEI-Maltose (1:10) as an example. 0.5ml of the stock solution was diluted with 9.5 ml of Millipore water as described. The titration with PES was carried out with different velocities (0.01 – 0.27 ml/min).

2.7. Influence of the pH on specific charge density. Aqueous solutions of PEI and OM-PEIs with different pH (between 2 and 11) were prepared using hydrochloric acid or sodium hydroxide as described above. Then for each sample the specific charge density (q) was measured.

3. RESULTS SECTION

As already mentioned the titration procedure works very well and was broadly applied for the characterization of different polyelectrolyte solutions such as PDADMAC. But, whereas PDADMAC is well known as a “strong” polycation with high charge density, also at high pH, the charge of many other, so called “weak polyelectrolytes” such as PEI depends on pH in large extent. Therefore the IEP is very important and was measured at first.

3.1. Characterization of the isoelectric point (IEP).

3.1.1 IEP of (unmodified) PEI G 100. As already described, the IEP is the pH, at which the number of positive and negative charges are equal. It can be measured by “potentiometric” titration of the samples. When the streaming potential is positive, hydrochloric acid and for negative potential, sodium hydroxide is added.

As shown in Figure 1, the streaming potential of PEI, which is positive at low pH, decreases with increasing pH. The IEP is about 10, independent from the volume of the titrant added per titration step. But, the PEI-stock solution in millipore water (1g/l) has a pH of about 10. For the characterization different volumes of the stock solution were diluted with water in the measuring cell. Increasing PEI-volume (0.0005 ml, 0.005 ml or 0.01 ml in 15 ml) leads to an increase of pH and therefore to differences in the height of streaming potential. Because the streaming potential is an indicator for the charge, for correct charge determination it is necessary to adjust the pH.

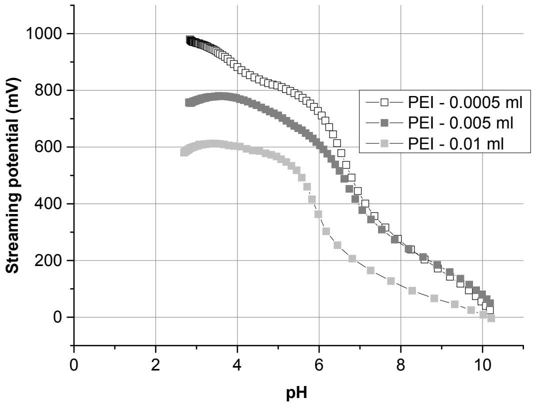


Figure 1. Determination of the streaming potential of PEI G 100 in dependence on the volume of the titrant added per titration step.

In another set of experiments the influence of the „titration direction“ on the IEP was tested. As mentioned above the pH of the stock solution is about 10. Then PEI was diluted with water. In one case the streaming potential was measured starting with pH of 10 whereas in the second case the pH was decreased to pH of 3 by addition of hydrochloric acid. Then the streaming potential was measured after adding NaOH. The titration was carried out 3 times in each direction. The influence on the IEP was low, but the absolute values of the streaming potential were different. Due to the high salt concentration in the second case the double layer is compressed and therefore the potential is lower.

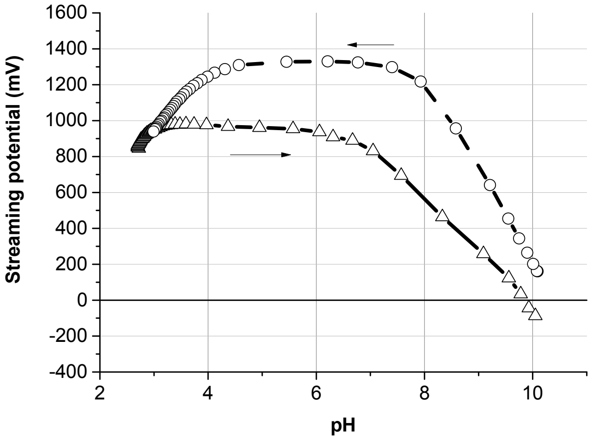


Figure 2. Determination of the IEP of PEI-G100 in dependence on the direction of the titration (triangels – from pH 3 to pH 10 or circles- from pH 10 to pH 3).

