

Thesis of Ph.D. Dissertation

ÁGNES ÁBRAHÁM

**INVESTIGATION OF THE BULK STABILITY AND
THE SOLUTION/AIR INTERFACIAL PROPERTIES
OF POLYELECTROLYTE/SURFACTANT MIXTURES**

Supervisors: Dr. Imre Varga, Ph.D.
Dr. Róbert Mészáros, D.Sc.

Doctoral School of Chemistry
Head of Doctoral School: Dr. György Inzelt, D.Sc.

Analytical, Colloid and Environmental Chemistry, Electrochemistry Program
Head of Program: Dr. Gyula Zárny, D.Sc.



Eötvös Loránd University, Faculty of Science
Institute of Chemistry, Department of Physical Chemistry
Laboratory of Interfaces and Nanosized Systems

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Introduction and aims of my study

Aqueous mixtures of oppositely charged macromolecules and amphiphiles are increasingly important in our common life. Numerous dyes, shampoos and domestic products contain cationic polyelectrolytes and anionic surfactants as main components. Solubilization of different organic materials or dyes in polyelectrolyte/surfactant complexes is used for waste water cleansing and chromatography procedures. These systems may also have a relevant role in some biotechnological and medical applications (e. g. nanoencapsulation, gene therapy). The interaction between polyelectrolyte/surfactant complexes and hydrophobic surfaces plays a dominant part in several practical applications, thus its deeper understanding is important.

The mixtures of oppositely charged macromolecules and surfactants form two-phase systems in a certain composition range because of the aggregation of the primer polyelectrolyte/surfactant particles (associative phase separation). Though, it has been widely accepted that the transparent polyelectrolyte/surfactant systems form thermodynamically stable solutions outside the surfactant concentration range of the associative phase separation, recently it has been shown that at certain compositions polyelectrolyte/surfactant systems can form trapped non-equilibrium states with considerable kinetic stability. It has been proved that the hyperbranched poly(ethyleneimine) (PEI) and sodium dodecylsulfate (SDS) system may form transparent electrostatically stabilized colloidal dispersions in surfactant excess that can explain the observed non-equilibrium properties of the system. At the same time the transparent systems of linear polyelectrolytes mixed with excess amount of surfactant have not been investigated before if they are equilibrium solutions or colloidal dispersions.

One of the aims of my thesis is to investigate if the formation of colloidal dispersion is valid only for the hyperbranched polyelectrolyte/surfactant systems or it can be extended for linear polyelectrolyte/surfactant systems as well. I studied the aggregation of polyelectrolyte/surfactant complexes that are formed in mixtures of linear poly(vinylamine) (PVAm)/SDS and poly(diallyldimethylammonium chloride) (PDADMAC)/SDS in excess of surfactant, and the prepared systems were studied by coagulation kinetics measurements. My results were compared to the previous observations of PEI/SDS systems.

In the literature of the solution/air interfacial behaviour of polyelectrolyte/surfactant mixtures the occurring associative phase separation is usually mentioned, but the systems are treated as *equilibrium* systems in the interpretations. The newest results have proved that polyelectrolyte/surfactant systems behave as *non-equilibrium* systems in bulk in excess surfactant.

Campbell and Varga proved that the interfacial behaviour of PDADMAC/SDS mixtures – which are well-known type 2 systems – show type 1 interfacial behaviour immediately after mixing (surface tension plateau on the isotherm), while the aged and settled samples behave as type 2 systems (surface tension peak on the isotherm).

My aim was to study if this behaviour which can be connected to the bulk phase transitions is present only in PDADMAC/SDS systems or it is a general feature of polyelectrolyte/surfactant mixtures. For this aim I investigated the poly(sodium 4-styrenesulfonate) (PSS)/DTAB mixture which is a typical type 1 system to find out how the slow phase separation process in bulk influences the interfacial properties. Finally, I studied if my results can be extended to the biomacromolecule/surfactant systems which are important in practical applications. Furthermore, I worked out a simple method to estimate quantitatively the peak (magnitude, position) which appears in the surface tension isotherms of polyelectrolyte/surfactant systems.

Methods

Mixing protocols

For the preparation of the polyelectrolyte/surfactant samples two mixing protocols were used (at $25.0 \pm 0.5^\circ\text{C}$). During the *simple mixing* method the solutions of the same ionic strength were mixed in equal volume with magnetic stirring (~ 1000 rpm). In the *fast mixing* application the polyelectrolyte/surfactant mixtures were prepared with Applied Photophysics stopped-flow equipment. In case of this latter method, the solutions were passed through a special, small-volume flowing cell which enables the very fast mixing of the components ($t < 10$ ms). The volume ratio of the polyelectrolyte and surfactant solutions was 1:1 in this mixing protocol as well.

