Polyanion–polycation complex formation as a function of the position of the functional groups

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A method consisting of the combination of turbidimetry and conductometry was investigated to detect polyanion–polycation complex formation. We used 'strong acid' polyelectrolytes varying in charge density and 'strong basic' polyelectrolytes varying in the length of the spacer groups and in the accessibility of the quaternary ammonium function. Our systematic investigations have shown a predominantly 1:1 stoichiometry at the turbidimetric as well as the electrochemical titration endpoints. Deviations were observed when the individual components were significantly less soluble, i.e. when the polymers had units with long hydrophobic spacer groups and/or with quaternary ammonium functions that are sterically less accessible. Colloid stability as well as the type of turbidity curve are discussed on the basis of a two-step mechanism of symplex formation. The results are also compared with our earlier investigations. We previously found a general trend that a 1:1 stoichiometry could only be achieved with 'strong' polyelectrolyte components. Independently of the molar ratio of the cationic to anionic functional groups at the titration endpoint, the stability of the colloids of the symplex system was found to depend also on the molar mass, the charge density and the hydrophobicity of the comonomer units. Copy © 1996 Elsevier Science Ltd.

(Keywords: polyelectrolytes; complexes; symplex formation)

INTRODUCTION

Polyanion–polycation complex (symplex) formation is a well known phenomenon. It is based predominantly on Coulombic interactions[1]. Symplex formation is of practical relevance to flocculation processes in water treatment[2]; it is also of interest from the analytical point of view for the determination of the degree of substitution and/or of the concentration of polyelectrolytes in aqueous systems[3].

Very often, a 1:1 stoichiometry of cations and anions in polyanion–polycation complexes of polyelectrolytes is assumed without further experimental evidence. However, we have in the past[4] observed deviations from a 1:1 stoichiometry due to structural features of the polyelectrolytes. Specifically, branched polyelectrolytes with 'weak' functional groups of low charge density have been observed to form non-stoichiometric polyelectrolyte complexes. We have therefore investigated the different effects of the complex stoichiometry of symplex formation in detail.

A combination of polyelectrolyte titration techniques in the concentration range just prior to phase separation has been employed with great success. These techniques consisted of potentiometry, conductometry and turbidimetry and allowed the detection of the electrochemical rather than the turbidimetric titration endpoints. We have described some of these results previously[4]. We thus directed our research activities using this combination of titration techniques to investigate 'steric' effects, i.e. the influence of the accessibility of the functional groups, and have used for that purpose previously reported, but for our purpose specially synthesized, polyelectrolytes.

The polycations varied in: (i) the type and length of the alkyl units surrounding the ammonium ions; (ii) the length of the spacer groups that connected the functional groups with the polymer backbone chain; and (iii) the charge density of the functional groups. In addition, sulfonate and sulfopropyl group containing polyanions were also synthesized, which varied predominantly in the charge density of the functional groups. In comparison to our earlier investigations, these charged macromolecules can be classified as 'strong' polyelectrolytes with

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Table 1 Cationic polyelectrolyte components used

