CONTROLLING THE POLYELECTROLYTE/SURFACTANT ASSOCIATION WITH NONIONIC SURFACTANTS AND POLYMERS

EDIT FEGYVER

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Introduction and aims of study

Multicomponent systems, which contain oppositely charged polyelectrolytes (PE) and ionic surfactants (S) with nonionic additives are applied in home and personal care products, cosmetics, as well as in wastewater treatment and biotechnological processes. Such systems have complex physical and chemical properties which determine their utilization for practical formulations, therefore their mixtures were thoroughly investigated in the past few decades.

Most previous studies dealt with the association of ionic and nonionic surfactants with oppositely charged macromolecules assuming thermodynamic equilibrium. An important finding of these investigations is that at an appropriate excess of the uncharged amphiphile the associative phase separation (i.e. when the oppositely charged components separate out from a dilute solution) of the oppositely charged components diminishes. This observation was interpreted by various approaches. The studies of Dubin and coworkers are pioneering in this field.\(^1\) They considered the mixed micelles as rigid, charged spheres to which the polyelectrolyte chains bind by electrostatic interaction. In this physical model the change in the chemical potential of the surfactants is neglected, therefore their chemical properties are merged and they are handled as one component. According to this approach, below a critical surface charge density of the bulk free mixed micelles they do not interact with the oppositely charged macromolecules. This model provides an elegant way to estimate the phase properties of polyion/mixed surfactant (S\(_{\text{mix}}\)) systems under certain circumstances. However, it is limited to a high excess of the mixed micelles in relation to the polyelectrolyte molecules and cannot interpret the nonequilibrium behavior of PE/S systems.

An alternative explanation for the suppression of precipitation is given by Corbyn et al. based on their studies on DNA/cationic surfactant mixtures in nonionic surfactant excess.\(^2\) The authors suggested that the binding of the uncharged amphiphile and the mixed surfactant assemblies onto the DNA molecules can be ignored. In this case the redissolution of the precipitate with increasing nonionic-to-ionic surfactant ratio can be attributed to the stripping of the ionic amphiphile molecules from the complexes into the polyelectrolyte-free mixed micelles. This model explains the diminishing phase separation only with the change of the bound amount of the cationic surfactant at sufficient excess of the nonionic amphiphile. However, several studies revealed that in the presence of nonionic surfactant both types of surfactants bind to the macromolecules.

Janiak and his coworkers proposed a third interpretation for the suppression of associative phase separation in PE/S systems via the addition of nonionic surfactants.\(^3\) The authors investigated the solubility of stoichiometric polyelectrolyte/ionic surfactant salts in the

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\(^1\) Dubin, P. L.; Oteri, R. J. Colloid Interface Sci. 1983, 95, 453-461.
aqueous solutions of nonionic amphiphiles. They found that in the presence of high amount of nonionic amphiphile the insoluble salt can be resolubilized due to the largely increased hydrophilicity of the PE/S complexes through the incorporation of the nonionic surfactant. In these studies however, the electrolyte and counterion effects – which are very important in practical applications – were not investigated.

In contrast with the previously mentioned studies others found that in the dilute composition range (for both surfactants) with the addition of nonionic surfactant the two-phase concentration range increases compared to the nonionic amphiphile-free ones.\(^4\)

During my scientific work I principally investigated the effect of nonionic surfactants on the association of polyelectrolytes and ionic surfactants. My goal was to interpret the role of nonionic surfactant additives both in dilute and concentrated systems in a general framework. Furthermore, my aim was to understand and control the nonequilibrium behavior of PE/S systems in the presence of nonionic surfactants.

