Theses of Ph.D. dissertation

THE EFFECT OF ADDITIVES ON THE PHASE PROPERTIES OF OPPOSITELY CHARGED POLYELECTROLYTE/SURFACTANT SYSTEMS

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Budapest, 2011

Introduction and aims of study

Aqueous mixtures of oppositely charged macromolecules and amphiphiles are relevant in numerous industrial applications. Apart from their extensive use as the main ingredients of different cosmetic and domestic products, these systems play an important role in some biotechnological applications (e. g. sewage treatment) as well as gene therapy. Therefore, the understanding of the phase behavior of polyelectrolyte/surfactant (P/S) systems is of paramount importance. However, several contradictory observations hinder the deeper understanding in this field.

For example, although the theoretical and simulation studies consider equilibrium association between the polyelectrolyte and the surfactant, certain P/S systems are frequently observed to be trapped in nonequilibrium states.

It is also not well-understood, how the addition of inert electrolyte affects the association between oppositely charged macromolecules and surfactants. It is well-known that P/S mixtures form two-phase systems in a certain composition range. In some P/S systems precipitation was reported in a wider composition range in the presence of electrolyte. However, in other cases, the addition of electrolyte was found to suppress the precipitation concentration range.

Recently, it has been shown that the nonequilibrium character observed for the mixtures of different cationic polyelectrolytes and sodium dodecyl sulfate (SDS) in a certain composition range is attributable to the formation of electrostatically stabilized colloidal dispersions of these systems.

The colloidal dispersion state of the polycation/SDS mixtures provides several options to manipulate the phase properties of these systems. It has been shown that the solution preparation method, the charge density and concentration of the polyelectrolyte as well as the presence of a nonionic surfactant may influence the width of the kinetically stable composition range of polycation/SDS systems.

In principle, the kinetic stability of P/S dispersions can be enhanced if the adsorption of a suitable neutral polymer sterically stabilizes the dispersion of the P/S nanoparticles. However, the effect of polymer additives on the kinetic stability of P/S dispersions has not been tested yet.

In my thesis, the effect of different additives on the bulk behavior of sodium poly(styrenesulfonate) (PSS)/ hexadecyltrimethylammonium bromide (CTAB) and poly(ethyleneimine) (PEI)/sodium dodecyl sulfate (SDS) systems has been investigated. On one hand, the effect of inert electrolyte (NaCl) on the phase properties of the PSS/CTAB mixtures was studied, and comparisons with the behavior of PEI/SDS systems under the same conditions were made. Furthermore, my aim was to test the validity of the colloidal dispersion concept in the case of the PSS/CTAB system. On the other hand, my motivation was to investigate how the addition of different neutral polymer additives (such as poly(ethylene oxide) (PEO), poly(vinyl pyrrolidone) (PVP), dextran, and the poly(ethylene oxide)-poly(propylene oxide)- poly(ethylene oxide) triblock copolymer (Pluronic F108)) affects the kinetic stability of PEI/SDS dispersions.

Methods

Mixing methods

During my experiments two mixing methods were used (at 25.0 ± 0.5 °C). In the *slow-mixing* protocol, the surfactant solution was added to the polyelectrolyte solution (in equal volume) slowly, drop by drop under continuous stirring. By the application of the *stop-flow-mixing* method the equal volumes of polyelectrolyte and surfactant solutions were mixed within 10 ms using a stop-flow apparatus.

In the case of additives, both the polyelectrolyte and the surfactant solution contained the additive in equal concentrations during the application of *stop-flow-mixing*.

In some experiments the effect of the order of addition of the additive was also tested. In these cases the final composition of the mixtures was attained in two steps. First, the P/S systems were prepared (without additive) by the *slow-mixing* method. After 24 hours, appropriate amount of additive was added to the mixtures under continuous stirring either in a solution (*two-step-mixing-I.*) or in a solid form (*two-step-mixing-II.*)

Methods of characterization

The P/S association was characterized by the mean electrophoretic mobility and the apparent mean hydrodynamic diameter of the formed P/S complexes (via electrophoretic mobility and dynamic light scattering measurements). The aggregation of the P/S nanoparticles was investigated by coagulation kinetics measurements. In the case of PEI/SDS mixtures the changes in the amount of bound surfactant to the polyelectrolyte were monitored by pH measurements. The measurements were carried out at 25.0 ± 0.1 °C.

