The effect of binary mixtures of cationic and anionic polyelectrolytes (PE) on the electrokinetic potential of monodisperse carboxylated polystyrene (PS) particles as a function of the mixture dose, its composition and way of adding the polymers to the suspension has been studied in mixtures of cationic and anionic PE, the ζ-potential of particles is determined by the adsorbed amount of the anionic polymer independently of the charge density of polyelectrolytes, the ratio between positively and negatively charged segments and the sequence of addition of the mixture components. It has been shown that the isoelectric point of the surface is reached at the adsorbed amount of positive charges that is only a small fraction of the “total” surface charge density. The laws observed were explained by features of macromolecules conformation in adsorbed mixed polyelectrolyte layers.

**Keywords:** polystyrene, particles, suspension, anionic and cationic polyelectrolytes, mixture, electrokinetic potential, isoelectric point, polyelectrolyte layers, conformation.

**Introduction**

Polymers are widely used as flocculants for suspensions in many industrial applications, such as mineral processing, papermaking, water treatment and biotechnology. In recent years there has been considerable interest in the use of multi-component flocculants, especially dual-polymer systems. In the latter case, there can be significant advantages over the use of single polymers. The effect of non-ionic polymer mixtures on flocculation of hydrophobic sols has been studied in detail by Csempesz et al. [1, 2]. A short review on the issue is given in our recent papers [3-5].

The effect of polymers on colloidal stability is mainly due to adsorption of macromolecules onto the particles surface and the structure of adsorbed layers formed [6-8]. Electrokinetic measurements are a powerful tool to investigate the structure of interfacial polymer layers [9-11]. At low ionic strength, formation of fairly thick hydrodynamically impermeable adsorbed layers of non-ionic polymers shifts the slip plane further out into the bulk liquid phase, which causes a decrease in zeta-potential and hence a reduction in the electrical repulsion forces between particles with adsorbed polymer. However, such adsorbed layers can also
give appreciable steric repulsion [6, 7, 12], which would often outweigh the electrokinetic effect. From the difference between electrokinetic potentials of bare particles and those with adsorbed nonionic polymer, the ‘electrophoretic’ thickness of the adsorbed layer can be evaluated.

It is also well known that addition of oppositely charged polyelectrolytes to a colloidal dispersion usually leads to a significant decrease in the $\zeta$-potential and to a change in the sign of the particle charge, which is accompanied by destabilization of the system. Adsorption of polyelectrolytes bearing charges of the same sign as the particles is responsible for the increase in the electrokinetic potential and stability of dispersions[11, 12]. So, electrokinetic data provide valuable information about the effect of adsorbed polymers on the parameters of the electrical double layer and mechanisms of destabilization of colloids by polymers.

Suspension of polystyrene latex particles is an excellent model system to study the effect of polymer mixtures adsorption on the electrokinetic potential and mechanism of flocculation of dispersions. In this paper, the results on the electrokinetic measurements of monodisperse carboxylated polystyrene particles in solution of cationic and anionic polyelectrolytes of different charge density and their binary mixtures of different composition are presented.

1. Materials and methods

Monodisperse carboxylated polystyrene (PS) particles with 4.2 $\mu$m in diameter were synthesized as described in paper [13]. The sample was kindly provided by Prof. A. Menshikova, Institute of Macromolecular Compounds, Saint-Petersburg, Russia. The particles surface contains polyvinyl pyrrolidone (PVP) grafted by PS chains, which anchored in PS matrix. Commonly, surface concentration of carboxylic groups originated from the initiator (4,4'-azobis, 4-cyanoisovaleric acid) for such samples reaches about $2\times10^{-6}$ mol/m$^2$. The surface charge density determined by conductometric titration for our sample was $0.9\times10^{-6}$ mol/m$^2$ (repeated twice). This smaller value in comparison with $2\times10^{-6}$ mol/m$^2$ might be a result of storage of the microspheres in pure water, when some carboxylic groups could migrate into particle volume. The calculated specific surface area of particles was $S=65$ m$^2$.g$^{-1}$.