Methods of characterization

To characterize the aggregation of the primer polyelectrolyte/surfactant complexes in bulk, turbidity and dynamic light scattering measurements were performed, while the overall charge of the polyelectrolyte/surfactant aggregates was monitored using electrophoretic mobility measurements. The stability of the particles was studied with coagulation kinetics measurements. The surface tension isotherm was determined to characterize the interfacial properties with pendant drop method.

Results

1. It has been shown with coagulation kinetics measurements that independent of the polyelectrolyte structure (linear or hyperbranched), electrostatically stabilized colloidal dispersion is formed in the mixtures of polyelectrolytes and oppositely charged surfactants in excess surfactant.
2. The stability of the PVAm/SDS and the PDADMAC/SDS dispersions increases with increasing surfactant/polyelectrolyte ratio due to the increasing adsorption of the surfactant on the surface of polyelectrolyte/surfactant nanoparticles. The kinetic stability of the PVAm/SDS dispersions increases with decreasing pH at a given surfactant activity due to the increasing protonation of the polyelectrolyte resulting in the formation of more compact (hydrophobic) PVAm/SDS particles and as a consequence in increased surfactant adsorption on the particle surface.
3. It has been shown that the interfacial properties of the PSS/DTAB mixture - which is considered as a typical example of type 1 systems on the basis of its interfacial behaviour - are determined by the instantaneous state of the associative phase separation taking place in the bulk. Immediately after the mixing of the components the PSS/DTAB mixture shows a surface tension plateau which is a characteristic feature of type 1 systems. However, when the mixed systems are aged for sufficiently long time a surface tension peak appears in the surface tension isotherm that could be unambiguously connected to the precipitation in the bulk phase.
4. In the case of PSS/DTAB system the ionic strength of the medium practically does not influence the equilibrium surfactant concentration where stoichiometric surfactant binding occurs. At the same time the *cmc* of the surfactant decreases with increasing ionic strength. Thus, it has also been shown that the appearance and magnitude of the surface tension peak can be controlled by the addition of inert electrolytes.
5. It has been shown that the interfacial behaviour of a rigid biomacromolecule (DNA)/surfactant system is controlled by the same principles as in the case of flexible, synthetic polyelectrolyte/surfactant mixtures. The freshly prepared samples behave as a

type 1 system and the aged mixtures show a type 2 interfacial behaviour due to the slow bulk precipitation taking place in the system.

6. I proposed a model to predict the appearance and size of the surface tension peak in the aged polyelectrolyte/surfactant systems. The model is based on the assumption that the interfacial properties of the polyelectrolyte/surfactant system are determined by the equilibrium surfactant solution, because the polyelectrolyte moves from the solution to the solid phase during the aging of the sample due to associative phase separation. The estimation of the expected surface tension values requires only the determination of the surface tension isotherm of the pure surfactant and the characterization of the bulk phase behaviour of the polyelectrolyte/surfactant system (binding isotherm and phase diagram).

List of publications on the subject of the dissertation

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

The Impact of Electrolyte on the Aggregation of the Complexes of Hyperbranched Poly(ethyleneimine) and Sodium Dodecyl Sulfate

Langmuir **2009**, 25 (13), 7304–7312

Impact factor: 3,898

The article is shared with Katalin Pojják (25%) and Amália Mezei (25%).

2. **Ágnes Ábrahám**, Amália Mezei, Róbert Mészáros

The effect of salt on the association between linear cationic polyelectrolytes and sodium dodecyl sulfate

Soft Matter **2009**, 5 (19) 3718-3726

Impact factor: 4,869

3. **Ágnes Ábrahám**, Richard A. Campbell, Imre Varga

New method to predict the surface tension of complex synthetic and biological polyelectrolyte/surfactant mixtures

Accepted, Langmuir **2013**

Impact factor: 4,186

Poster presentations or oral presentations on the subject of the dissertation

1. Imre Varga, **Ágnes Ábrahám**, Richard A. Campbell

„Generalizing the quantitative link between the interfacial properties and bulk phase behavior of polyelectrolyte / surfactant mixtures”

Oral presentation, 26th Conference of the European Colloid and Interface Society, Malmö, September 2012

2. **Ágnes Ábrahám**, Amália Mezei, Katalin Pojják, Róbert Mészáros

„The effect of salt on the association between cationic polyelectrolytes and anionic surfactants”

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

3. **Ágnes Ábrahám**, Amália Mezei, Tibor Gilányi, Róbert Mészáros

„Aggregation of the Nanocomplexes of Oppositely Charged Poly(ethyleneimine) and Sodium Dodecyl Sulfate in the Presence of Supporting Electrolyte”

Poster presentation, 21st Conference of the European Colloid and Interface Society, Geneva, September 2007 and Baltic Polymer Symposium, Druskininkai, September 2007

Other poster presentations

1. Ágnes Ábrahám, Imre Varga

„Preparation of High Buffer Capacity Composite Nanoparticles”

3rd International CDTM Symposium “Cellular Delivery of Therapeutic Macromolecules 2010”, Cardiff, June 2010

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

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

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