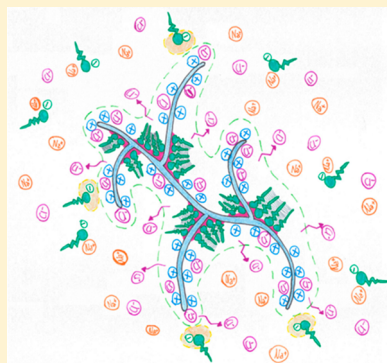


Polycation–Sodium Lauryl Ether Sulfate-Type Surfactant Complexes: Influence of Ethylene Oxide Length

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S Supporting Information

ABSTRACT: Polyelectrolyte–surfactant complexes (PESC) are a class of materials which form spontaneously by self-assembly driven by electrostatic and hydrophobic interactions. PESC containing sodium lauryl ether sulfates (SLES) have found wide application in hair care products like shampoo. Typically, SLES with only one or two ethylene oxide (EO) groups are used for this application. We have studied the influence of the size of the EO block (ranging from 0 to 30 EO groups) on complexation with two model polycations: linear polyDADMAC and branched PEI. PESC size and electrostatic properties were determined during stepwise titration of buffered polycation solutions. The critical aggregation concentration (CAC) of PESC was determined by surface tension measurements and fluorescence spectroscopy. For polyDADMAC, there is no influence of the size of the EO block on the complexation behavior; the stiff polycation governs the structure formation. For PEI, it was seen that the EO block size does affect the structure of the complexes. The CAC value of the investigated complexes turns out to be rather independent of the EO block size; however, the CMC/CAC ratio decreases with increasing size of the EO block. This latter observation explains why the Lochhead–Goddard effect is most effective for small EO blocks.



INTRODUCTION

Self-assembly of polymers and especially polyelectrolytes in solution offers the possibility to build composite mesoscopic structures, with specific functionalities.^{1–3} The absence of covalent bonds between the building blocks makes self-assembly a spontaneous, versatile, and reversible process allowing the formation of complex architectures. The main driving force in self-assembly involving polyelectrolytes is the electrostatic interaction between the charges on the polyelectrolyte chain and oppositely charged ions, which may be other polyelectrolytes,^{4,5} surfactants,^{6–8} counterions, or even charged surfaces.^{9,10} The binding motif, and thus the structure of a self-assembled system, does not require extensive synthesis. It can be tuned by the structure and composition of the polyelectrolyte and proper choice of the other component(s). Because self-assembly is thermodynamically driven, it is relatively defect-free and can exhibit self-healing properties. Nature employs self-assembly for the formation of functional structures which are crucial to biological functions.^{11,12} A rapidly growing number of industrial applications of self-assembled structures are seen with increasing importance, for instance, in the fields of coatings, optical materials, drug delivery, food, and personal care products.^{13–17} Also, in industrial processes, self-assembly is becoming a more common

tool like, e.g., in waste (water) treatment and bioremediation.^{18–20}

Polyelectrolyte–surfactant complexes (PESC) are a particular class of self-assembled structures, which may exist at interfaces,^{21,22} as dispersed colloidal particles,^{23,24} or in the dry state.²⁵ Their formation involves, besides electrostatic interactions between the polyelectrolyte's charges and the charged head groups of the surfactant, a second driving force being the hydrophobic or van der Waals interaction between the apolar tails of the surfactant molecules. This second interaction allows for the formation of complex shapes, this in contrast to polyelectrolyte–polyelectrolyte complexes derived from synthetic polyelectrolytes which only show ordering in planar structures. The formation of PESC is thermodynamically driven, and during formation, it is seen that the binding of the surfactant molecules is highly cooperative. In order to allow a hydrophobic interaction between the surfactant tails, close proximity is required; i.e., surfactants preferentially bind adjacent to an already bound surfactant molecule in the PESC.^{26,27} We define the relative amounts of polycations and

Received: March 2, 2015

Revised: April 23, 2015

Published: May 4, 2015



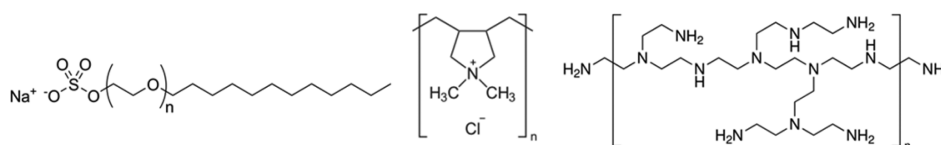


Figure 1. Chemical structures of (from left to right) SLES, polyDADMAC, and PEI.