Contrary to nonionic surfactants, only a few studies are available which describe the role of neutral polymers on the PE/S association. These studies report the investigations of hyperbranced poly(ethyleneimine) (PEI)/sodium dodecyl sulfate (SDS) dispersions.\(^5\) The results showed that the PEI/SDS dispersions can be sterically stabilized with certain nonionic polymers even at high ionic strength, where electrostatically stabilized PE/S dispersions cannot be prepared. My question was whether these observations are general or specific to this system and these certain polymers. Therefore my goal was to examine the impact of the previously studied neutral polymers on the stability of linear polycation/anionic surfactant dispersions, and compare the results with the observations made in the PEI/SDS system.

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Investigated systems

The structure of the applied polyelectrolytes, ionic and nonionic surfactants and neutral polymers are shown below.

poly(diallyldimethylammonium chloride) (PDADMAC)

sodium poly(styrenesulfonate) (PSS)

sodium dodecyl sulfate (SDS)

dodecyltrimethylammonium bromide (DTAB)

hexadecyl(cetyl)trimethylammonium bromide (CTAB)

n-dodecyl-β-D-maltoside (C₁₂G₂)

n-dodecyl-hexaethylene-glycol (C₁₂E₆)

poly(ethylene oxide) (PEO)

poly(vinylpyrrolidone) (PVP)

dextran (Dx)
Mixing methods

Various mixing methods were used for the preparation of the PE/S systems. By means of *stopped-flow mixing* equal volumes of the polyelectrolyte and surfactant solutions were mixed by an Applied Photophysics (Model RX 1000) apparatus. In this mixing method the two solutions are mixed within 10 ms. In the case of *rapid-mixing* 2 ml ionic surfactant solution was added rapidly to 2 ml polyelectrolyte solution using an automatic pipette under continuous stirring with a magnetic stirrer at 2000 rpm. This is a simple method but not as fast as the *stopped-flow mixing*, although, quite efficient to prepare colloidal dispersions. Via application of *slow-mixing* the ionic surfactant solution was added slowly, drop by drop to the polyelectrolyte solution under continuous stirring with a magnetic stirrer. In all of the mixing methods in the case of added nonionic additive the polyelectrolyte and surfactant solutions contained the additive at the same concentration.

When the effect of order of addition of the components on the final state of the systems was investigated, several two-step mixing protocols were applied:

*Two-step-(rapid)-mixing I:* First, the PDADMAC/SDS mixtures were prepared via rapid-mixing of the polyelectrolyte and anionic surfactant solutions in equal volumes. Next, these mixtures were mixed in equal volumes with dodecyl maltoside solution utilizing the rapid-mixing protocol again.

*Two-step-(rapid)-mixing II:* First, the PDADMAC/C$_{12}$G$_2$ mixtures were prepared via rapid-mixing of the polyelectrolyte and nonionic surfactant solutions in equal volumes. Next, these mixtures were mixed in equal volumes with SDS solution utilizing the rapid-mixing protocol again.

*Two-step-mixing I:* First, the PDADMAC/SDS systems were prepared with the stopped-flow apparatus, then after 24 hours the neutral polymer solutions were added to equal volumes of PDADMAC/SDS mixtures in a dropwise manner under stirring with a magnetic stirrer.

*Two-step-mixing II:* First, the PDADMAC/SDS systems were prepared by stopped-flow mixing, then after 24 hours these mixtures were added to equal volumes of neutral polymer solutions in a dropwise manner under stirring with a magnetic stirrer.

Methods of characterization

The interactions between the solution components were characterized by fluorescence and electrical conductivity measurements. The apparent mean hydrodynamic diameter of the PE/S complexes and nanoparticles was measured by dynamic light scattering measurements, while their charged nature was determined by electrophoretic mobility measurements. The turbidity of the systems was also measured. The aggregation of the nanoparticles in colloidal dispersions due to added electrolyte was monitored by coagulation kinetics measurements.
Results

I. A new alternative interpretation has been proposed describing the effect of nonionic surfactant on polyelectrolyte (PE)/surfactant (S) association, which also considers the nonequilibrium features of PE/S mixtures. The approach is based on the two distinct effects of the nonionic surfactant on the binding of the ionic surfactant to the polyelectrolyte molecules. The applied PE/S system, ionic strength and concentration range determine which of these impacts (enhancement or reduction of the binding of ionic surfactant) dominate.