Results

1. It has been shown that the transparent PSS/CTAB systems are not thermodynamically stable solutions in excess of surfactant (where the amount of surfactant ions considerably exceeds the number of charged polyelectrolyte segments). At high surfactant concentrations electrostatically stabilized colloidal dispersions of the PSS/CTAB nanoparticles are formed due to the adsorption of the surfactant cations on the surface of the PSS/CTAB nanoparticles by making use of the *stop-flow-mixing* protocol. The kinetically stable composition range decreases with increasing PSS concentration. However, the application of *slow-mixing* results in the formation of precipitates in the presence of excess surfactant. In this latter case the slightly charged PSS/CTAB nanoparticles formed in the intermediate stage of the mixing process irreversibly coagulate.

2. The effect of salt on the phase properties of the PSS/CTAB system is twofold. At small and moderate NaCl concentrations the impact of electrolyte is manifested in the reduction of the kinetically stable composition range of the PSS/CTAB dispersions. However, the application of high salt concentrations has an impact on the equilibrium phase properties. Namely, the amount of surfactant bound to the polyelectrolyte decreases in the presence of large NaCl concentrations which results in the formation of thermodynamically stable one-phase systems in the investigated concentration range.

3. It has been shown that at a fixed PEI concentration the kinetic stability of the PEI/SDS dispersions formed in the presence of surfactant excess increases with increasing surfactant concentration (at a fixed ionization degree of PEI) as well as with increasing PEI charge (at a given surfactant activity). These findings can be qualitatively explained by the largely increased surface charge of the PEI/SDS nanoparticles leading to considerably enhanced repulsive forces between the nanoparticles. This effect is superior compared to the variation of the attractive interparticle forces under the same experimental conditions.

4. The kinetic stability of the PEI/SDS dispersions can be enhanced by the addition of a suitable neutral polymer (by making use of the *stop-flow mixing* protocol, provided that the polymer additive/SDS interaction is negligible). At high surface coverage of PEO and PVP thick adsorbed layers are formed on the PEI/SDS nanoparticles, which sterically stabilize the dispersion. The sterically stabilized PEI/SDS dispersions have considerable kinetic stability

even at high ionic strength where precipitation occurs in a wide concentration range of PEI/SDS systems (in the absence of neutral polymer).

5. The applied homopolymer additives have different impact on the kinetic stability of the PEI/SDS dispersions. The addition of high molecular weight PEO in small amount enhances the aggregation of the PEI/SDS nanoparticles. However, at high surface coverage of PEO thick adsorbed polymer layers are formed on the nanoparticles resulting in sterically stabilized dispersions. The steric stabilizing effect of the PVP additive is the most pronounced, and can be observed from lower polymer concentrations compared to PEO. This difference can be explained by the different adsorption affinity and adsorbed layer structure of PEO and PVP on the surface of the PEI/SDS nanoparticles. In contrast, the addition of dextran or low molecular weight PEO do not affect the kinetic stability of the PEI/SDS dispersions because these additives can not form thick adsorbed layers on the nanoparticles.

6. At a given PEI/SDS composition and additive concentration, the adsorption of the PEO and PVP molecules on the surface of the nanoparticles and therefore their stabilizing effect increases with increasing ionization degree of PEI. This can be rationalized by the enhanced adsorption affinity of the polymers to the PEI/SDS nanoparticles which contain larger amount of bound surfactant at high protonation degrees of PEI.

7. It has been shown that among the investigated polymer additives only the amphiphilic Pluronic F108 could prevent the aggregation of the electroneutral complexes of PEI/SDS systems, and therefore completely suppress the precipitation compostiton range (in the absence of electrolyte). This finding is related to the different adsorption kinetics, adsorption affinity and adsorbed layer structure of the investigated uncharged macromolecules. By making use of an appropriate mixing protocol, in the presence of Pluronic F108 the PEI/SDS systems are not thermodynamically stable solutions but sterically stabilized dispersions of the PEI/SDS/F108 nanoparticles (apart from a narrow concentration range at very low surfactant-to-polyelectrolyte ratios).

Possible applications of the results

These results might be exploited at different applications of P/S systems. The observed impact of electrolyte on the P/S association may be used to apply the P/S nanoparticles as carriers of different apolar substances, which can be released by a sudden increase of the electrolyte concentration.

In other applications the P/S dispersions should preserve their kinetic stability even at high salt concentrations. A possible way to achieve this goal is to sterically stabilize the dispersions by the adsorption of a suitable polymer. Thus, the sterically stabilized P/S dispersions maintain their kinetic stability even at high ionic strength. In some processes, the aim is to prevent the aggregation of both the uncharged and charged P/S nanoparticles. This can be achieved by the adsorption of an amphiphilic Pluronic-type triblock copolymer. The sterically stabilized P/S dispersions can be used as drug-delivery systems as well as to enhance the efficiency of different cosmetic products.