anionic surfactants in terms of the charge stoichiometry Z_s/Z_p , where Z_s and Z_p are the number of charged groups on the surfactants and on the polycations per unit volume. Charge stoichiometric PESC ($Z_s = Z_p$) only form when the actual distance between two neighboring charges along the polycation matches the optimal distance between two surfactant head groups. The optimum distance between two neighboring surfactant head groups includes both solvation as well as the spatial requirements to allow the most favorable hydrophobic interaction between the surfactant's apolar tails. When the charged groups along neighboring groups are too far apart, stoichiometric complexation may only occur at higher surfactant to polycation ratio ($Z_s/Z_p > 1$); in case the polycation charges are too close, a lower surfactant to polycation stoichiometry ($Z_s/Z_p < 1$) may be observed to reach effectively neutral complexes, as not all surfactant molecules may actually be able to bind to the polycation's charged groups.

In this study, we focused on the formation of PESC consisting of polycations and sodium lauryl ether sulfates (SLES). These SLES–PESC have an interesting application in personal care products in so-called dilution–deposition shampoos. These dilution–deposition shampoos are based on the Lochhead–Goddard effect,^{28,29} which is described in the literature as the formation of a gel-like PESC precipitate on the hair's surface when the ionic strength I , by dilution, is lowered below a critical value, I_{crit} . PESC formation in the formulation, and during application, is avoided by the addition of salt at a level sufficient to achieve an ionic strength above I_{crit} . Although, still not fully understood, it is assumed that an increased ionic strength prevents PESC formation by weakening the electrostatic interaction between SLES and polycation. In the appropriate ionic strength range, a minimum surfactant concentration is observed where PESC can form. PESC typically forms at a critical aggregation concentration (CAC) that is orders of magnitude smaller than the critical micelle concentration (CMC). The variation in the recipes for these shampoos is almost exclusively found in the architecture of the polycation, i.e., the binding motif. The majority of the compositions contain the same SLES-type surfactants with only one or two ethylene oxide groups. Suitable polycations for this application are often tested in high-throughput experimentation,³⁰ but fundamental knowledge on the mechanism of complexation is mostly lacking. The interest in this study was to investigate whether SLES-type surfactants with larger EO blocks also form stoichiometric complexes with polycations, and, if so, whether the physicochemical properties of these complexes reveal whether they are also suitable materials for capture, encapsulation, and release of sparingly soluble solutes. For this purpose, the complexation of commercially available SLES surfactants (with variable size of the EO block) with two model polycations, linear poly(diallyldimethylamine hydrochloride) (polyDADMAC) and highly branched poly(ethylenimine) (PEI), was investigated. Of main interest are the hydrodynamic radius and electrokinetic properties as a

function of stoichiometry and the critical aggregation concentration of PESC with SLES. Such a study contributes both to the insight into the preferred type of surfactant (low EO blocks) used in dilution–deposition shampoos and the most preferred type of surfactant for capture, encapsulation, and release of apolar solutes.

EXPERIMENTAL SECTION

Chemicals. In our experimental studies, the following polyelectrolytes were used: (1) poly(di allyldimethyl amine hydrochloride) hereafter referred to as polyDADMAC. Three grades were used: DB45 (molar mass 450 kDa) and DB45VHM (molar mass 2000 kDa) both kindly supplied by SNF Floerger and polyDADMAC Titrant (molar mass 107 kDa) supplied by BTG Müttek GmbH further denoted as Müttek. (2) Highly branched poly(ethylenimine hydrochloride), further on denoted as PEI (molar mass 55 kDa), which was purchased from Acros. The stated molar masses of the polycations are weight-averaged molar masses; the polydispersity indices are unknown. polyDADMAC is considered to be a strong polycation with $pK_a \approx 12$, whereas PEI is considered a weak polycation with $pK_a = 9.7$. The SLES used were commercial Disponil series surfactants, kindly supplied by BASF: (1) Disponil FES27, lauryl(EO)₂ sulfate, (2) Disponil FES32, lauryl(EO)₄ sulfate, (3) Disponil FES993, lauryl(EO)₁₁ sulfate, and (4) Disponil FES77, lauryl(EO)₃₀ sulfate. Sodium lauryl sulfate, of highest purity (99.6%) available, was purchased from Merck. The chemical structures of the surfactants and polyelectrolytes used are given in Figure 1.