Sample designation		Average distance between charge centres (nm)
PMAPy E-0	Poly(methacrylatoethylpyridinium bromide)	0.26
PMAPy E-1	copolymer with methyl methacrylate	0.40
PMAPy E-2	copolymer with methyl methacrylate	0.52
PMAPy E-3	copolymer with methyl methacrylate	0.84
PMAPy E-4	copolymer with methyl methacrylate	1.19
PMAPy P-0	Poly(methacrylatopropylpyridinium bromide)	0.29
PMAPy P-1	copolymer with methyl methacrylate	0.36
PMAPy P-2	copolymer with methyl methacrylate	0.45
PMAPy P-3	copolymer with methyl methacrylate	0.94
PMAPy B-0	Poly(methacrylatobutylpyridinium bromide)	0.29
PMAPy B-1	copolymer with methyl methacrylate	0.33
PMAPy B-2	copolymer with methyl methacrylate	0.49
PMAPy B-3	copolymer with methyl methacrylate	0.82
PMAPy H-0	Poly(methacrylatohexylpyridinium bromide)	0.26
PMAPy H-1	copolymer with methyl methacrylate	0.35
PMAPy H-2	copolymer with methyl methacrylate	0.50
PMAPy H-3	copolymer with methyl methacrylate	0.79
PMAE TM-0	Poly(methacrylatoethyltrimethylammonium chloride)	0.23
PMAAP TM-0	Poly(methacrylamidopropyltrimethylammonium chloride)	0.23
PVB TM-0	Poly(vinylbenzyltrimethylammonium chloride)	0.23
PVB TE-0	Poly(vinylbenzyltriethylammonium chloride)	0.23
PVB TB-0	Poly(vinylbenzyltributylammonium chloride)	0.23
PVB DMO-0	Poly(vinylbenzyldimethyloctylammonium chloride)	0.23
PDADMAC-0	Poly(diallyldimethylammonium chloride)	0.38

Table 2 Anionic polyelectrolyte components used

Sample designation		Average distance between charge centres (nm)
PSPM-0	K salt of poly(sulfopropyl methacrylate)	0.23
PSPM-MMA-1	copolymer with methyl methacrylate	0.38
PSS-0	Na salt of poly(styrenesulfonate)	0.23
PSS-MMA-1	copolymer with methyl methacrylate	0.35
PSS-MMA-2	copolymer with methyl methacrylate	0.56
PSS-MMA-3	copolymer with methyl methacrylate	1.07
PAA-0	Na salt of poly(acrylate)	0.23

regard to the acidity of the polyanions as well as the basicity of the polycations.

EXPERIMENTAL

The polyelectrolytes used in this work are shown in *Tables 1* and *2*. The sample designation was based on the chemical structure in combination with the average distance between the charged centres assuming an ideal distribution of the monomer units along the backbone chain.

3-Sulfopropyl methacrylate and *p*-styrenesulfonic acid were copolymerized with methyl methacrylate by free-radical polymerization according to ref. 5 with azobisisobutyronitrile (AIBN) as initiator and toluene as solvent at 60°C. The chlorinated methacrylates (chloroethyl, chloropropyl, chlorobutyl and chlorohexyl methacrylate) synthesized according to ref. 6 were polymerized in a quite similar way to the above described anionic components[5]. The *r* values and *Q*–*e* values are shown in *Tables 3* and *4*. The Cl atoms of the resulting polymers were exchanged by Br atoms according to ref. 7 for enhancing their reactivity in the following quaternization process with pyridine, which was realized in pyridine solution at 65°C in 6–10 h. The quaternary ammonium salts are insoluble in pyridine and can then be isolated.

Table 3 The r values calculated by the Kelen–Tüdös method; $M_2 = MMA$

M_1	r_1	r_2
2-Chloroethyl methacrylate	0.80 ± 0.12	0.70 ± 0.11
3-Chloropropyl methacrylate	0.56 ± 0.13	0.85 ± 0.16
4-Chlorobutyl methacrylate	1.02 ± 0.05	0.91 ± 0.05
6-Chlorohexyl methacrylate	0.71 ± 0.10	0.82 ± 0.07
PSPM	0.76 ± 0.15	0.57 ± 0.16
PSS	0.61 ± 0.15	0.59 ± 0.19

Table 4 The Q–e values calculated with $Q = 0.78$, $e = 0.40$ for MMA (M_2)

M_1	Q	e
2-Chloroethyl methacrylate	1.10	0.36
3-Chloropropyl methacrylate	1.29	1.26
4-Chlorobutyl methacrylate	0.95	0.67
6-Chlorohexyl methacrylate	0.97	0.34
PSPM	1.43	0.51
PSS	0.88	-0.61