II. By means of fluorescence measurements it has been shown that in all of the investigated systems, in that concentration range where mixed micelles do not exist, in the presence of nonionic surfactant hydrophobic PE/mixed surfactant (S_{mix}) assemblies are formed from lower ionic surfactant concentration than in the nonionic surfactant-free systems. This reveals the synergistic binding of the two types of surfactant onto the polyelectrolyte chain.

III. One of the main consequences of the synergism between the ionic and nonionic amphiphiles is that the ionic surfactant/polyion ratio which is needed for the charge neutralization of the polyelectrolyte is reduced, therefore, the equilibrium two-phase composition range becomes more extended. The enhanced surfactant binding and increased phase separation concentration range is in contrast with earlier observations of diminishing PE/S interaction in the presence of nonionic surfactant.

IV. It has been shown that at polyelectrolyte excess (where the charged polymer segments are in excess compared to the surfactant ions) as well as in the case of PSS/CTAB mixtures at ionic surfactant excess (where the surfactant ions are in excess compared to the charged polymer segments), with increasing nonionic surfactant concentration the precipitate formed in the intermediate C_{12}G_{2} concentrations redissolves and a thermodynamically stable solution is formed. The reason behind this process is that the nonionic amphiphile incorporates into the PE/S complexes, changing its composition and hydrophilicity as well as ionic surfactants are stripped to mixed micelles, therefore the bound amount of the ionic surfactant significantly decreases. The redissolution of PDADMAC/SDS and PSS/DTAB precipitates – formed in ionic surfactant excess – in the presence of nonionic surfactant can be observed only via the addition of electrolyte. This is due to the order of magnitude higher concentration of ionic surfactants in these mixtures contrary to the PSS/CTAB system.

V. It has been shown that in the PDADMAC/SDS/C_{12}G_{2} and PSS/CTAB/C_{12}G_{2} systems in the presence of low amount of nonionic surfactant, via the application of appropriate mixing protocol electrostatically stabilized colloidal dispersions can be obtained in ionic surfactant excess. On the other hand, in case of the PSS/DTAB or PSS/DTAB/C_{12}G_{2} systems –
containing a cationic surfactant with shorter alkyl chain – the preparation of kinetically stable colloidal dispersions cannot be obtained at ionic surfactant excess even via the application of the ultrafast stopped-flow mixing protocol, due to the low surface charge of the formed nanoparticles.

VI. It has been shown that the synergism between the ionic and nonionic surfactants influences the extension of the kinetically stable concentration range. In the PDADMAC/SDS and PSS/CTAB systems in the absence of nonionic surfactant at a certain composition range even via application of a rapid mixing protocol, PE/S nanoparticles with low surface charge are formed, which coagulate. However, due to the synergistic surfactant binding onto the macromolecule in the presence of C12G2, the charge of the particles increases, therefore their dispersion becomes kinetically stable in that certain composition range. Therefore via the application of low amount of nonionic surfactant the concentration range of electrostatically stabilized colloidal PE/S dispersion can be increased.

VII. It has been shown that via the application of intermediate and high concentration of dodecyl maltoside the stability of PSS/CTAB/C12G2 and PDADMAC/SDS/C12G2 dispersions decreases. This can be explained by the stripping of ionic surfactant molecules to the mixed micelles, which results in the reduced bound amount of ionic surfactant as well as decreased charge of the PE/S nanoparticles. This leads to the aggregation of the polyelectrolyte/surfactant nanoparticles resulting in macroscopic phase separation. Above a certain polyelectrolyte concentration, the extension of the kinetically stable composition range can be modified by the order of addition of the components. The reason behind this is that the coagulation rate of the particles is strongly dependent on the adsorption kinetics of the two types of surfactants on the PE/Smix nanoparticles. Therefore in this concentration range new types of PE/Smix nanoparticles can be prepared, which were not investigated so far.