The auxiliary materials used were: Hyamine 1622 titrant solution (0.004 N) purchased from VWR/Merck; Nile Red technical grade purchased from Sigma-Aldrich and poly(sodium ethylene sulfate) hereafter referred to as NaPES (molar mass 19.1 kDa), purchased from BTG Müttek GmbH. All other materials were of the highest purity available and have been used without further purification. Ultrapure water, used throughout the investigation, was obtained using a Milli-Q Advantage A10 purification system from Millipore SA Molsheim, France.

Sample Preparation and Model System. All reagents were prepared as stock solutions in ultrapure water. These stock solutions, at a concentration of 10 mM, were freshly prepared and stored in the dark for the duration of the study. Since commercial products were used, some of which in the form of concentrated solutions, the actual concentrations in the stock solutions were determined by titrimetric methods and expressed as mM of charged groups. In order to maintain a constant pH and ionic strength, all experiments were performed in an acetic acid buffer at $c(\text{buffer}) = 5$ mM and pH 4.0.

Standardization Stock Solutions of Reagents. The actual polyDADMAC and PEI concentrations were determined by streaming potential titration employing a Müttek PCD03 streaming potential detector and a standardized NaPES 1.00 mM titrant solution. All analyses were performed in 5 mM

Table 1. Characteristics of PEI, polyDADMAC, and Surfactants Used in This Study

polymer	monomeric molar mass (g mol ⁻¹)	content by supplier w/w%	content determined w/w%
PEI Acros	43.0	50	46.4
polyDADMAC DB45	161.7	99	88.4 ^a
polyDADMAC DB45VHM		99	98.7
polyDADMAC Müttek		not specified	45.1
surfactant trade name	EO groups	content supplier w/w%	content determined w/w%
sodium dodecyl sulfate	0	99.6	99.5
Disponil FES 27	2	10–30	26.9
Disponil FES 32	4	30–50	30.4
Disponil FES 993	11	29–31	29.6
Disponil FES 77	30	30–35	31 ^b

^aThe opened container may have shown moisture uptake and was not previously dried. ^bDry weight was used.

acetic acid buffer solution (pH 4.0) in triplicate. Actual concentrations of the surfactants were determined using a monotonous turbidimetric titration employing a Metrohm 907 Titrand titrator fitted with a SpectroSense photometric detector and a standardized Hyamine 1622 4.0 mM titrant solution. The characteristics of the materials used in this study are shown in Table 1. All stock solutions were first prepared at a slightly higher concentration than expected from materials' purity. Next, the actual concentration was determined, after which the solutions were diluted to yield solutions that had an exact concentration of 10.0 mM. Prior to use, all stock solutions have been reanalyzed and were found to contain the desired concentration of 10.0 mM within the 2% accuracy of the employed titration methods.

Hydrodynamic Diameter and ζ -Potential. In order to get insight into the size and charge of the complexes, we performed dynamic light scattering (DLS) and ζ -potential measurements. DLS is based on measuring fluctuations in the scattered intensity as a function of time. These fluctuations arise from the Brownian motion of particles. The fluctuations in the scattered intensity yield a correlation function which is fitted, giving a diffusion coefficient of the complexes. For dilute suspensions, the diffusion coefficient can be turned into a (z -averaged) hydrodynamic size using the Stokes–Einstein equation. The ζ -potential is derived from electrophoretic mobility measurements, by using the Smoluchowski equation. By applying an electrical field, the electrophoretic mobility of particles was determined by laser Doppler velocimetry. The Zetasizer Nano ZS Malvern instrument allows the hydrodynamic diameter d_H and the ζ -potential to be simultaneously measured by using a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) in a patented technique called M3-PALS.

The influence of the stoichiometry Z_s/Z_p on PESC size and charge was investigated by addition of surfactant stock solution to a 1.0 mM polycation solution buffered at pH 4.0 (5 mM acetic acid buffer) by using the Malvern Instruments MPT-titrator. After each dosing step, the PESC solution was thoroughly mixed, the sample cell flushed, and subsequently a 2 min temperature equilibration (25 °C) was applied. The ζ -potential measurements were performed in threefold, allowing the instrument to determine the optimal number of submeasurements. A reproducible execution of the titrations was achieved by programming full instrument and titrator control into a detailed program in the instrument's software called a "play-list".

Critical Aggregation Concentrations. The CACs of PESC were determined by fluorescence spectroscopy and surface tensiometry.