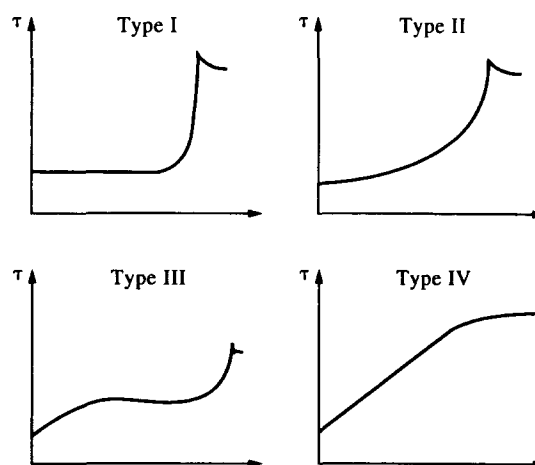**Figure 1** Characteristic types of titration curves

Vinylbenzyl chloride is a commercial mixture containing about 90% plus of the *para* isomer. On distillation and subsequent substitution, the amounts of the isomers decrease and, at the end, only a small amount of isomer impurity other than the *para* isomer remains.

Synthesis of poly(vinylbenzyltrialkylammonium chloride)s was carried out as follows. The trialkylmethylstyrylammonium salts were prepared by reacting vinylbenzyl chloride with trimethylamine, triethylamine, tri-n-butylamine and *N,N*-dimethyl-*N*-n-octylamine in an inert solvent. The monomers were polymerized in 20–30% water solutions with 4,4'-azobis(4-cyanovaleric acid) (ACVA) as the initiator for most monomers. Vinyl(*N,N,N*-dimethyl-n-octyl)ammonium chloride was polymerized in methanol using AIBN as the initiator. The polymer yields were in excess of 90%. The inherent viscosities varied, in part because of their change in hydrophilic character, but were between 5 and more than $10 \, dl \, g^{-1}$. For details see refs. 8 and 9.

Methacrylatoethyltrimethylammonium chloride (MAE TM-0) was synthesized from 2-dimethylaminoethyl methacrylate and methyl iodide followed by treatment of the methacrylatoethyltrimethylammonium iodide with silver chloride. MAE TM-0 was polymerized in an about 30% aqueous solution with ACVA and after the usual work-up white polymer was obtained in 94% yield; $\eta = 10.4 \, dl \, g^{-1}$ (0.2% in water).

Methacrylamidopropyltrimethylammonium chloride (MAAP TM-0) was obtained from a commercial source. It was polymerized in 50% aqueous solution with ACVA as the initiator and gave the polymer in 93% yield; $\eta = 8.4 \, dl \, g^{-1}$ (0.2%).

Poly(diallyldimethylammonium chloride) used as a cationic standard was obtained by radical polymerization of diallyldimethylammonium chloride with radical initiators[10]. Anionic poly(sulfopropyl methacrylate)s as well as the copolymers of styrenesulfonate with methyl methacrylate were synthesized by copolymerization of the respective comonomers. Commercially available homopolymers of sodium styrenesulfonate and sodium acrylate were purchased from Polyscience and from Aldrich Chemical Co.

The polyelectrolyte titration experiments were carried out in a 100 ml glass vessel equipped with a pH electrode, a conductivity sensor and a turbidity sensor. The titrations were performed at pH 7 with 50 ml of a 0.05% solution (w/v) of the polyelectrolyte component in excess. The titrant solution (1% w/v) was continuously added with stirring to the oppositely charged component at a dose rate of $2–10 \, ml \, h^{-1}$; this rate of addition ensured equilibrium conditions for the process of complex formation.

The endpoint of the turbidimetric titration was judged as the maximum of turbidity or as the break in the curve of turbidity vs. titrant consumption. In addition, the electrochemical endpoint, i.e. the break in the curve of conductivity, was determined. The molar ratio (C)/(A) of the charged groups of the titrant at the titration endpoint to the total number of oppositely charged groups of the given polyelectrolyte was defined as the symplex stoichiometry.