3.1.2. IEP of OM – PEIs. As already mentioned, dendritic OM-PEIs have a great application potential, for instance as RNA- or DNA carrier systems for metal ions or inorganic particles or for surface modification. They are water soluble and combine ionic with nonionic structures. Therefore charge characterization is very important. The isoelectric point of OM-PEIs was determined by titration with hydrochloric acid as described above for PEI. As shown in Figure 3, the isoelectric point of monosubstituted PEI-Maltose (1:0.2) is about 9.8, independent from the polymer concentration in the measuring cell, which was varied in a broad range. In contrast to Figure 1, the streaming potential-pH-profiles do not have big differences because the pH for all the concentrations was adjusted to the same value. Compared with unmodified PEI, the IEP of OM-PEIs is slightly lower due to the modification and the bad accessibility of charges. The protonation of the amino groups of monosubstituted PEI-maltose starts at pH of about 10 and covers a large area of pH (ΔpH= 6), because the molecule has a large number of basic groups and the electrostatic potential during titration is influenced by all these groups. In the beginning the primary amino groups (pH= 9.5) of PEI-maltose are protonated. Later, when secondary amino groups were protonated (pH=8.5), the interactions between charged groups further increase. At pH 4 (and lower) the protonation of PEI-maltose is going to complete. The maximum is reached at pH=3 [19]. According to [20-22] only 2/3 of the amino groups can be protonated, due to the high density of amino groups on the molecule and due to the branched structure, which is responsible for a very compact molecule structure.

As shown, the IEP of PEI-maltose is about 9.8. Therefore this polymer has a large amount of basic (16% primary, 53% secondary und 31% tertiary) amino groups at the surface. For other types of modified PEIs (mono-substituted as well as di-substituted) the curves are similar, but the isoelectric points are shifted to lower values, due to their different quantity of primary, secondary and tertiary amino groups. In Tab. 1 the IEPs of different OM - PEIs are summarized.

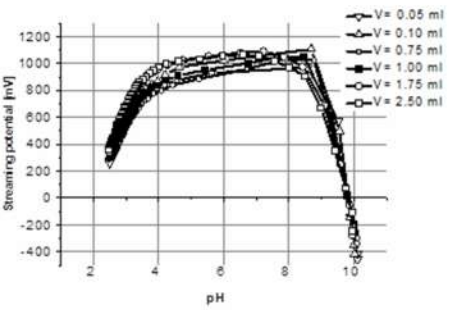


Figure 3. Determination of the isoelectric point (IEP) of monosubstituted PEI-Maltose (1:0.2): Streaming potential in dependence on pH; the volume of PEI-stock solutions in the titration cell was varied between 0.05 ml and 2.5 ml.

Table 1. IEPs of different OM-PEIs with their ratio of primary, secondary and tertiary amino groups.

Sample	Ratio, PEI:OS	Degree of Functionalization, [%]	Ratio of amino groups, [%]			IEP
			prim.	sec.	tert.	
PEI-5000	-	-	32	37	31	10
PEI-Lactose	1:0.4	30	2	67	31	9.8
PEI-Lactose	1: 5	80	-	21	79	8.8
PEI-Maltose	1:0.2	16	16	53	31	9.8
PEI-Maltose	1:0.5	36	-	66	34	9.5
PEI-Maltose	1:10	90	-	11	89	8.8
PEI-Maltotriose	1:0.2	13	17	52	31	9.8
PEI-Maltotriose	1:0.5	32	-	69	31	9.5
PEI-Maltotriose	1:4.25	75	-	24	76	9.0
PEI-Maltoheptaose	1:0.4	21	17	52	31	9.6