Fluorescence Spectroscopy. For the CAC determination by fluorescence, each model system was investigated by the analysis of individual samples prepared for each data point. For this, polycation and buffer were added to yield a concentration, in the final solution for analysis, of 1.00 mM in acetate buffer 5 mM, pH 4.0. Next, varying amounts of SLES stock solutions and diluted solutions were added by means of calibrated pipettes. All samples were made up to a final volume of 9.98 mL to which 20 μ L of a 4.5 μ M Nile red solution in ethanol was added.³⁷ After equilibration of the solution (15 min at room temperature), fluorescence analyses were performed on a Shimadzu RF5301 spectrofluorometer, using high performance quartz cuvettes supplied by Hellma. Excitation of the samples was done at 550 nm; emission spectra were recorded in the range 560–750 nm in slow scanning plus high sensitivity modes. The instrument's software was used to analyze the spectra to obtain the peak position and intensity. As a check on instrument performance, the Raman peak (position and intensity) of water was recorded.

Surface Tensiometry. Static surface tension measurements were performed using a KSV Sigma-70 tensiometer equipped with a Wilhelmy plate. Titrations were performed in precleaned and tested titration beakers by verifying the correct measurement of the surface tension of water (72.8 mN/m at 23 °C). Next, the beakers were rinsed with buffer solution, prior to the addition of the buffered polycation solution at 1.00 mM. The surface tension was derived from the equilibrium force obtained in the force–time curve after dipping the Wilhelmy plate to a depth of 2.0 mm. The first dip was used to wet the plate; next, a set of four measurements were performed at each point in the titration. The Wilhelmy plate was not cleaned between titration points.

RESULTS AND DISCUSSION

A prerequisite for studying PESC is a proper characterization of the constituting components. The reason for this characterization is twofold. First, as industrial grade surfactants and polyelectrolytes were used, only approximate concentrations of active matter were given by the suppliers, and second, the actual amount of active matter may differ from our purpose in this study. As we selected the surfactants and polyelectrolytes with the purpose of investigating the formation of complexes as a function of the stoichiometric ratio Z_s/Z_p , the amount of charged groups present was characterized for both species.

The amount of equivalent charged groups per polycation was determined using streaming potential titration.^{31,32} For this purpose, stock solutions were prepared with concentrations slightly above 10 mM, based on the mass per monomeric charged unit. These solutions were titrated using a Mutek PCD03pH streaming potential detector fitted with a Titrino titration unit using a calibrated NaPES titrant solution of 1.0 mM. The titration of polyDADMAC is independent of the solution pH, owing to the fact that polyDADMAC is a strong polycation which remains charged within the observed range of pH values during titration. For PEI, however, the regular solution pH at the start of the titration was about 6.5 at which not all monomeric groups are protonated. Only 70% of the maximum amount of charge equivalents could be recovered from titration. It was therefore decided to fix the pH of the titration medium to pH 4.0 using a 5 mM sodium acetate buffer which was able to maintain a pH of 4.0 for the duration of the titration. For the polycations used in this study, the expected charge equivalents, based on weight and purity, were confirmed. On the basis of the charge equivalents found in the stock solutions, dilutions were made (if needed) to bring the charge equivalents to 10.0 ± 0.2 mM.

The surfactants used in this study were, apart from SDS, industrial grade commercial Disponil products. It is known for these compounds that the proposed molecular formula represents an average composition, as there is distribution in the alkyl-chain length as well as in the number of EO groups per molecule. There may also be species present that do not carry a sulfate group. Also here, stock solutions were prepared at a concentration based on the average composition of the surfactants, slightly above 10 mM which were characterized using potentiometric titration³³ employing a Metrohm "Anionic surfactant electrode" and a standardized Hyamine 1622 solution of 4.0 mequiv/L. Alternatively, for the surfactants with the larger EO blocks (FES993 and FES77), also a turbidimetric titration³⁴ with Hyamine 1622 was applied. It was found that for Disponil FES77 also this method does not give an identifiable equivalence point, neither in direct titration nor in back-titration of an excess of Hyamine 1622 using a calibrated SDS solution. Also, the attempt to determine the Disponil FES77 content by streaming potential titration failed. The FES77 content was therefore estimated by determining the dry matter content of the solution. This yielded a value close to the purity stated on the product's certificate of analysis. The surfactant stock solutions were diluted to yield a concentration of 10.0 ± 0.3 mM.

