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SALT EFFECT ON SURFACE MODIFICATION OF SILICA BY INTERPOLYELECTROLYTE COMPLEXES

Heide-Marie Buchhammer*, Klaus Lunkwitz
Institut für Polymerforschung Dresden e.V.
Hohe Straße 6, D-01069 Dresden, Germany

Dmitry V. Pergushov
Department of Polymer Science, Faculty of Chemistry, Moscow State University
Vorob'evy Gory, 119899 Moscow, Russia

Abstract: The effect of a low-molecular-mass salt on the properties of interpolyelectrolyte complexes formed as a result of interactions between poly(diallyldimethylammonium chloride) and copolymers of maleic acid with propylene or α-methylstyrene in their salt containing non-stoichiometric mixtures has been studied. Properties of such interpolyelectrolyte complexes were found to be determined by the chemical nature of the polyelectrolytes and by the salt concentration. The effect of salt on the surface modification of silica particles *via* their interactions with interpolyelectrolyte complexes has been examined. Two different ways of the surface modification of silica particles were used: **(i)** silica particles were contacted with previously prepared interpolyelectrolyte complexes and **(ii)** silica particles were contacted with cationic polyelectrolyte at first and then anionic polyelectrolyte was added. The efficiency of the surface modification was shown to be also dependent on the salt concentration and the chemical nature of polyelectrolytes. Turbidimetry, quasi-elastic light scattering, laser microelectrophoresis, and polyelectrolyte titration were used to characterize studied systems.

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INTRODUCTION

Polyelectrolytes belong to the class of reactive polymers. They are widely used to modify surface properties of various substrates and to stabilize or to destabilize colloidal dispersions. Interactions between oppositely charged macromolecules lead to the formation of interpolyelectrolyte complexes (**PECs**) that can be considered as new promising polymeric reagents and materials for industry, biotechnology and medicine (Refs. 1, 2).

In our previous studies, we considered interactions between oppositely charged polyelectrolytes in a solution or at a solid-liquid interface in the relation to a surface modification of various organic and inorganic substrates (Refs. 3, 4). It was shown that surface charge can be changed more effectively if a combination of oppositely charged polyelectrolytes rather than only a pure polyelectrolyte is used.

PECs formed as a result of interactions between oppositely charged macromolecules play also an important role for stabilization or destabilization of colloidal dispersions. Using a combination of polyelectrolytes that differ in their macromolecular masses or in their charge densities, an effective solid-liquid separation was demonstrated (Refs. 5-7). A flocculation of colloidal alumina in the presence of a mixture of oppositely charged macromolecules is considered in Ref. 8. It is surprising that only a few studies (Refs. 9, 10) have been devoted to investigations on the application of previously formed PECs as polymeric flocculants. It is important to note that the colloidal stability of dispersions can be either enhanced or reduced in dependence on the properties of PECs.

Low-molecular-mass salts exhibit a strong influence on the properties of PECs as demonstrated in Refs. 11-13. However, the effect of low-molecular-mass salts on the abilities of PECs to modify surfaces of colloidal particles and to be flocculants of their dispersions has not been studied yet in detail.

In this work, our first results on the effect of a low-molecular mass salt on the properties of PECs formed in salt containing non-stoichiometric mixtures of oppositely charged polyelectrolytes are presented. In particular, our main purpose has been to find how the abilities of such PECs to modify surfaces of silica particles and to be flocculants of their dispersions depends on the salt concentration and chemical nature of used polyelectrolytes.

EXPERIMENTAL PART

Materials

Poly(diallyldimethylammonium chloride) **(PDADMAC)** with $M_W \approx 580\ 000$ g/mol ($M_W/M_n \approx 1.6$) synthesized and characterized by Dr. W.Jaeger (Fraunhofer Institut für Angewandte Polymerforschung, Teltow, Germany) was used as a cationic polyelectrolyte.

