Thesis book

INTERACTIONS BETWEEN CATIONIC POLYELECTROLYTES AND ANIONIC SURFACTANTS

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**Introduction**

Aqueous mixtures of oppositely charged surfactants and polyelectrolytes are frequently used in many commercial products and have been studied for a wide range of applications in the home and personal care, paint and pharmaceutical industry.

With regard to the practical applications of polyelectrolyte/surfactant mixtures, their bulk and surface properties are of paramount importance. These properties, however, are significantly affected by the complex phase properties of these mixtures.

Surfactant/polyelectrolyte mixtures may associate into different nanostructures depending on the composition of the species in the system. The mechanism of the association between oppositely charged polyelectrolytes and surfactants are much more complicated compared to the mixtures of ionic surfactants with neutral polymers. Both non-cooperative and cooperative surfactant binding is possible for oppositely charged macromolecules and surfactants due to the strong electrostatic interactions between the compounds. At constant polyelectrolyte concentration the association between macromolecules and amphiphiles results in phase separation (precipitation) at intermediate surfactant concentrations. At higher or lower polyelectrolyte-to-surfactant ratios transparent systems might be formed.

The majority of the theoretical studies on the phase properties of polyelectrolyte/surfactant systems relies on the concept of cooperative surfactant binding as well as on the direct interaction between the polyelectrolytes and surfactant micelles. The general phase behavior emanating from these studies can be summarized as follows. At an intermediate polyelectrolyte-to-surfactant ratio, the charges of the polyelectrolytes are compensated by the bound surfactant molecules, which results in phase separation. At higher or lower polyelectrolyte-to-surfactant ratio, stable one-phase systems are predicted due to the significant net charge of the polyelectrolyte/surfactant complexes. It is important to emphasize that according to these approaches at high surfactant-to-polyelectrolyte ratio the significant charge reversal of the polyelectrolyte is explained by the excess charges of the bound micelles. This means that a re-swelling of the polyelectrolyte/surfactant complexes e.g. the resolubilization of the precipitate in concentrated surfactant solutions and the formation of a thermodynamically stable solution is predicted at large excess of the oppositely charged surfactant.

Some experimental observations, however, are in contrast with these predictions. For instance, it was observed for the mixtures of several cationic polyelectrolytes and anionic surfactants that the precipitate can not be resolubilised even at very large excess of the
surfactant. Furthermore, all the theoretical studies refer to equilibrium systems whereas the real mixtures of polyelectrolytes and oppositely charged surfactants are frequently observed to be trapped in non-equilibrium states. Last, but not least according to recent studies the effect of inert electrolyte on the phase properties of polyelectrolyte/surfactant mixtures seems to be controversial: i.e. it is not clear whether the added salt enhances or suppresses the two-phase composition region of these mixtures.

Recently a new interpretation was given for the phase properties of hyperbranched poly(ethyleneimine)/sodium dodecyl sulfate (PEI/SDS) mixtures at low charge density of the polyelectrolyte. The so-called colloid dispersion concept partly resolves the above mentioned discrepancies. According to this approach, the system is a thermodynamically stable solution of the solvated PEI/SDS complexes at low surfactant concentrations. Above a critical surfactant concentration, the mixture is considered as an unstable colloid dispersion of the PEI/SDS particles. At even higher surfactant concentrations, the surfactant molecules may adsorb on the surface of the neutral PEI/SDS particles resulting in a kinetically stable colloid dispersion of the polyelectrolyte/surfactant particles.

This thesis was intended to study the general validity of the above mentioned colloid dispersion concept with respect to the bulk- and surface properties of oppositely charged cationic polyelectrolytes and anionic surfactants in aqueous mixtures. Since the main information about the interaction between polyelectrolytes and surfactants is given by the binding isotherms, an important aim of my work was to develop new methods for the estimation of the bound amount of surfactant on oppositely charged polyelectrolytes. Because of the non-equilibrium nature of these systems, the study and control of the solution preparation are of paramount importance both in fundamental research and in technical applications. Therefore, one of the major goals of my investigation was to explore the effect of different mixing protocols on the bulk and surface properties of the aqueous mixtures of the linear poly(vinylamine)/sodium dodecyl sulfate (PVAm/SDS) and the hyperbranched poly(ethyleneimine) PEI/SDS system at different experimental conditions (concentration and charge density of the polyelectrolytes, as well as the ionic strength of the medium etc.).