PEI-polyethyleneimine
OS-Oligosaccharide

The highest IEP with 10.0 is found for PEI, which has 32% primary amino groups. The value of the IEP decreases with decreasing number of primary amino groups**.** The primary amino groups have the highest basicity. Therefore the unmodified PEI has the highest IEP (about 10) because due to its branched structure it has the largest number of primary groups (32%). Because of the modification with oligosaccharides the bascity decreases. Therefore we find a correlation between IEPs and the content of primary amino groups. The IEPs of monosubstituted PEI-Lactose (1:0.4), PEI-Maltose (1:0.2) and PEI-Maltotriose (1:0.2) are 9.8, according to 2% (PEI-Lactose), 16% (PEI-Maltose) and 17% (PEI-Maltotriose) primary amino groups. But, the IEP is much lower for “disubstituted” PEIs which have a PEI:OM ratio > 1. We found 8.8 for PEI-Lactose 1:5 and PEI-Maltose 1:10. The IEP of PEI-Maltotriose 1:4.25 is 9. The reduction of the basicity is caused by the fact that disubstituted PEIs have a big number of tertiary amino groups (ca. 80-90%) and a low content of secondary amino groups (10-20%). Further, the degree of functionalization is high. In contrast, monosubstituted PEIs have a lower oligosaccharide content (30% for 1:0.5 and 15% for 1:0.2). Therefore not so many PEI-groups were blocked and the basicity is higher than for disubstituted PEIs.

3.2. Determination of the specific charge density. The titration procedure was applied for charge characterization of different polyelectrolyte solutions – unmodified PEI (Polymin P and G) with low, respectively high molecular weight and, on the other side, highly branched OM - PEIs. Usually an automatic titration regime, which is relatively fast, is used. Results were obtained in several minutes. But we noticed that different factors can have an influence on measured specific charge density such as the polymer concentration in the measuring cell which has an influence on pH. So the pH of a freshly prepared stock solution (about 10) decreases by dilution with water by a factor of 10 to pH 8.5, or by a factor 1:100 to pH 7.8. Therefore results without a clear description of measuring conditions are not useful. As an example in Tab. 2 the charge densities of different PEIs as found in references are summarized. PEI is an important polyelectrolyte which is used for instance for surface modification of wood [23], or in the paper industry [24].

Table 2. Specific charge densities of PEI determined by polyelectrolyte titration.

PEL-sample	Supplied by	pH*	Specific charge density, q [meq/g]	Reference
PEI	Sigma Aldrich	9.0	+16.6	[23]
Polymin SK	BASF	8.0	+4.3	[24]
PEI, G100	BASF	11	+17.9	[23]
PEI-P	BASF	11	+17.7	[23]
Lupasol G 100	BASF	11	+16 (BASF-Method at pH 4.5)	[25]
Lupasol P	BASF	11	+17 (BASF-Method)	[25]

Polymin or Lupasol are trade names of PEI,
pH* -is the pH as it is mentioned in the reference

In Table 2, the importance of "pH" for the detected charge is obvious. It is essential to make a difference between the pH of the PEI-stock solution in water and the pH at which the titration was carried out. Therefore it is very difficult to compare titration results of different working groups.

To our knowledge the influence of the velocity during PEI-titration was not significant because the molecular weight of the PEI, used for oligosaccharide modification, was relatively low (5000 g/mol). Therefore the solubility of PEI was good and the accessibility of the molecules during titration was well. But the influence of concentration was tested for different OM-PEIs too. Their solutions were titrated as described in the experimental part (the pH was adjusted to 6-7). The results are shown in Tab. 3 for PEI-Maltotriose as example.

Table 3. Specific charge density (q) of three different modifications of PEI-Maltotriose in dependence on polymer volume.