Besides these titration endpoints, the shape of the turbidimetric curve was evaluated in a qualitative manner according to the curve types, schematized in *Figure 1*.

The phase behaviour of the systems, after passing the turbidimetric titration endpoint, was characterized with regard to their colloid stability as: (i) stable dispersion (D); (ii) film-forming system (FF); and/or (iii) flocculating system (F). It had a time-dependent phase separation, which can be subdivided further with regard to the structure of the flocculant into (a) large voluminous (F1) and (b) small sticky (F2) flocculant systems. It must be stated here that this deviation from the phenomenological point of view depended on the conditions of the titrations. In some 'borderline' cases such a classification is problematic.

RESULTS

Our results showed good agreement between the electrochemical and turbidimetric titration endpoints. This means that the endpoint of the conductivity curve and the turbidity maximum always coincided in the range of accuracy (about 4%) between the two methods. Both kinds of endpoints could not be determined in all cases. The turbidity maximum becomes flattened with decreasing charge density of the components and the
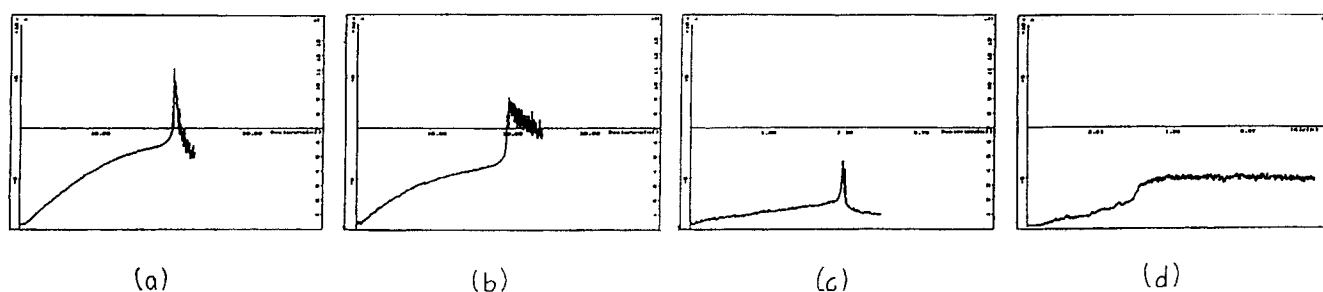
Figure 2 Turbidimetric titration curves observed by titrating quaternary polycations of varying hydrophobicity with poly(sulfopropyl methacrylate) (PSPM-0): (a) PMAPy P-0; (b) PMAPy B-0; (c) PMAPy H-0; (d) PVB TB-0
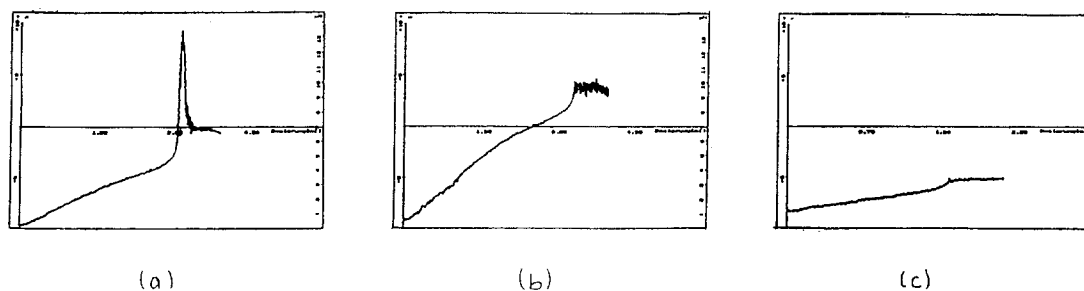
Figure 3 Turbidimetric titration curves observed by titrating quaternary polycations of varying charge density with poly(sulfopropyl methacrylate) (PSPM-0): (a) PMAPy E-0; (b) PMAPy E-2; (c) PMAPy E-4

break point in the conductivity curve becomes less noticeable or even non-distinct. The pH curves showed a small but significant shift, which corresponded to the conductometric as well as to the turbidimetric endpoint.