Publications on the subject of the dissertation:

1. Amália Mezei, Ágnes Ábrahám, Katalin Pojják and Róbert Mészáros

„*The Impact of Electrolyte on the Aggregation of the Complexes of Hyperbranched Poly(ethyeleneimine) and Sodium Dodecyl Sulfate*"

Langmuir **2009**, *25*, 7304-7312. Impact factor: 3,898
The article is shared with Amália Mezei (25%) and Ágnes Ábrahám (50%).

2. Katalin Pojják and Róbert Mészáros

„*Novel Self-Assemblies of Oppositely Charged Polyelectrolytes and Surfactants in the Presence of Neutral Polymer*"

Langmuir **2009**, *25*, 13336-13339. Impact factor: 3,898

3. Katalin Pojják and Róbert Mészáros

„*Association between Branched Poly(ethyleneimine) and Sodium Dodecyl Sulfate in the Presence of Neutral Polymers*"

J. Coll. Int. Sci. **2011**, *355*, 410-416. Impact factor: 3,066 (2010)

4. Katalin Pojják, Edit Bertalanits and Róbert Mészáros

„Effect of Salt on the Equilibrium and Nonequilibrium Features of Polyelectrolyte/Surfactant Association"

Langmuir **2011**, *27*, 9139-9147. Impact factor: 4,268 (2010)

5. Katalin Pojják and Róbert Mészáros

„Preparation of Stable Electroneutral Nanoparticles of Sodium Dodecyl Sulfate and Branched Poly(ethyleneimine) in the Presence of Pluronic F108 Copolymer"

submitted (*Langmuir*)

Oral presentations on the subject of the dissertation:

1. Katalin Pojják, Edit Bertalanits and Róbert Mészáros

„*Kinetically Stable Colloidal Dispersions of Sodium Poly(styrene-sulfonate)/Alkyl Trymethyl Ammonium Bromide Nanoparticles*"

24th Conference of the European Colloid and Interface Society – COST D43, Prague, September 2010.

2. Katalin Pojják and Róbert Mészáros

"*Association of Oppositely Charged Polyelectrolytes and Surfactants in the Presence of Neutral Polymers*"

24th Conference of the European Colloid and Interface Society, Prague, September 2010.

Posters presentations on the subject of the dissertation:

1. Ágnes Ábrahám, Amália Mezei, Katalin Pojják, Róbert Mészáros

„The Effect of Salt on the Association Between Cationic Polyelectrolytes and Anionic Surfactants"

23rd Conference of the European Colloid and Interface Society, Antalya, September 2009.

2. Katalin Pojják and Róbert Mészáros

„*Effect of Neutral Polymer Additives on the Association between Oppositely Charged Polyelectrolytes and Surfactants*"

57th Sepawa Congress and European Detergents Conference, Fulda, October 2010.

3. Katalin Pojják and Róbert Mészáros

„Self-Assemblies of Oppositely Charged Polyelectrolytes and Surfactants in the Presence of Neutral Amphiphilic Block Copolymers"

25th Conference of the European Colloid and Interface Society, Berlin, September 2011.

Other publications:

1. Amália Mezei, Katalin Pojják and Róbert Mészáros

„*Nonequilibrium Features of the Association between Poly(vinylamine) and Sodium Dodecyl Sulfate: The Validity of the Colloid Dispersion Concept*"

J. Phys. Chem. B **2008**, *112*, 9693-9699. Impact factor: 4,189

2. Mária Darvas, Katalin Pojják, George Horvai, Pál Jedlovszky

„Molecular Dynamics Simulation and Identification of the Truly Interfacial Molecules (ITIM) Analysis of the Liquid-Vapor Interface of Dimethyl Sulfoxide"

J. Chem. Phys. **2010**, *132*, 134701. Impact factor: 2,920

3. Katalin Pojják, Mária Darvas, George Horvai, Pál Jedlovszky

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J. Phys. Chem. C **2010**, *114*, 12207-12220. Impact factor: 4,520

Other poster presentations:

1. Róbert Mészáros, Amália Mezei, Katalin Pojják, Tibor Gilányi

„The Effect of Solution Preparation Protocols on the Bulk and Surface Properties of Oppositely Charged Polyelectrolytes and Surfactants"

21th Conference of the European Colloid and Interface Society, Geneva, September 2007.
és 9th Conference on Colloid Chemistry, Siófok, September 2007.

2. Augusztina Benák, Katalin Pojják, Ágnes Ábrahám, Róbert Mészáros

„The Thermodynamic Stability of the Mixtures of Hyperbranched Poly(ethyelenimine) and Sodium Dodecyl Sulfate at Low Surfactant-to-Polyelectrolyte Ratios"

23rd Conference of the European Colloid and Interface Society, Antalya, September 2009.