Copolymers of maleic acid with propylene **(P(MS-P))**, and α-methylstyrene **(P(MS-α-MeSty))** were used as anionic polyelectrolytes. They were prepared by a basic hydrolysis of corresponding anhydrides with a solution of NaOH. These anhydrides with $M_W \approx 50\ 000$ g/mol (P(MS-P)) and $M_W \approx 24\ 000$ g/mol (P(MS-α-MeSty)) were obtained from Leuna AG (Germany). Because a degree of dissociation of the carboxylic groups is pH-dependent, P(MS-P)) and (P(MS-α-MeSty) are considered as weak polyelectrolytes.

Cristobalit quartz powder *Silmikron* with the average size of particles 3 µm and a BET surface area ≈16 m^2/g was purchased from Quarzwerke GmbH (Frechen, Germany). To prepare a silica dispersion, 10 g of Silmikron was dispersed in 500 mL of water by ultrasonification for 15 min. After standing of such dispersions for about a day in order to let heavy particles to settle down, modification and flocculation tests were carried out.

NaCl was used as the low-molecular-mass salt.

The water deionized and purified by a Milli-Q reagent grade water system (Millipore GmbH, Eschborn, Germany) was used as a solvent.

The concentrations of charged groups of the polyelectrolytes in their stock solutions determined by polyelectrolyte titration were the same and equal to 0.005 basemol/L. The pH-values of stock solutions of polyelectrolytes were about 7.5.

Methods

Turbidity was measured by a LS-50 spectrofluoremeter (Perkin Elmer Ltd., UK) at the wavelength 625 nm as the intensity of light scattered at 90°.

Quasi-elastic light scattering by a Zeta Master S (Malvern Instruments Ltd., UK) was carried out to determine z-average diffusion coefficient of particles and to calculate their *z*-average hydrodynamic radius.

Laser microelectrophoresis by a Zeta Master S (Malvern Instruments Ltd., UK) was carried out to determine electrophoretic mobility of particles and to calculate their zeta-potential.

Polyelectrolyte titration allowing the determination of the amount of charges in a system was carried out by a particle charge detector PCD 02 (Mütek GmbH, Germany).

All measurements were made at room temperature.

Preparation of interpolyelectrolyte complexes

To prepare PECs, salt containing solutions of the oppositely charged polyelectrolytes were directly mixed each other under continuous stirring. In our experiments, the constant amount of polycationic charges ($n_+ = 0.1$ mmol) was used. A desired amount of a solution of the anionic polyelectrolyte was slowly added to a continuously stirred solution of the cationic polyelectrolyte. By changing the molar ratio between anionic and cationic charges (n_-/n_+) in the mixtures of oppositely charged polyelectrolytes or by the variation in the NaCl concentration up to 1.0 mol/L, PECs whose particles differed in their charges characterized by values of zeta-potential and their sizes characterized by values of *z*-average hydrodynamic radius were prepared.

All measurements, modification and flocculation tests were carried out 15-30 min after salt containing solutions of the oppositely charged polyelectrolytes were mixed each other.

Modification and flocculation tests

Two different principles of the surface modification of silica particles by PECs, discribed in detail in Ref. 4 have been used :

(i) silica particles were contacted with previously prepared PECs .

For each test, 10 mL of a salt containing silica dispersion (the solid content was 0.1 g) were added to 40 mL of a mixture of oppositely charged polyelectrolytes with the same salt concentration for 15 min under continious stirring.

(ii) silica particles were contacted with cationic polyelectrolyte at first and then anionic polyelectrolyte was added.

For each test, 10 mL of a salt containing silica dispersion (the solid content was 0.1 g, the NaCl concentration was 0.1 M) were added to 20 mL of a solution of the cationic polyelectrolyte with the same salt concentration. Then after 5 min of stirring , 20 mL of a solution of the anionic polyelectrolyte also with the same salt concentration were added.

Dispersions of modified silica were transferred into 50 mL graduated cylinders for settling measurements under static conditions. After 10 min, 5 mL were taken from the supernatant at the position of 2 cm under the liquid-air surface to determine turbidity of the supernatant.

The modified silica particles were separated by centrifugation at 5 000 rpm for 10 min. Then, they were washed, dried at room temperature, and redispersed in a 0.001 mol/L solution of KCl to carry polyelectrolyte titration out.