Because of the general good agreement between the electrochemical and the turbidimetric endpoints of the symplex formations, only the turbidimetric endpoints are discussed in more detail. We shall consider the results of the titrations when cationic polyelectrolytes in excess were titrated with various different polyanions. With a 'strong' acid component of high charge density (PSPM-0), a stoichiometry of 1:1 was obtained predominantly, but not in all cases. Deviations from a 1:1 stoichiometry were observed in the case of the comonomer units with n-hexyl side chains (PMAPy H samples) as well as in the case of the poly(vinylbenzylammonium) salts (PVB samples).

The largest effect was observed when PVB TB-0 as the polycation salt was used, which means a polycation with an ammonium ion surrounded by three n-butyl groups, which gave $(C)/(A) = 1.53$. The deviations from a 1:1 stoichiometry were accompanied by a change in the type of the titration curves from type III to type II or IV (compare *Figure 2*). Similar changes in the titration curves were observed by decreasing the charge density of the components as shown in *Figure 3*. In general, flocculation occurred after passing the titration endpoint.

Systems with voluminous flocculation were formed only in those cases where methylene spacer groups separated the polycation from the polymer chain in the polyelectrolytes. An increase of the spacer length (propyl spacer groups) was found to be related to a transition to more sticky systems. A further increase of the spacer unit was accompanied by a change to a more compact system (hexyl spacer). A weakening of the Coulombic interaction forces by decreasing the charge density of the component in excess (PMAPy-0)–(PMAPy-3) and the

dosage component (PSPM-0)–(PSPM-MAA-1) was found to be related to a change in the type of the titration curve (type III → II) (see *Figure 3*). The behaviour of the more colloidal sticky systems (F2–F1) was observed. By decreasing the acidity of the dosage component, the general trend showed: (i) deviations from a 1:1 stoichiometry, (ii) a turbidity curve of type I and (iii) the formation of a stable dispersion.

The average molar ratio of cationic to anionic groups at the titration endpoint was always nearly 0.77. Significant deviations from this value were observed only in samples with a n-hexyl spacer group and in the sample of PVB TB-0. These results seem to be in good agreement with the results obtained earlier from titration experiments of PSPM. Generally, two trends should be mentioned here: (a) an increase in the dispersion stability with increasing spacer length; and (b) a decrease in the steepness of the turbidity curve before passing the τ maximum, indicating that the charge density decreased drastically. The last trend could be understood by looking at *Figure 4*.

When the component which was in excess (PSPM-0 in excess) was changed, no significant effects with regard to symplex stoichiometry, type of turbidity curve, as well as the behaviour of the precipitate as colloid were observed.

We now describe anionic polyelectrolytes that have different charge densities and have strong acids as functional groups. Poly(diallyldimethylammonium chloride) was used as the cationic standard component for titration. *Tables 5* and *6* summarize the results of these experiments. Independent of the component that was in excess, a 1:1 stoichiometry was found at the endpoint of the titration when strong acid polyelectrolytes of varying charge density were used. When the charge density of the components was decreased, we observed a change of the titration curve from type I → IV and a different phase behaviour was observed after passing the endpoint.
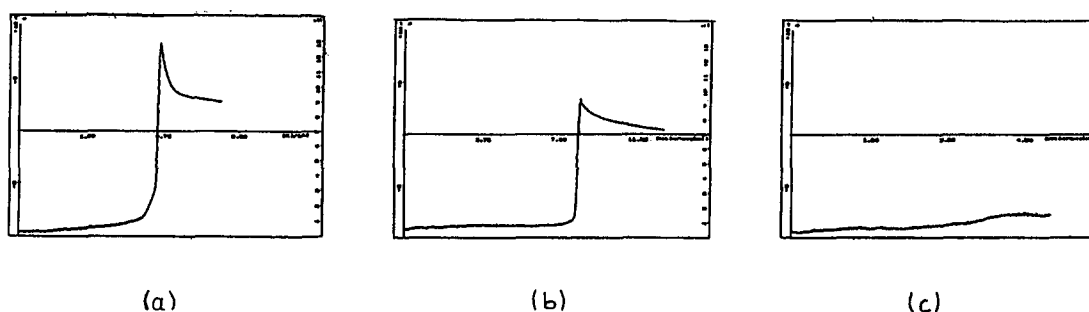
Figure 4 Turbidimetric titration curves observed by titrating quaternary polycations of varying charge density with Na-poly(acrylate) (PAA-0): (a) PMAPy E-0; (b) PMAPy E-2; (c) PMAPy E-4