As high-molecular substances SNF FO type cationic polyelectrolytes, and SNF AN grade anionic polyelectrolytes of different charge density (CD) produced by SNF A.S., France, have been used. Stock solutions of polymers with concentration 0.5 g/l have been prepared, then working solutions of designated concentration (typically 0.1-0.05 g/l) were prepared by dilution. The latter were used within 5 days after dilution of stock solutions. Preliminary tests showed that within this period of time the viscosity of polymer solutions remained practically constant.
Characteristics of the polyelectrolytes applied are presented in Table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>MW/10⁶</th>
<th>Charge density (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNF FO 4125 SH</td>
<td>Cationic</td>
<td>6–7</td>
<td>6</td>
</tr>
<tr>
<td>SNF FO 4400 SH</td>
<td>Cationic</td>
<td>6–7</td>
<td>30</td>
</tr>
<tr>
<td>SNF AN 905 SH</td>
<td>Anionic</td>
<td>8–9</td>
<td>5</td>
</tr>
<tr>
<td>SNF AN 956 SH</td>
<td>Anionic</td>
<td>8–9</td>
<td>50</td>
</tr>
</tbody>
</table>

The electrokinetic potential of particles was measured using ZetaPlus, Brookhaven Inc. instrument. Determination of the electrophoretic mobility in this instrument is based on the Doppler-effect. The program used in this instrument converts the electrophoretic mobility of particles into electrokinetic potential using the classical Smoluchowsky formula. This procedure is acceptable for our systems with relatively big particles as the criterion $\text{Rel} (\text{or } Du)= \exp[(\psi_1/2-1)/\kappa a]$ in our experiments was much less than unity (where $\psi_1$ is the Stern potential, $\kappa$ is the reciprocal Debye length and $a$ is the particle radius, the magnitude of the initial $\zeta$-potential was taken for $\psi_1$). As shown by Dukhin [14], the magnitude of $\text{Rel} (\text{or } Du)$ characterizes the contribution of the electric double layer polarization to the electrosurface phenomena and this contribution can be neglected for $\text{Rel}<<1$. The values of $\zeta$ indicated below typically represent an average from five individual measurements.

2. Effect of individual polyelectrolytes

As a first stage, for comparison reasons, we have investigated the effect of individual polyelectrolytes on the electrokinetic potential of particles under study.

The effect of weakly charged FO 4125 and medium charged FO 4400 cationic polyelectrolytes on the electrokinetic potential of PS particles is demonstrated by curves 1, 2 on Fig. 1. As expected, addition of oppositely charged polyelectrolytes to the suspension results in a significant decrease in the $\zeta$-potential and to a change in the sign of the charge of particles. Changes in the $\zeta$-potential are more pronounced for the sample with higher CD, the rise in $\zeta$ before and after the isoelectric point (iep) is much steeper and the final positive value reached in this case is +40 mV, while for weakly charged sample the maximum positive zeta-potential reached is only about +7-8 mV. This is
obviously due to accumulation of higher amount of cationic charges in the Stern layer in the first case. Similar behaviour we observed for kaolin and bentonite particles having adsorbed cationic polymers of different charge density [3, 15]. It is interesting to note that there is a good correlation between the charge densities of the cationic PE (30 % for FO 4400 and 6% for FO 4125) and its amount (0.6 mg/g and 3 mg/g, correspondingly) at which the iep is observed. A five-fold decrease in the CD of the polymer results in a five-fold increase of the PE amount that is necessary to add to reach the iep of particles. This is an evidence of the important role of electrostatic factor in cationic PE adsorption and its effect on the electrical double layer structure of PS particles.

Addition of anionic polyelectrolytes in amount of 0.5–5.0 mg/g gives an approximately 1.5-2.0-fold rise of the $\zeta$-potential of PS particles, from -18 mV to about -22 mV and -30 mV for weakly and highly charged samples, respectively (curves 3, 4 on Fig. 1). Adsorption of anionic polymers on the PS surfaces is mainly due to hydrophobic interactions between hydrocarbon parts of the repeated units and the surface (see below).

![Fig.1. Dependence of the electrokinetic potential of polystyrene particles on the added amount of FO 4400 (1) and FO 4125 (2) cationic polymer, AN 956 (3) and AN 905 (4) anionic polymer](image)

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3. Effect of cationic and anionic polyelectrolyte mixtures