The polarity of a PCD signal corresponds to the sign of the surface charge. However, for the quantitative determination of the surface charge a polyelectrolyte titration is necessary to be done. The specific surface charge q (C/g) can calculated from the consumption of a titrant according to Eq. (1).

$$q = \frac{V \cdot c \cdot F}{m} \tag{1}$$

where V is the consumption of a titrant (mL), c is the concentration of a titrant (base mol/L), F is the Faraday constant (C/mol), and m is the mass of the sample (g).

RESULTS AND DISCUSSION

Formation and characterization of interpolyelectrolyte complexes

Depending on the salt concentration, salt containing non-stoichiometric mixtures of the oppositely charged polyelectrolytes was observed to be

- relatively stable (at least for a few days) dispersions whose turbidity is nearly independent of time (low salt concentrations),
- unstable dispersions whose turbidity decreases with time due to precipitation of a product of interpolyelectrolyte complexation (moderate salt concentrations),
- transparent solutions, no formation of precipitate is observed when the salt concentration exceeds a certain „critical“ value (high salt concentrations).

The dependences of turbidity (measured as the intensity of light scattered at 90°) on the salt concentration for mixtures of PDADMAC and P(MS-P) or P(MS-α-MeSty) are given in Fig.1.

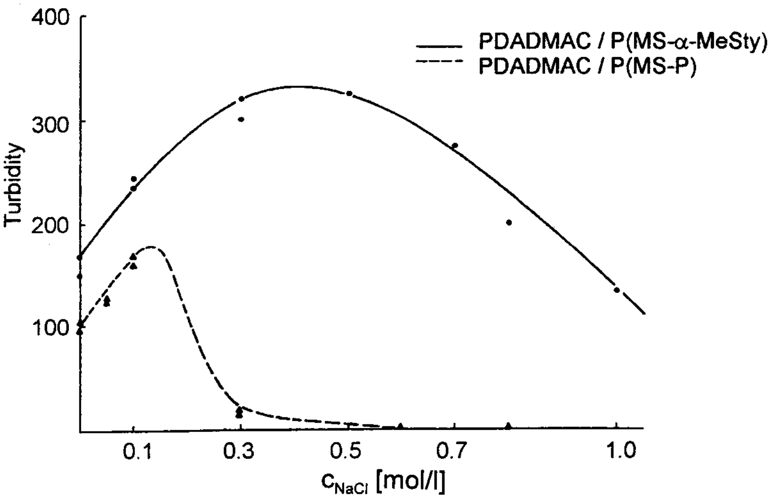

Fig. 1. Turbidity of non-stoichiometric mixtures ($n_-/n_+ = 0.3$) of PDADMAC and P(MS-P) or P(MS-α-MeSty) as a function of the NaCl concentration. The concentration of PDADMAC is 0.002 basemol/L.

Precipitation of PECs formed due to interactions between PDADMAC and P(MS-P) or P(MS-α-MeSty) was observed to begin at ≈ 0.3 mol/L NaCl in the case of P(MS-P) and ≈ 0.6 mol/L NaCl in the case of P(MS-α-MeSty).

The dependences of *z*-average hydrodynamic radius and zeta-potential of particles formed due to interpolyelectrolyte complexation between PDADMAC and P(MS-P) or P(MS-α-MeSty) at low salt concentrations are shown in Fig. 2 and in Fig. 3 respectively.

These results evidence that stable dispersions prepared at low salt concentrations contain positively charged particles whose *z*-average hydrodynamic radius is in the range of a few hundreds nm. Relatively large size of these particles that significantly exceeds sizes of individual chains of the used polyelectrolytes indicates that they are aggregates of a plenty of macromolecules. Such positively charged aggregates are considered to be particles of non-stoichiometric interpolyelectrolyte complex that incorporates charged groups of the polycationic components in an excess as compared to charged groups of the polyanionic component.