Sample	pH	Volume [ml]	q [meq/g]
PEI-Maltotriose 1:0.2	6.98	0.15	(+)4.90
		0.30	(+)4.51
		0.50	(+)4.44
PEI-Maltotriose 1:0.5	6.09	0.15	(+)2.52
		0.30	(+)2.50
		0.50	(+)2.50
PEI-Maltotriose 1:4.25	6.22	0.50	(+)0.91
		1.00	(+)0.69
		1.50	(+)0.63

As expected, a clear correlation between oligosaccharid-content and titrated cationic charge was found. The higher the degree of modification with maltotriose, the lower the detected cationic charge. In contrast to PEI whose charge is about 10 meq/g at pH of about 6 (Figure 7), the charge of OM-PEIs is much lower, depending on the degree of modification. The influence of polymer volume in the measuring cell on detected charge density is different and depends on the PEI-OM-ratio. In some cases (ratio 1:0.5) the influence is small, but at high oligosaccharide content the deviations are significant. In all cases the highest charge was found at the lowest polymer concentration. As one reason the better accessibility of charged groups is considered. In the third example (1:4.25), where the volumes were larger than in the first and second example, big deviations of the specific charge density were found.

3.2.1 Influence of titration velocity on the detected specific charge density q. The influence of kinetic effects on the specific charge density was measured for the unmodified PEI and also for disubstituted PEI- maltose (1:10), using the "static mode" of PCD. The velocity of PES-addition was varied between 0.01 ml/min and 0.27 ml/min. The solutions were prepared as described. Because the streaming potential was positive at this pH, PES was used as titrant. For PEI the influence of the titration velocity on PES consumption is small, but the rate of polymer addition should be neither too low nor too high. The slowest mode (0.01 ml polymer per 1 minute) is not effective, because one titration would take about 30 minutes. Further, it was noticed that the pH significantly changed during such a long titration (from 6.9 to 6.4). Therefore, as already described [14] an optimum of titration velocity is necessary.

In contrast to PEI, the titrated charge of PEI-Maltose decreases with increasing titration velocity. The results are shown in Figure 4.

It is obvious that for these modified PEIs with an excess of oligosaccharide and therefore with a dense shell the measured charge is significantly influenced by the titration velocity because the polyanion needs time for diffusion into the molecule. The slower the titration process, the higher the detected charge. As already described [14] an optimum of titration velocity is necessary. The titration velocity should be neither to high nor too low. Therefore in our further work a velocity of 0.04ml/min was used. Similar topics were described by Sezaki and Hubbe. For characterization of acrylamide polyampholytes they preferred a manual titration method in which streaming current signals were observed 5 minutes after each addition of titrant instead of an automatic titration with low titration velocity [15].

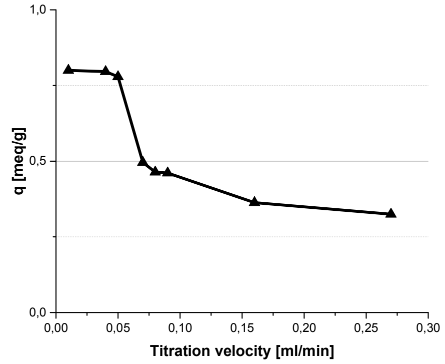


Figure 4. Specific charge density q of PEI-Maltose in dependence on the titration velocity.

3.2.2. Influence of pH on specific charge density q. The specific charge density is an important, application relevant parameter, especially for weak polyelectrolytes such as PEI or OM-PEIs, because the cationic charge decreases with increasing pH. Therefore different stock solutions were prepared in water and then the pH was varied in the range from 2 to 11. In Figure 5 the streaming potential of these solutions is shown in dependence on the volume of the titrant. In neutral media it is possible to detect acidic or basic groups at the interface. Therefore PEI-maltotriose has basic groups (amino groups) because the streaming potential at the beginning of titration (volume=0ml) is positive. At first the pH of the PEI stock solution was decreased by adding different quantities of hydrochloric acid (0.1M). The lower the pH, the more H^{+}-Ions are in the solution. Then the titration was carried out by adding PES-Na. Due to the reaction with H^{+} the signal slowly decreases. When the reaction between H+ and PES-Na is completed, the signal dramatically decreases. Then, as described in Part 2, the specific charge density can be calculated.