Table 5 Characteristics of symplex formation by titrating polyanions of varying constitution with poly(diallyldimethylammonium chloride) (PDADMAC-0)

Excess component	Turbidity curve type	Molar ratio (C)/(A) at the endpoint	Phase behaviour after passing the endpoint
PSPM-0	III	1.07	D
PSPM-MMA-1	II	1.12	D
PSS-0	I	1.01	F2
PSS-MAA-1	II	1.01	F1
PSS-MAA-3	IV	1.02	D

Table 6 Characteristics of symplex formation by titrating poly(diallyldimethylammonium chloride) (PDADMAC-0) with polyanions of varying constitution

Dosaged component	Turbidity curve type	Molar ratio (C)/(A) at the endpoint	Phase behaviour after passing the endpoint
PSPM-0	III	1.04	D
PSPM-MMA-1	II	1.12	D
PSS-0	I	1.00	F1
PSS-MAA-1	II	1.01	F1
PSS-MAA-2	II	0.99	F1
PSS-MAA-3	IV	1.07	F1

Table 7 Phase behaviour of symplex systems, consisting of poly-(diallyldimethylammonium chloride) (PDADMAC-0) and poly(sodium acrylate) (PAA-0), after passing the turbidimetric endpoint as a function of the molar mass of the components used

Molar mass of the components (g mol^{-1})		
Excess component PDADMAC-0	Dosaged component PAA-0	Phase behaviour
5 000	6 000	Dispersion
5 000	60 000	Dispersion
5 000	200 000	Weak film formation
40 000	6 000	Dispersion
40 000	60 000	Dispersion
40 000	200 000	Dispersion
90 000	6 000	Weak film formation
90 000	60 000	Dispersion
90 000	200 000	Dispersion

For a more comprehensive discussion of the phenomena that we observed, we investigated the influence of the molar mass of the polymers systematically by using different, but well characterized, PAA and PDADMAC samples. Before passing the τ maximum of the titration curve, a general trend to, primarily, larger aggregates (τ increase at the beginning of the dosage) could be observed, when the molar mass of the components was increased, as demonstrated in *Figure 5*. *Table 7*

characterizes the phase behaviour of the resulting systems after passing the maximum of turbidity. In general, a rather insignificant tendency of flocculation could be observed. Instead of flocculation, films were predominantly formed.

The systems described above could be further subdivided into systems of weak and systems of strong film-formation tendency; they could be related to the structure of the precipitate (*Table 7*). The film-forming tendency (comparable to the flocculation tendency) increased when two components were titrated which differed significantly in their molar mass. When two components were used that have low charge density, stable dispersions were formed.