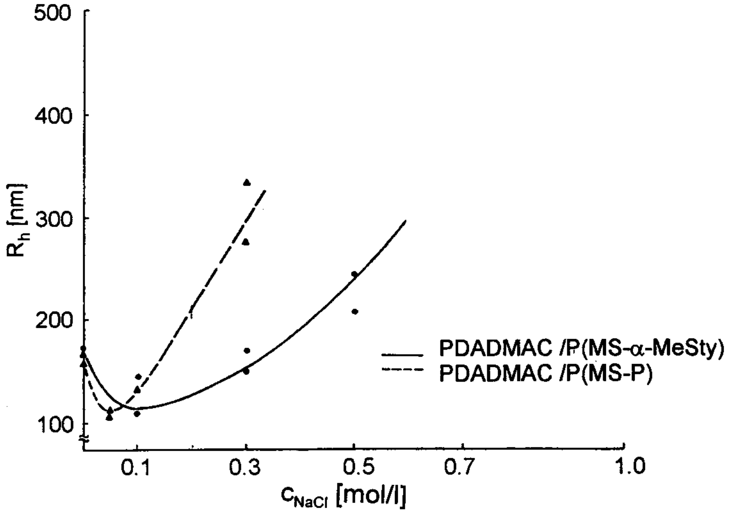

Fig. 2. *Z*-average hydrodynamic radius of particles formed in salt containing non-stoichiometric mixtures ($n_-/n_+ = 0.3$) of PDADMAC and P(MS-P) or P(MS-α-MeSty) as a function of the NaCl concentration. The concentration of PDADMAC is 0.002 basemol/L.

A progressive increase in size and a concomitant decrease in the charge of particles of PECs are supposed to promote precipitation of the products of interpolyelectrolyte complexation observed at moderate salt concentrations.

A formation of transparent solutions at hight salt concentrations is related to the dissociation of interpolymer salt bonds formed by oppositely charged macromolecules because of binding of counterions with charged groups of corresponding polyions incorporated into PECs.

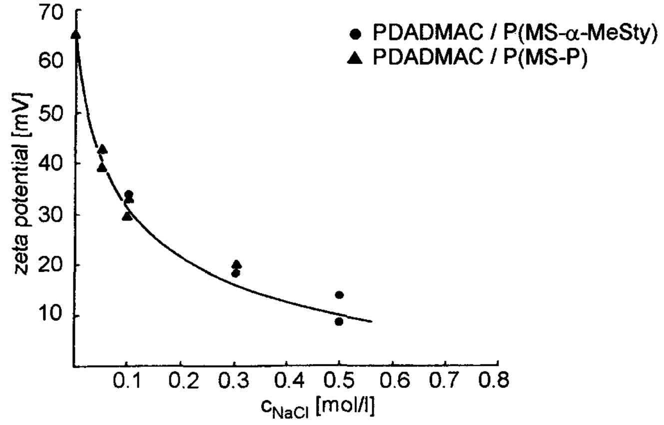

Fig. 3. Zeta-potential of particles formed in salt containing non-stoichiometric mixtures ($n_-/n_+ = 0.3$) of PDADMAC and P(MS-P) or P(MS-α-MeSty) as a function of the NaCl concentration. The concentration of PDADMAC is 0.002 basemol/L.

The „critical" value of the salt concentration was found to be ≈ 0.5 mol/L NaCl in the case of P(MS-P) and > 1 mol/L NaCl in the case of P(MS-α-MeSty). This tendency can be attributed to the stabilisation of PECs (in relation to the dissociation of interpolymer salt bons) due to possible hydrophobic interactions that can be superimposed on the electrostatic attraction between oppositely charged macromolecules and can modify it.

Modification of silica by pure polycation

Polycation adsorption on silica was estimated by determining its depletion from the solution. The samples were treated in a fashion similar to that used for the modification and flocculation tests.

In Fig. 4 the data for PDADMAC adsorption at pH = 7.5 as a function of the ionic strength are presented.