PESC formation using SLES-type surfactants is influenced by the ionic strength of the solution and can only take place at an intermediate salt concentration (depending on the type of salt and polycation). In the limit of low ionic strength, Manning condensation⁹ of the polycation's counterions prevents PESC formation, whereas, in the high ionic strength limit, PESC formation is prevented by screening the electrostatic interactions between surfactant and polycation, resulting in the Lochhead–Goddard^{28,29} effect (described in the Introduction). In order to avoid variation in ionic strength, all experiments were performed using a buffer solution. As was shown before, for PEI, the pH needs to be buffered at a value well below PEI's $pK_a = 9.7$ in order to maintain fully charged PEI molecules. Since all surfactants and polycations were characterized in a 5 mM acetic acid buffer at pH 4, it was decided to use the same buffer for all subsequent experiments.

When rapidly mixing equimolar charge quantities of SLES and polycation ($Z_s = Z_p$) at 1.0 mM level, there is an increase in turbidity, which can be detected by the eye. This suggests that PESC formation indeed took place, since neither micellization of the surfactants nor precipitation of the polycation is expected at this concentration. For all SLES species, there is a marked increase in turbidity when mixed with either polyDADMAC or PEI, indicating that even with an EO block of 30 units PESC formation still takes place. The turbidity, observed by the eye, develops within seconds and remains fairly unchanged over a time span of several hours, indicating that the PESC formation is completed almost instantaneously. However, upon gradual addition of SLES surfactant to polycation solutions, the onset of complexation is not readily visible and will only appear at higher stoichiometry. For instance, for polyDADMAC, this occurs at $Z_s/Z_p > 0.8$.

In order to follow the evolution of PESC formation, both the size and ζ -potential of PESC with increasing Z_s/Z_p charge stoichiometry were measured in a titration setup. In the sample vessel, 9.00 mL of a 1.10 mM polycation solution was placed, to which a SLES surfactant solution of 10.0 mM was sequentially added in 0.1 mL steps. After each addition, the vessel was stirred, circulated, and allowed to temperature equilibrate to 25 °C, prior to analyzing the size and ζ -potential of the mixture. In Figure 2, we plotted the evolution of the hydrodynamic diameter (d_H) and ζ -potential of PESC consisting of polyDADMAC DB45 and SDS or the selected Disponil FES

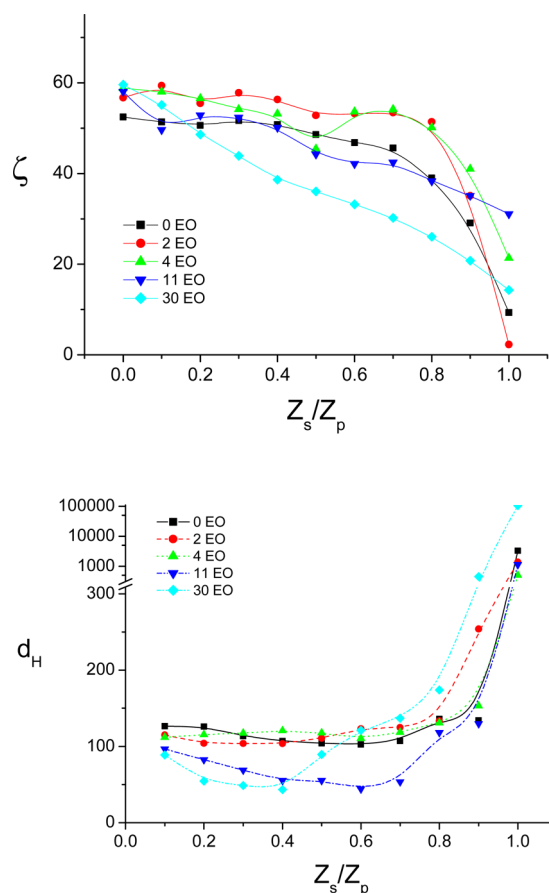


Figure 2. ζ -Potential (ζ in mV) and hydrodynamic diameter (d_H in nm) of PESC for polyDADMAC DB45, as a function of Z_s/Z_p stoichiometry at pH 4.0 using 5 mM acetic acid buffer.

types. In Figure 3, the results for the ζ -potential and d_H are shown for PESC with PEI as polyelectrolyte.