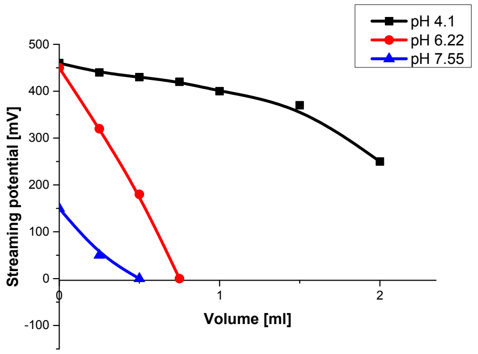


Figure 5. Streaming potentials of disubstituted PEI-Maltotriose in dependence on the volume of titrant (0.001 M PES-Na) at different pH.

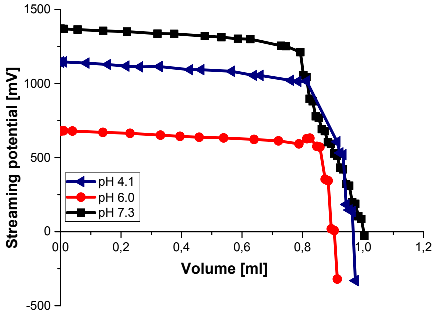


Figure 6. Streaming potentials of PDADMAC (c=0.001 mol/l) in dependence on the volume of titrant (0.001 mol/l PES-Na) at different pH; pH 6 is the pH of the stock solution).

Positive charges are found in all cases (at pH of 4.1, 6.0, 7.3 or also higher).

In the following chapter the measured charge density in dependence on pH is compared for PEI and different structures of OM - PEIs. First results of charge determination of OM-PEIs are presented in [18], but here these investigations were completed. For polymer addition during titration a velocity of 0.04 ml/min was used. The following influences were varied:

- Ratio between PEI- and OS-units: from 1:0.2 up to 1:10
- Type of polysaccharide: Lactose (La) compared with Maltose (Ma)
- Polysaccharide structure: The size of the substituents increases with increasing number of OS-units: Maltose (Ma) < Maltotriose (Ma-III) <Maltoheptaose (Ma-VII)

At first the influence of PEI-OS ratio is shown for PEI-Lactose (Figure 7).

In contrast, at higher pH (>7.55) the streaming potential is negative (not shown here). For comparison the behavior of the strong polycation PDADMAC is shown in Figure 6.

Table 4. Comparison of the charge in dependence on pH; unmodified PEI and two samples of PEI-Lactose.

(+) positve charge (titrated with PES-Na); (-) negative charge (titrated with PDADMAC)

pH	Sample		
	PEI-5000 q [meq/g]	PEI-Lactose 1:0.4 q [meq/g]	PEI-Lactose 1:5 q [meq/g]
2.0	(+)16.534	(+)6.410	(+)3.007
3.0	(+)16.163	(+)5.833	(+)2.910
4.0	(+)14.660	(+)5.582	(+)2.669
4.5	(+)11.431	(+)4.978	(+)2.560
5.0	(+)11.253	(+)4.270	(+)1.559
6.0	(+)10.229	(+)3.886	(+)1.300
7.0	(+)8.441	(+)3.413	(+)0.987
7.5	(+)8.381	(+)3.212	(+)0.854
8.0	(+)7.265	(+)3.012	-
8.5	(+)5.137	(+)2.775	(-)0.036
9.0	(+)4.343	(-)0.020	(-)0.040
10.0	(+)1.313	(-)0.190	(-)0.217
10.5	(-)0.360	-	-

In most cases the polyelectrolytes are positively charged. With increasing pH the charge decreases, however, a strong influence of the molecule structure can be noticed. The charge of unmodified PEI compared with PEI-Lactose is significantly higher due to the screening effect of large substituents. The detected charge of monosubstituted PEI-Lactose (1:0.4) is much higher (about 2 times) compared with PEI-Lactose (1:5). According to [18] the structure of such polymers with an excess of OS is characterized by a dense shell. The dependenceof charge on pH will be shown in Figure 7-11 too.