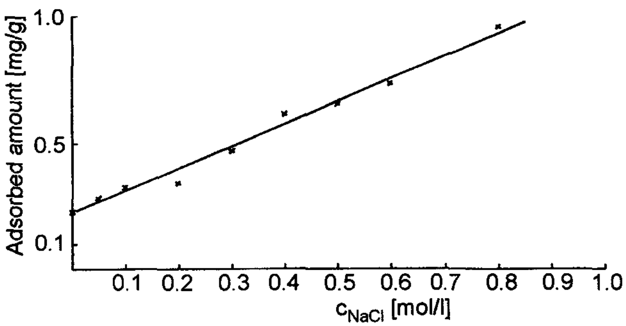

Fig.4. Adsorbed amounts of PDADMAC as a function of the salt concentration at pH = 7.5. The concentration of PDADMAC is 0.002 basemol/L.

From the results it can be concluded that at low salt concentrations the polymer molecules assume a flat conformation at the surface because of the mutual repulsion of the segment charges. The adsorbed amounts are dominated by electrostatic interactions between the polyelectrolyte and the surface. With increasing salt concentration the electrostatic contributions are screened. Loops and tails are formed leading to an increase of the adsorbed amount. In this case the adsorption becomes influenced by the chemical interaction between the surface groups and the adsorbing polymer segments in contrast to pure electrosorption. An experimental evidence for this explanation is given in Ref.15. It could be shown that at high salt concentration the hydrodynamic thickness of the adsorbed layer rises with the molar mass of the PDADMAC.

Modification of silica by previously formed interpolyelectrolyte complexes

In these experiments, we studied how the salt concentration and chemical nature of polyanion influence the ability of PECs to be flocculants of silica dispersions. The ratio between concentrations of oppositely charged groups of the polyelectrolyte components was kept constant and equal to 0.3 ($n_-/n_+ = 0.3$).

To obtain a reference for the flocculation ability of PECs, a flocculation of silica by pure PDADMAC of the same concentration was examined.

The dependences of turbidity of silica dispersions in the presence of pure PDADMAC, PEC formed in salt containing non-stoichiometric mixtures of PDADMAC and P(MS-P) or P(MS-α-MeSty) on the salt concentration are given in Fig. 5.

As is seen, no significant flocculation is observed in the presence of pure PDADMAC and silica dispersions are stable at all salt concentrations studied. At the same time, an efficiency of flocculation of silica dispersions in the presence of PECs depends on the salt concentration. At low salt concentrations, no significant flocculation is observed as in the case of pure PDADMAC and silica dispersions are stable. However, flocculation of silica dispersions becomes to be more and more pronounced with increasing salt concentration. It is noteworthy that the flocculation optima were found to be in the range of moderate salt concentrations where precipitation of the products of interpolyelectrolyte complexation is observed. At high salt concentrations, a partial restabilisation of silica dispersions was observed.

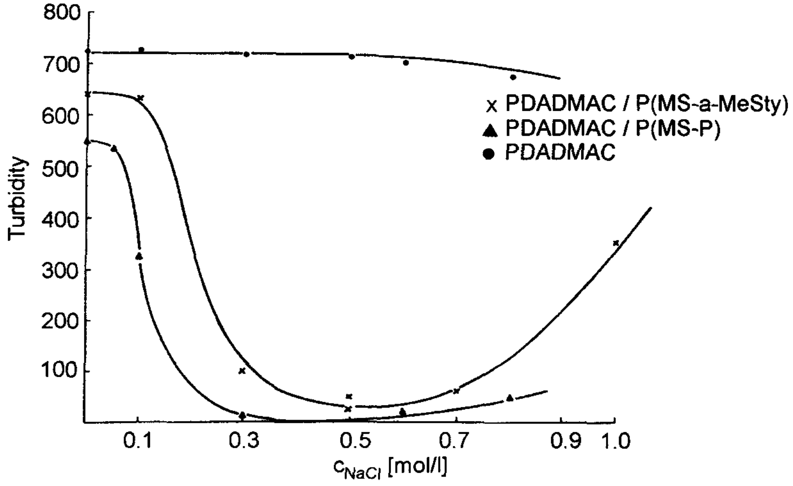

Fig. 5. Turbidity of silica dispersions in the presence of PDADMAC, PEC formed due to interactions of PDADMAC with P(MS-P), and PEC formed due to interactions of PDADMAC with P(MS-α-MeSty) as a function of the NaCl concentration. The concentration of PDADMAC is 0.002 basemol/L.