Figure 2 shows the variation of the $\zeta$-potential of PS particles at different modes of addition of the polyelectrolyte mixture components to the suspension: 1. pre-adsorption of increasing amount of medium charged FO 4400 cationic PE (contact time 1 h), then addition of 2 mg/g of weakly charged AN 905 anionic PE to the samples, and 30 min later measurements of the zeta-potential; 2. vice versa, addition of permanent amount (2 mg/g) of cationic polymer to particles 1 h after their contact with increasing amount of anionic polyelectrolyte, and 3. simultaneous addition of increasing amount of a 1:1 mixture of FO 4400 cationic and AN 905 anionic polyelectrolytes. The following features should be stressed. In mixtures of anionic and cationic polyelectrolytes of different composition, of different ratios between positive and negative charges and different ways of components addition, the particles always acquire negative zeta-potential. In mixtures of middle charged cationic and weakly charged anionic polyelectrolytes, the dependence of $\zeta$-potential on the amount of added mixture goes through a maximum at low polymer contents. This can be explained by partial neutralization of negative charges of the anionic PE by the adsorbed cationic segments which results in a decrease in the absolute (negative) zeta-potential values. For example, minimal $|\zeta|$-potential (-8 mV) is observed at cationic/anionic segments ratio of 3:1 if we adsorb anionic polymer onto particles pre-treated with cationic PE (1 mg/g of FO 4400 cationic PE with CD 30% and 2 mg of AN 905 anionic PE with CD 5%, see curve 1 on Fig.2). In the event of addition first the anionic polymer, then the cationic one (curve 2) or simultaneous addition of the mixture components (curve 3), the minimum value of $|\zeta|$ is observed at ratio of positive/negative charges 6:1 and 12:1, correspondingly.

Fig.3 demonstrates the effect of a strongly charged anionic/weakly charged cationic polyelectrolyte mixture on the electrokinetic potential of PS particles at different sequences of components addition to the suspension (the same as described above). Despite the apparent differences between Figs. 2 and 3, the main feature of behaviour of mixed polyelectrolytes layer on the surface is the same as described above: namely, $\zeta$-potential of particles is always negative, independently of the ratio between positive and negative segments and the sequence of addition of the mixture components. This system is characterized by domination of the effect of the anionic polyelectrolyte on $\zeta$, and the observed changes in the $\zeta$-potential are less pronounced. For example, in the presence of increasing amount of 1:1 (by mass) mixture of AN 956 anionic and FO 4125 cationic polyelectrolyte, there is practically no change in the negative value of the zeta-potential (cca –16 - 18 mV), see curve 1 on Fig.3. Similarly, adding 2 mg/g of the cationic PE to samples pre-treated with increasing amount of
strongly charged anionic polymer, results only in a slight decrease in the electrokinetic potential of particles (curve 2). Pre-adsorption of increasing amount of weakly charged cationic PE has an insufficient influence on the ζ-potential of particles having adsorbed 30 min later 2 mg/g of AN 956 anionic polyelectrolyte (compare curve 4 on Fig.1 and curve 3 on Fig. 3).

*Fig. 2.* Dependence of the electrokinetic potential of polystyrene particles on the added amount of medium charged FO 4400 cationic and weakly charged AN 905 anionic polymer mixtures at different sequences of addition of the mixture components: 1. pre-adsorption of increasing amount of the cationic PE (contact time 1 h), then addition of 2 mg/g of the anionic PE; 2. addition of permanent amount (2 mg/g) of cationic polymer to particles 1 h after their contact with increasing amount of anionic polyelectrolyte, and 3. simultaneous addition of increasing amount of a 1:1 (by mass) mixture of cationic and anionic polyelectrolytes

Summarising the above described results, one can say that the electrokinetic potential of polystyrene particles in anionic/cationic polyelectrolyte mixtures is mainly determined by the adsorbed amount of the anionic PE independently of the mixture composition, ratio of positive/negative charges in the mixed adsorbed layers and the sequence of the mixture components addition to the suspension.
Fig. 3. Dependence of the electrokinetic potential of polystyrene particles on the added amount of weakly charged FO 4125 cationic and strongly charged AN 956 anionic polymer mixtures at different sequences of addition of the mixture components (the same as described on the legend to Fig. 2.).

4. Discussion

There are several mechanisms of polyelectrolytes adsorption onto surfaces of dispersed particles and its effect on the electrical double layer structure. Interactions that may be responsible for attachment of polymer segments to surfaces are:

 Electrostatic. Polyelectrolytes will always adsorb on surfaces of opposite charge, simply because of electrostatic attraction. This gives very high adsorption affinity and can lead to an adsorbed configuration that is considerably ‘flatter’ than that typical for non-ionic polymers (“trains”, long loops and tails [9]).

 Hydrogen bonding. Polymers such as polyacrylamide (PAM) [16] and polyethylene oxide (PEO) [17] can adsorb on surfaces with suitable H-bonding sites (e.g. silanol groups on silica), since these can form bonds with the amide groups of PAM and the ether oxygens of PEO [17].