DISCUSSION AND CONCLUSIONS

We will now discuss the results that have been obtained
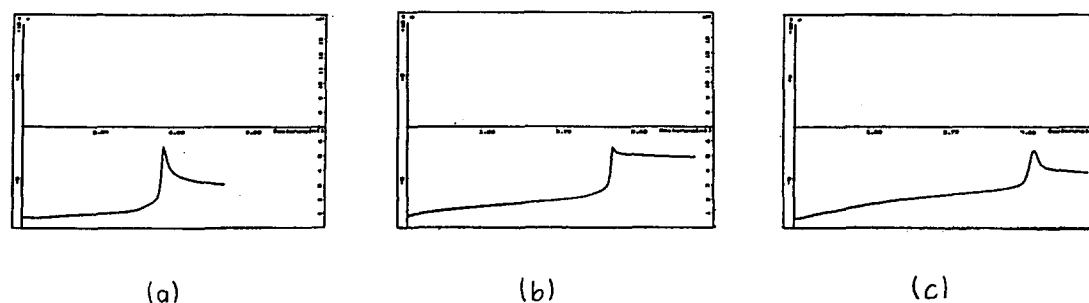
Figure 5 Turbidimetric titration curves observed by titrating Na-poly(acrylate) (molar mass of 60 000 g mol^{-1}) with different poly(diallyldimethylammonium chloride) samples of varying molar mass (g mol^{-1}): (a) $MW = 5000$; (b) $MW = 40\,000$; (c) $MW = 90\,000$

during this research on polyelectrolyte complex formation with special emphasis on: (i) symplex stoichiometry; (ii) colloidal behaviour of the resulting systems; and (iii) the mechanism of symplex formation.

When analysing our experimental data, the stoichiometry of complex (symplex) formation shows a general 1:1 stoichiometry when 'strong acid' polyanions are titrated with a 'strong basic' polycation, independent of the charge density. Deviations from a 1:1 stoichiometry were observed only when strong polyelectrolytes with longer spacer length, longer than five methylene units (PMAPy H samples, PVB DMO-0), were used: see the discussion about flexible methylene spacer length between polymerizable group or polymer main chain and functional groups[11].

The direct environment of the quaternary ammonium ion is of special importance. It relates to the molar ratio of cationic to anionic functional groups that is obtained at the endpoint of the titration. The substitution of the methyl groups (i.e. PMAE TM-0 or PMAAP TM-0) surrounding the ammonium ion by ethyl (i.e. PVB TE-0) or n-butyl groups (i.e. PVB TB-0) is also accompanied by a deviation from the 1:1 stoichiometry. It must be pointed out that those polyelectrolytes which show deviation from a 1:1 stoichiometry are also significantly less soluble in water as compared to the trimethylammonium polycations.

The stoichiometry of the polycation–polyanion complex with hydrophobic groups is sufficiently different from the exact 1:1 stoichiometry even when two strong polyelectrolytes were titrated. The polyelectrolytes were found to be more hydrophobic because of the increase in the spacer hydrocarbon length and/or the length of the alkyl groups surrounding the ammonium group. In contrast to the strong acid sulfopropyl groups of the PSPM-0 sample, poly(acrylic acid) is a polyelectrolyte that has carboxyl groups which are much weaker acid groups than the sulfonic acid groups. We found in this case, in good agreement with our earlier investigations, that deviations from 1:1 stoichiometry occurred even at pH 7. A molar ratio of 0.72 was obtained for PMAPy H and PVB samples for the stoichiometry of the titration results, independently of the spacer length and of the charge density of the components. For the more hydrophobic PMAPy samples with n-hexyl spacer groups and also for the PVB samples, an increase in the molar ratio of cationic to anionic functional groups at the endpoint of titration was observed. These results were analogous to the results obtained by using PSPM-0 as our titration agent.

The titration of the PSPM and PSS samples with varying charge densities showed no significant deviations from the 1:1 stoichiometry; it was observed even when the titrating agent was in excess. Our results indicate that the 1:1 stoichiometry of polycations and polyanions was favoured when two components were used that were different in the type of acidity. By increasing the length of the side chain or the accessibility of the charge centre, the solubility of the component solutions becomes more unfavourable. This change results in a non-stoichiometric symplex formation due to the additional presence of non-Coulombic interactions, i.e. hydrophobic–hydrophobic interactions in water. The weaker Coulombic forces of interactions are then accompanied by a tendency to form symplex systems that are non-stoichiometric. This seems to be caused by the incomplete dissociation of the functional groups and the weak Coulombic interactions, which makes a complete charge compensation between the oppositely charged polyions impossible. This trend was found to be accentuated by additional steric hindrance.