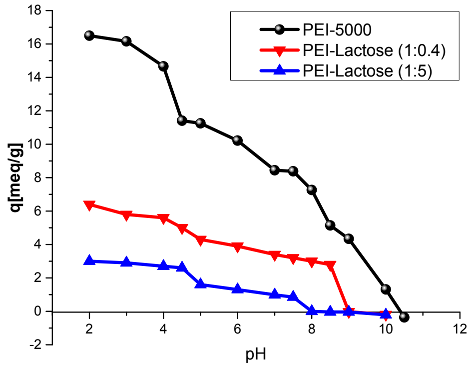
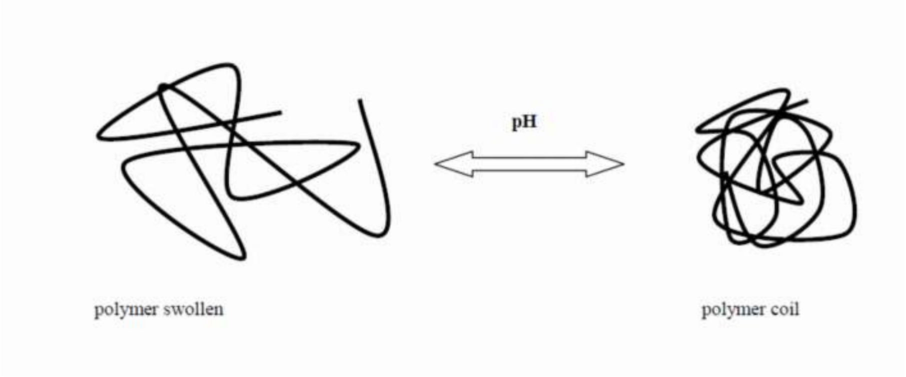


Figure 7. Measured specific charge density q in dependence on pH; Comparison between unmodified PEI and PEI-Lactose.

For instance PEI-Lactose is deprotonated at pH >>7 (Figure7). The polymer in aqeous solution is a coil. At lower pH, the functional groups are protonated and the charge density is increased. Therefore the forces between charged segments increase and polymer coils swell. (Scheme 1). At lower pH PEI-Lactose has the maximum of charge density and the polymer is (theoretically) stretched. But for branched PEI the protonation is not complete. Only 2/3 of the amino groups can be protonated.

The maximum of charge density is reached at pH 3 [22]. Therefore the charge density of the molecule is influenced by the pH. For branched PEI only 2/3 of the amino groups are protonated. Maximum charge density is obtained at pH of about 3. [22]. Similar results, compared with Lactose, were found for PEI-Maltose or PEI-Maltotriose (Figure 8 and 9). A direct comparison between different oligosaccharides will be shown later in Figure 10 and 11. As a result we can say: the larger the substituent (the oligosaccharide), the more complex is the system. Therefore the reaction between the charged polymer and the titrant is hindered.



Scheme 1. Schematic structure of polymer at low (left) or high pH (right).

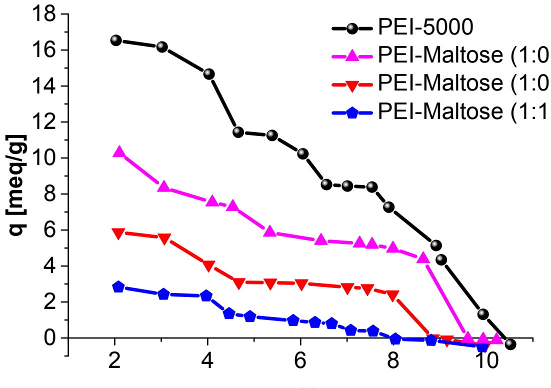


Figure 8. Measured specific charge density q in dependence on pH; Comparison between unmodified PEI and PEI-Maltose with different PEI-OS-ratios.