Another important goal of the investigations was to test the colloid dispersion character of polyamine/SDS mixtures at high surfactant concentration range. Furthermore, surface tension measurements were carried out in order to explore the effect of solution preparation methods on the surface properties of polyamine/SDS systems. Last, but not least I also attempted to
explore novel ways of manipulating the phase properties of oppositely charged polyelectrolytes and surfactants with the addition of non-ionic, environmentally friendly surfactants. For this purpose the phase properties of PEI/SDS mixtures was investigated in the presence of n-dodecyl-β-D-maltoside (C\textsubscript{12}G\textsubscript{2}).

**Methods**

Two kinds of mixing protocols were applied for the preparation of the polyelectrolyte/surfactant solutions. a) *Gentle mixing*: equal volumes of pH-preadjusted polyelectrolyte and surfactant solutions were added into the same dish simultaneously and mixed by repeatedly turning the test tubes upside down. b) *Stop-flow mixing*: equal volumes of pH-preadjusted polyelectrolyte and surfactant solutions were mixed by the stop-flow mixing equipment of Applied Photophysics Ltd. (Model RX. 1000). This apparatus is designed to monitor the kinetics of chemical reactions and/or the coagulation of colloid particles. This mixing method is very efficient, since the two solutions are completely mixed within 10 ms.

Electrophoretic mobility measurements were used to monitor the charged nature of the polyelectrolyte/surfactant complexes. The average apparent hydrodynamic diameter of the complexes was determined from dynamic light scattering measurements. Furthermore, coagulation kinetics measurements were performed to monitor the colloid dispersion character of the systems. Surface tension measurements were also carried out by the pendant drop method in order to characterize the interfacial behaviour of the mixtures at the air/water interface.

All the measurements were performed at 25 ± 0.1 °C and 24 hours after the preparation of the mixtures. During the experiments, double distilled water was used for the solution preparation. The surfactant binding isotherms were determined only for the PEI/SDS system.

**New scientific results**

The major scientific achievements of my Ph.D study are summarized below:

1. A novel method based on electrophoretic mobility measurements has been developed for the estimation of the binding isotherms of ionic surfactants on oppositely charged
polyelectrolytes. The method can be generalized for the binding of surfactants or small ligands on different polyelectrolytes or biomacromolecules.

2. The variation of the initial coagulation rate of the PVAm/SDS and PEI/SDS complexes formed at large excess of the surfactant with the electrolyte concentration is consistent with the predictions of the DLVO theory. These results provide an unambiguous evidence for the formation of an electrostatically stabilized colloid dispersion of the polyamine/SDS nanoparticles at high SDS concentrations.

3. The kinetic stability of the colloid dispersion and the critical coagulation concentration increases with increasing surface charge density of the polyamine/SDS complexes.

4. The results of the coagulation kinetics measurements on PEI/SDS and PVAm/SDS mixtures clarify the earlier controversial results with respect to the effect of inert electrolyte on the phase properties of oppositely charged polyelectrolyte/surfactant systems. It was shown, that the increasing ionic strength – in the applied concentration range of NaCl – results in a decreasing kinetically stable composition range and not in an increasing equilibrium two-phase region of the mixtures.

5. The applied mixing protocols do not affect the electrophoretic mobility of the polyelectrolyte/surfactant complexes and the bound amount of the surfactant. This means that the same primary polyamine/surfactant complexes are formed via the application of both mixing methods.

6. At large excess of the surfactant a kinetically stable colloid dispersion of the polyamine/SDS particles are formed via the stop-flow mixing method. The application of the less efficient gentle mixing results in large aggregates in addition to the primary complexes. The observed differences between the mixtures prepared by the different mixing protocols persist over a long time provided that the charge of the primary complexes is large enough.

7. Via the application of the stop-flow mixing protocol the kinetically stable colloid dispersion of polyamine/SDS particles is formed in a larger surfactant concentration
range e.g. the precipitation region is less extended compared with the polyamine/SDS mixtures prepared by gentle mixing.

8. The effect of mixing on the bulk properties of polyamine/SDS mixtures depends on the local rate of coagulation of the primary complexes which is enhanced in the case of a less efficient mixing method. The effect of mixing becomes more pronounced at large concentration and charge density of the polyelectrolytes as well as at high ionic strengths.

9. The applied solution preparation methods have no major impact on the surface tension vs. surfactant concentration curves of polyamine/SDS mixtures. This observation is attributable to the hindered adsorption of the large polyelectrolyte/surfactant aggregates, formed via the application of the gentle mixing, at the air/water interface.