 Hydrophobic interaction. This is responsible for the adsorption of non-polar segments of polymer chains on hydrophobic surfaces, as in the case of polyvinyl alcohol on silver iodide [18] or adsorption of modified PAM on gold substrates with different degrees of hydrophobicity [19].

 Ion binding. With anionic polyelectrolytes and negative surfaces, electrical repulsion may prevent adsorption in some cases. It is often found that a certain
salt concentration is needed to promote adsorption (and flocculation). Salts with divalent cations such as calcium and magnesium are especially effective. These are known to bind quite strongly to carboxylate groups and may serve as links between these groups and negative sites on a particle surface [20].

We can suppose that the negative segments of anionic polyelectrolytes interact with the surface mainly due to hydrophobic interactions and H-bonds formation between the surface -COOH and functional groups of the polymer. This results in formation of long loops and tails of adsorbed macromolecules because of the small number of contacts of the chain to the surface. At the same time cationic polyelectrolytes, due to electroadsorption of positive segments on numerous negative sites, form an adsorbed layer with big number of contacts to the surface. The thickness of this layer is less than that for anionic polyelectrolytes but it is thick enough to separate a considerable amount of positively charged segments from the surface. This conclusion can be deducted from the comparison of the number of surface charged group and the total charge of cationic segments adsorbed. The surface charge density of PS particles is 0.9x10⁻⁶ mol.m⁻², i.e. (xS=65 m².g⁻¹) 5.8x10⁻⁵ mol.g⁻¹. The molar concentration of positive segments on the surface at the iep for FO 4125 polymer is 3x10⁻³ g.g⁻¹ (the adsorbed amount) x 6x10⁶ (M of the PE)/6x10⁶ x 226 (M of the repeated unit) =1.3x10⁻⁵ mol.g⁻¹. The CD of this sample =6%, i.e. we have at the iep on the surface 1.3x10⁻⁵ x 0.06=8x10⁻⁷ mol/g positive charges. The same results we obtain for FO 4400 polymer with CD=30 % and adsorption of 0.6 mg.g⁻¹ at the iep. It means that the isoelectric point of PS particles is reached at almost two orders of magnitude less amount of added positive charges (8x10⁻⁷ mol/g) than the “total” (negative) surface charge density (5.8x10⁻⁵ mol.g⁻¹). Similar relationships we have found in the case of adsorption of cationic polyelectrolytes of different CD onto clay mineral particles surface [15]. At the same time we have to keep in mind that for surfaces and (weak) polyelectrolytes with pH-dependent charge, the situation is more complicated. The feature of weak surface/PE functional groups is that their charge is a function of the local pH which, close to the surface, is different from that in the bulk solution [9]. Carboxylic groups on the PS surface, having dissociation constant in the form of acidic acid 1.75x10⁻⁵, at neutral pH values are in ionic form probably less than 1 %. We do not know how the dissociation of the carboxylic groups is changed on the surface as a result of adsorption of trimethyl ammonium groups of the cationic polymer. Typically, the dissociation of polyelectrolytes on an oppositely charged surface is higher than that in the bulk and this can be applied also to the surface functional groups [9]. It might be that the real surface charge is low enough to be fully compensated by charges of the adsorbed cationic polyelectrolytes. We can state definitely only that at the iep the adsorbed amount of positive charges is only a small fraction of the “total” surface charge density determined by conductometric/potentiometric titration.
The zeta potential of polymer-covered particles is determined by the charge of the peripheral part of the adsorbed layer and not by the charges in the immediate neighborhood to the surface. This shows also that the most of adsorbed cationic polyelectrolyte segments are not connected directly to the surface, i.e. the conformation of the macrochain on the surface is far from the flat.

It is logical to suppose that in the case of polyelectrolyte mixture adsorption, the layer of the cationic polymer will be hidden inside (behind) the much more extended anionic polymer layer. The latter determines the properties of the peripheral part of the adsorbed layers that are responsible for the electrokinetic potential of particles bearing mixed polyelectrolyte layer. This explains our results showing that $\zeta$-potential of PS particles in polymer mixtures depends first of all on the adsorbed amount of anionic polyelectrolyte on the surface.

Acknowledgements

The author cordially thanks Prof. Jiri Skvarla, Technical University of Kosice, for providing the Brookhaven zeta-sizer instrument and useful discussions, as well as L. Marcinova for participation in electrokinetic measurements.

This work was carried out as part of the TÁMOP-4.2.1.B-10/2/KONV-2010-0001 project in the framework of the New Hungarian Development Plan. The realization of this project is supported by the European Union, co-financed by the European Social Fund.

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