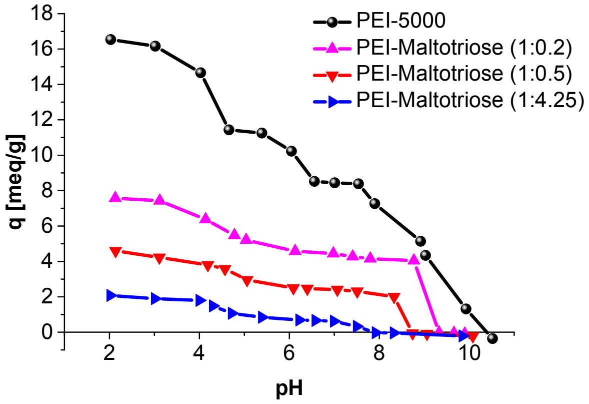


Figure 9. Measured specific charge density q in dependence on pH; Comparison between unmodified PEI and PEI-Maltotriose with different PEI-OS-ratios.

By comparing the charge density of OM-PEIs with the same degree of substitution, but different oligosaccharides, the following results were obtained (Figure 10). The PEI-OS-ratio is more important for the charge density than the size of molecule. Therefore the differences between PEI, modified with Maltose or Maltotriose with the same DS are small.

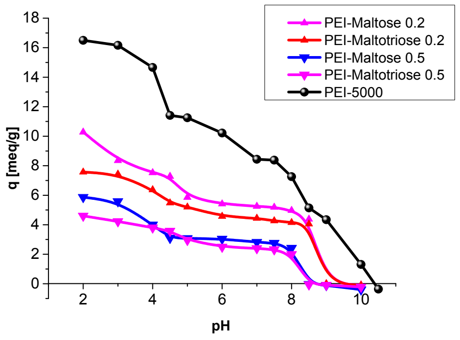


Figure 10. Measured specific charge density q in dependence on pH; Comparison between unmodified PEI, PEI-Maltose and PEI-Maltotriose with low and medium PEI-OS-ratios.

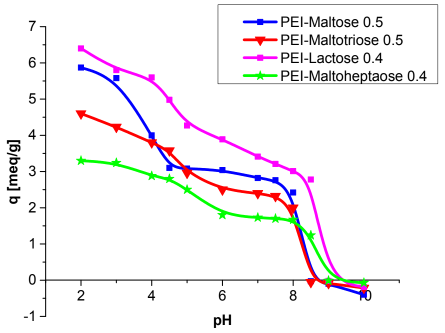


Figure 11. Measured specific charge density q in dependence on pH; Comparison between different OM-PEI structures with the same, “medium” PEI:OS-ratios (0.4-0.5).

The lowest charge is found for products with very high degree of substitution, for instance PEI-Maltose (1:10); not shown here. When we compare molecules with four different oligosaccharides, but similar, “medium” PEI-OS-ratio, we find that PEI-Lactose has the highest, and PEI-Maltoheptaose has the lowest charge. But these differences in cationic charge were obtained up to pH of about 8. At higher pH the molecules are neutral or slightly negative.

4. CONCLUSIONS

The complete characterization of water soluble polymers is very important because of the great application potential in different fields. Due to their charges and therefore their electrostatic interactions their behavior in aqueous solution is different from non-charged polymers because the properties in solution are influenced by intra- and intermolecular interactions. Coulombic interactions are influenced by the charge density on the polymer chain. For strong PELs, the charge is determined by the structure of the molecule and does not change with pH. In contrast, the charge of weak PELs can be varied by changing the pH. This was demonstrated for PEI and for OM-PEI, which were modified with oligosaccharides. Unmodified PEI has the highest cationic charge density (about 17 meq/g at pH of about 2) whereas the charge density decreases with increasing number of oligosaccharide structures.

For characterization the polylectrolyte titration using streaming potential can be used. This method is easy to handle and robust, but the titration parameters (polymer concentration in the measuring cell and titration velocity) should be investigated and adapted to the structure of PEL. For branched polymers highly accurate and reproducible measurements were obtained with lower titration velocity than for “standard titration”.

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