The symplex systems that result from these interactions show a typical colloidal behaviour which agrees with the results of our systematic investigations of the general trends for flocculation when strong acid, fully ionized polyanions are introduced into the system. A voluminous flocculation was observed, which sediments, however, very readily. This result can be interpreted as being caused by a weakening of the strong Coulombic interactions, which is the result of a decrease of the charge density of the titrant. An increase of the hydrophobic portion of the polycations and polyanions results in the formation of so-called 'sticky' systems.

In the case of acid–base interactions involving the weaker carboxylic acid groups, the Coulombic forces were found to create the formation of stable dispersions.

Polyanion + polycation

Primary aggregat
(surface charge stabilized)

Titrant in excess
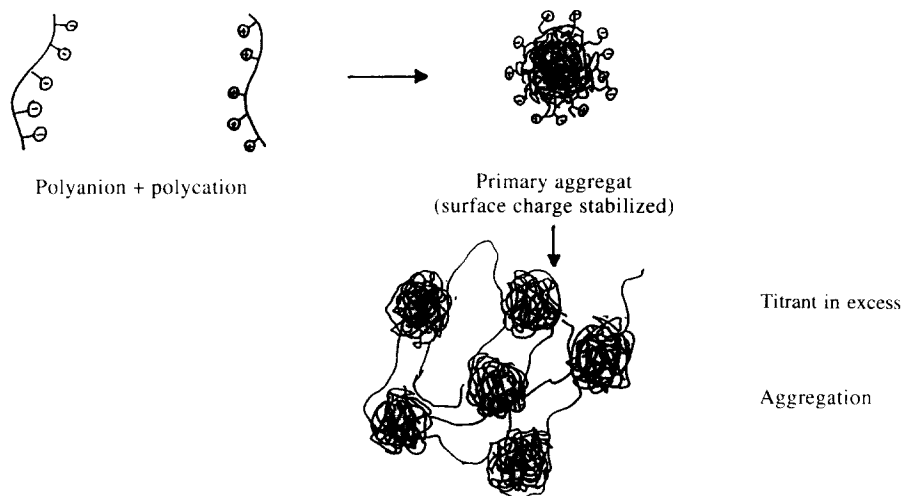
Aggregation

Figure 6 Two-step mechanism of symplex formation. First step: formation of surface charge stabilized primary symplex aggregates. Second step: bridging flocculation of the primary symplex aggregates

On the basis of a two-step mechanism for symplex formation, which has been outlined in more detail before[12] and shown in *Figure 6*, titration curves of general usefulness can be described as follows:

The curve of type I shows an increase of rapid turbidity before it reaches the τ maximum. This behaviour is characteristic of primary small symplex particles which aggregate to significantly larger, optically visible particles only near the maximum of turbidity. Stable dispersions of such complexes were predominantly observed when the two component polyions were of 'low molecular mass'. Films were formed and/or flocculation was observed when the two components of the titration varied significantly in molar mass. These cases can be interpreted by the model of bridging flocculation[12].

Curves of type II and III were commonly observed when the molar mass of the component polyions was increased and/or the acid strength between polyanions and polycations was substantially different. This behaviour is characteristic of the formation of significantly larger primary symplex particles.

The behaviour of the symplex system after passing the τ maximum mainly depends on the balance of these interactions. Coulombic interactions are dominant but non-Coulombic, e.g. 'hydrophobic', interactions also play a more or less significant role.

In contrast to curve types I–III, curve type IV can be interpreted by a continuous symplex formation independent of the degree of conversion of the polyanion–polycation complex formation. These kinds of interactions were observed predominantly by titrating polyanion–polycation polyelectrolyte components of low charge density.

ACKNOWLEDGEMENTS

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