Observed in our experiments effective flocculation of silica dispersions can be associated to the formation of layers formed by aggregates of oppositely charged macromolecules between silica particles. In other words, PEC acts as a binder of dispersed silica particles and provides the formation of flocs. The ability of PECs to play role of effective binders for various dispersed systems such as soils, sands, etc. is considered and discussed in Ref. 14 in detail.

The formation of such layers seems to be unfavorable at low salt concentrations where particles of PECs bear a significant excessive cationic charge. The electrostatic repulsion between similarly charged layers of PECs adsorbed onto surfaces of silica particles is thought to prevent the formation of flocs and to be responsible for the colloidal stability of silica dispersions. With increasing salt concentration, a charge of particles of PECs decreases and the formation of layers formed by aggregates of oppositely charged macromolecules between silica particles is assumed to become to be a favorable process.

However, additional experimens should be done to understand the mechanism of the flocculation of silica dispersions by previously formed PECs.

In Tab. 1, the values of specific surface charge of modified silica particles separated from salt containing dispersions with various salt concentrations, washed, dried, and redispersed in 0.001 mol/L solution of KCl are shown. These results evidence that the efficiency of the surface modification expressed in terms of the amount of PDADMAC incorporated into PEC that is adsorbed onto surfaces of silica particles increases with increasing salt concentration. It is important that the corresponding values of specific surface charge for silica particles modified by pure PDADMAC in the presence of the salt are much more less that the corresponding values obtained for those modified by previously formed PECs.

Tab. 1. Specific surface charge of complex modified silica [1)]

Salt con. mol/L	PDADMAC C/g	PDADMAC / P(MS-P) C/g	PDADMAC / P(MS-α- MeSty) C/g
0.0	+ 0.05	- 0.1	- 0.04
0.3	+ 0.15	+ 2.2	+ 1.80
0.6	+ 0.38	+ 2.4	+ 2.70

[1)] Detected by a particle charge detector after washing, drying and redispersing in 0.001 mol/L KCl.

Modification of silica by interactions of polycation previously adsorbed onto silica surface with polyanion in a mixed solution

In these experiments, we changed the molar ratio n_-/n_+ in the mixtures of oppositely charged polyelectrolytes whereas the salt concentration was constant and equal to 0.1 mol/L. The results obtained for salt containing mixtures of PDADMAC and P(MS-P) or P(MS-α-MeSty) are shown in Fig. 6 and Fig. 7 respectively.

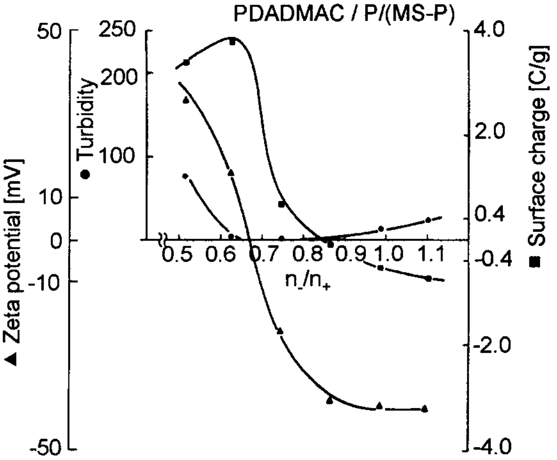

Fig. 6. Turbidity of silica dispersions (●) in the presence of the mixtures of PDADMAC and P(MS-P), zeta-potential of particles of PECs (▲) formed in the mixtures of PDADMAC and P(MS-P), and specific surface charge of modified silica particles (■) that were washed, dried, and redispersed in 0.001 mol/L solution of KCl as functions of the molar ratio n_-/n_+ (inital concentration of PDADMAC = 0.002 basemol/L, [NaCl] = 0.1 mol/L).