10. The presence of C\textsubscript{12}G\textsubscript{2} in the PEI/SDS mixtures results in a synergistic binding of the anionic and non-ionic surfactants to the PEI molecules. It was shown that in the PEI/SDS/C\textsubscript{12}G\textsubscript{2} mixtures the surfactant molecules bind to the charged and uncharged amine groups as well. An important consequence of the synergistic surfactant binding is the significant extension of the kinetically stable concentration range for PEI/SDS/C\textsubscript{12}G\textsubscript{2} mixtures compared with the PEI/SDS system.

List of publications

1. Amália Mezei and Róbert Mészáros
   “Novel Method for the Estimation of the Binding Isotherms of Ionic Surfactants on Oppositely Charged Polyelectrolytes”
   *Langmuir* 2006, 22, 7148-7151

2. Amália Mezei, Róbert Mészáros, Imre Varga and Tibor Gilányi
   “Effect of Mixing on the Formation of Complexes of Hyperbranched Cationic Polyelectrolytes and Anionic Surfactants”
   *Langmuir* 2007, 23, 4237-4247
3. Amália Mezei and Róbert Mészáros
“Novel nanocomplexes of hyperbranched poly(ethyleneimine), sodium dodecyl sulfate and
dodecyl maltoside”
Soft Matter 2008, 4, 586-592

4. 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”

5. Amália Mezei, Ágnes Ábrahám, Róbert Mészáros and Tibor Gilányi
“Aggregation of the Poly(ethyleneimine) and Sodium Dodecyl Sulfate in the presence of
coagulating electrolyte”
(in preparation)

List of poster and oral presentations

1. Amália Mezei, Róbert Mészáros – Practical aspects of polyelectrolytes/surfactants
interaction, „SIS 2006” Seoul, Korea, jun. 4-9 – talk

2. Amália Mezei, Róbert Mészáros – Determination of the binding isotherms of ionic
surfactants to oppositely charged polyelectrolytes based on electrokinetic
measurements, Orsay, France „Summer School SOCON”, 2006 jun. 12-16 – talk

3. Amália Mezei, Róbert Mészáros – Binding characteristics of oppositely charged
polyelectrolytes and surfactants, Budapest, Hungary „SOCON Mid-Term Review”,
2006 sept. 15-16 – talk

4. A. Mezei, R. Mészáros and T. Gilányi - Binding Characteristics of Ionic Surfanctants
to Hyperbranched Polyelectrolytes 20th ECIS 2006, Budapest, Hungary, sept. 17-22 –
poster
5. R. Mészáros, A. Mezei, A. Benák, I. Varga, and T. Gilányi - Non-equilibrium Features of Oppositely Charged Polyelectrolyte/Surfactant Complexes 20\textsuperscript{th} ECIS 2006, Budapest, Hungary, sept. 17-22 – poster

6. Amália Mezei, Róbert Mészáros – Practical aspects of polyelectrolyte/surfactant interaction, Stockholm, Sweden, 2007 oct. 10 – talk


9. Amália Mezei, Róbert Mészáros – Novel experimental routes to affect the phase properties of polyelectrolyte/surfactant systems, Stockholm, Sweden „3\textsuperscript{rd} Annual Meeting of the Marie Curie Research Training Network”, 2007 sept. 05-08 – talk

10. Amália Mezei, Róbert Mészáros – The effect of mixing protocols on the association of oppositely charged polyelectrolytes and surfactants, Siófok, Hungary „9\textsuperscript{th} Conference on Colloid Chemistry”, 2007 oct. 03-05 – talk

11. Amália Mezei, Róbert Mészáros – Interaction between cationic polyelectrolytes and anionic surfactants in bulk solution, Kolozsvár (Cluj-Napoca), Románia „XIII. Nemzetközi Vegyészkonferencia”, 2007 nov. 08-10 – talk


13. Ágnes Ábrahám, Amália Mezei, Tibor Gilányi, Róbert Mészáros - Aggregation of the nanocomplexes of oppositely charged poly(ethyleneimine) and sodium dodecyl
sulphate in the presence of supporting electrolyte, 21st ECIS 2007, Geneva, Switzerland, sept. 10-14 – poster

14. Ágnes Ábrahám, Amália Mezei, Tibor Gilányi, Róbert Mészáros - Aggregation of the nanocomplexes of oppositely charged poly(ethyleneimine) and sodium dodecyl sulphate in the presence of supporting electrolyte, Baltic Polymer Symposium 2007, Druskininkai, Lithuania, sept. 18-23 – poster


18. Amália Mezei, Róbert Mészáros – Effect of dodecyl maltoside on the phase properties of the mixtures of hyperbranched poly(ethyleneimine) and sodium dodecyl sulfate, 17th SIS 2008, Berlin, Germany, aug. 17-22 – talk