VIII. It has been shown that – in contrast to the earlier observations on PEI/SDS systems – the steric stabilization of PDADMAC/SDS dispersions cannot be obtained with the investigated nonionic PEO and PVP polymers, since they do not form a thick adsorbed layer on the surface of the PDADMAC/SDS nanoparticles. Moreover, they reduce the kinetic stability of the PDADMAC/SDS dispersion, since above a certain polymer concentration bridging or depletion flocculation occurs. It has been shown that the effect of neutral polymers depends on the extent and kinetics of polymer adsorption on the PE/S particles, which can be significantly determined by their composition and structure.
Publications on the subject of the dissertation:

1. Katalin Pojják, Edit Fegyver and Róbert Mészáros
   „Effect of Linear Nonionic Polymer Additives on the Kinetic Stability of Dispersions of Poly(diallyldimethylammonium chloride)/Sodium Dodecylsulfate Nanoparticles”

2. Edit Fegyver and Róbert Mészáros
   „The Impact of Nonionic Surfactant Additives on the Nonequilibrium Association between Oppositely Charged Polyelectrolytes and Ionic Surfactants”

3. Edit Fegyver and Róbert Mészáros
   „Fine-tuning the Nonequilibrium Behavior of Oppositely Charged Macromolecule/Surfactant Mixtures via the Addition of Nonionic Amphiphiles”

4. Edit Fegyver and Róbert Mészáros
   „Complexation between Poly(styrenesulfonate) and Alkyltrimethylammonium bromides in the Presence of Dodecyl maltoside”
   Submitted (J. Phys. Chem. B)

Oral presentations on the subject of the dissertation:

1. Róbert Mészáros, Edit Fegyver
   „Manipulation of the stability and composition of polycation/SDS nanoparticles with a sugar surfactant additive”
   COST Action CM1101 24-25. 01. 2013., Valletta

2. Edit Fegyver, Róbert Mészáros
   „Manipulation of the stability and composition of PDAC/SDS nanoparticles with a sugar surfactant additive”
   14th European Student Colloid Conference 10-13. 06. 2013., Potsdam
Poster presentations on the subject of the dissertation:

1. Edit Fegyver, Róbert Mészáros

"The Impact of Nonionic Surfactant Additives on the Nonequilibrium Association Between Oppositely Charged Polyelectrolytes and Ionic Surfactants”
26th Conference of the European Colloid and Interface Society 02-07. 09. 2012., Malmö, and
10th Conference on Colloid Chemistry 29-31. 08. 2012., Budapest

2. Katalin Pojják, Edit Fegyver, Róbert Mészáros

"Effect of Linear Nonionic Polymer Additives on the Kinetic Stability of Dispersions of Poly(diallyldimethylammonium chloride)/Sodium Dodecylsulfate Nanoparticles”
26th Conference of the European Colloid and Interface Society 02-07. 09. 2012., Malmö, and
COST Action 26-28. 05. 2013., Szeged

Other publications connected to the subject of the dissertation:

1. Beatrice Plazzotta, Edit Fegyver, Róbert Mészáros, Jan Skov Pedersen

"Anisometric polyelectrolyte/mixed surfactant nanoassemblies formed by the association of poly(diallyldimethylammonium chloride) with sodium dodecyl sulfate and dodecyl maltoside”
in progress

2. Katalin Pojják, Edit Bertalanits, Róbert Mészáros

"Effect of salt on the equilibrium and nonequilibrium features of polyelectrolyte/surfactant association”


Other poster presentations:

Katalin Bodnár, Edit Fegyver, Miklós Nagy, Róbert Mészáros

"The impact of the nature of polyelectrolyte charges on the nonequilibrium character of oppositely charged macromolecule/surfactant association”

COST Action 26-28. 05. 2013., Szeged