The optima of flocculation were reached at the molar ratio $n_-/n_+ \approx 0.7$ for P(MS-P) or $n_-/n_+ \approx 0.6$ for P(MS-α-MeSty). It is noteworthy that the formation of nearly uncharged particles of PECs takes place at these ratios.

It is important that the molar ratio n_-/n_+ at which the formation of nearly uncharged particles of PECs was observed is shifted to lower values of n_-/n_+ as compared to salt free mixtures of the corresponding oppositely charged polyelectrolytes (Ref. 4): $n_-/n_+ \approx 1.1$ for P(MS-P) and $n_-/n_+ \approx 0.75$ for P(MS-α-MeSty) in the absence of a salt. This effect can be related to the screening effect of low-molecular-mass counterions.

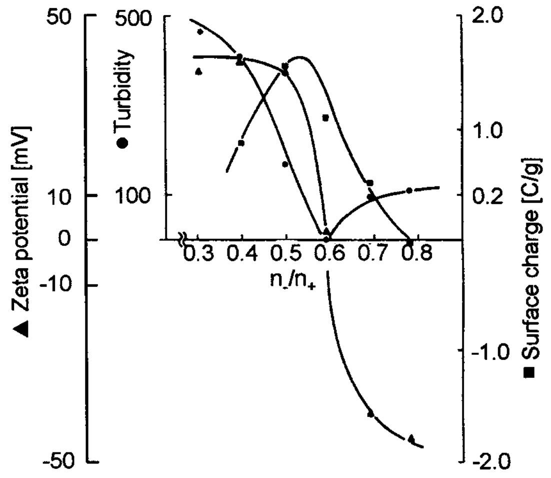

Fig. 7. Turbidity of silica dispersions (●) in the presence of the mixtures of PDADMAC and P(MS-α-MeSty), zeta-potential of PEC particles (▲) formed in the mixtures of PDADMAC and P(MS-α-MeSty), and specific surface charge of modified silica particles (■) that were washed, dried, and redispersed in 0.001 mol/L solution of KCl as functions of the molar ratio n_-/n_+ (inital concentration of PDADMAC = 0.002 basemol/L, [NaCl] = 0.1 mol/L).

For both anionic polyelectrolytes used in a combination with PDADMAC, a significant increase in the values of specific surface charge of the modified silica particles that were washed, dried, and redispersed in the 0.001 mol/L solution of KCl was observed at the ratios n_-/n_+ at which the optima of flocculation were reached.

The dependences of the flocculation efficiency on the molar ratio n_-/n_+ can be also explained if one takes into account the considerations discussed above. Indeed, the ability of used PECs to be flocculants of silica dispersions appears to increase with decreasing charge of aggregates of oppositely charged macromolecules. Since the charge of particles of PECs can be varied by changing the molar ratio n_-/n_+, the observed improvement of fllocculation with increasing n_-/n_+ is reasonable.

CONCLUSIONS

Obtained results demonstrate that in dependence on the salt concentration PECs previously formed in salt containing mixtures of oppositely charged polyelectrolytes can be successfully used both to stabilize and destabilize silica dispersions. The flocculation ability of PECs and the efficiency of the surface modification of silica particles by PECs are influenced by the salt concentration and chemical nature of polyelectrolytes. The optimum of flocculation was found to be in the range of the salt concentrations in which the formation of large aggregates of PECs and their precipitation take place. PECs are supposed to act as binders of silica particles and to promote the formation of flocs. The possibility to obtain a high positive charge onto surfaces of silica particles (after their separation, washing, and drying) modified by PECs previously formed in salt containing mixtures of oppositely charged polyelectrolytes was demonstrated.

By the simultaneous complexation of the oppositely charged polyelectrolytes in the bulk solution and at the silica surface, the influence of the salt on the colloidal stability of silica dispersions was examined. The molar ratios n_-/n_+ between concentrations of charged groups of anionic and cationic polyelectrolytes at which the flocculation optima observed were found to decrease with increasing salt concentration and to depend on chemical nature of used polyelectrolytes. A significant increase in a cationic surface charge of the modified silica particles was detected for the ratios n_-/n_+ at which the flocculation optima are reached.

ACKNOWLEDGEMENT

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