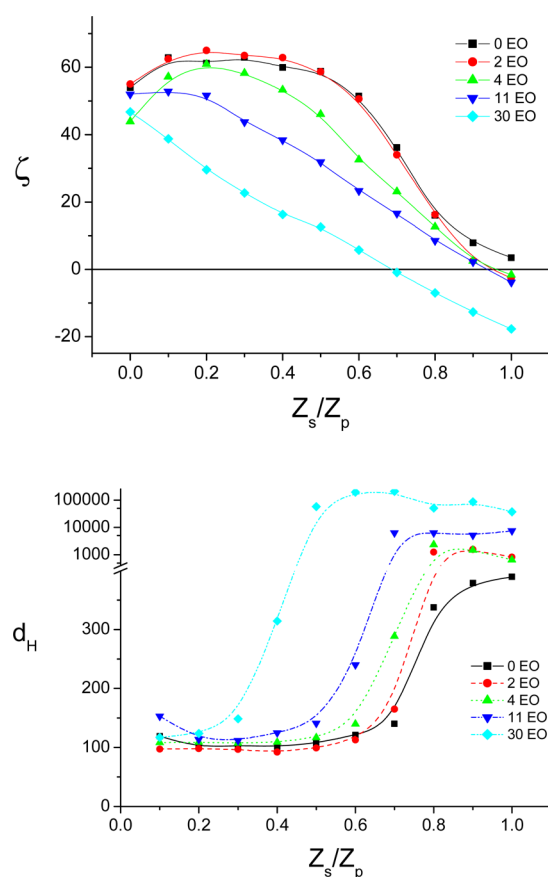


Figure 3. ζ -Potential (in mV) and hydrodynamic diameter (d_H in nm) of PESC of PEI, as a function of Z_s/Z_p stoichiometry at pH 4.0 using 5 mM acetic acid buffer.

The results presented in Figures 2 and 3 can be interpreted as follows. Upon adding surfactant, the first surfactant molecules will bind at random positions on the charged polyelectrolyte. The local segment concentration of a single polyelectrolyte chain in a salt solution will vary; it will have a maximum near the center of the polymer chain and gradually decrease as a function of the distance from the center. Hence, the probability that surfactant molecules will initially bind to locations close to the center of the polyelectrolyte is larger than on the outside. Therefore, the measured ζ -potential, which will mostly depend on the outer parts of the polyelectrolyte chains, will hardly be affected at low Z_s/Z_p . Followed by the first randomly bound surfactant molecules, the binding of the subsequently added surfactant molecules is considered to be cooperative and preferably on locations next to already bound surfactant molecules.²⁶ In that configuration, the hydrophobic tails can align in such a way that they benefit from the van der Waals interaction. Therefore, the charge as measured via the ζ -potential of most PESC, both polyDADMAC and PEI, only starts to decrease (except for the EO30 surfactant case) for values of $Z_s/Z_p \rightarrow 1$. Sometimes (PEI plus surfactants with small EO block lengths) the ζ -potential even increases initially as a function of Z_s/Z_p . The increase of the ζ -potential relative to the starting polycation solution may be the result of an improved measuring signal, thus overcoming analytical errors,

or may indicate the release of counterions attached to the polycation upon the interaction with the first surfactant molecules. It is noted that the measurements at small values of Z_s/Z_p show larger variation most likely due to measurement errors caused by low signal quality.

The addition of more surfactant molecules to the PESC probably also proceeds by cooperative binding near the center of the polycation. In the case of PEI, with a branched topology and therefore most likely in a more compact spherical arrangement, this will lead to a compaction of the center. For polyDADMAC, a linear polycation with a relatively more extended rod-like formation, this can be visualized by placing the surfactant molecules distributed along this rod with a higher preference for positions close to the center of the rod. For both polycations, this leaves the outermost segments free of surfactant molecules and thus leads to an overall positive ζ -potential. The sizes of the observed PESC are smaller with respect to the initial sizes, which also reflects a more condensed structure of the complexes due to the replacement of counterions (with their large hydration shells) by surfactant molecules.

Close to the condition $Z_s = Z_p$, one expects charge neutralization of PESC, which could be detected via either a vanishing ζ -potential or a steep increase in PESC size. Suspended PESC are stabilized by double layer interactions between them. When the PESC become effectively uncharged, the repulsive double layer interactions disappear and one can imagine that the surfactant molecules bound to the polyelectrolytes of different PESC will engage in van der Waals interactions by bringing their hydrophobic tails close to one another. Charge neutralization at $Z_s = Z_p$ is however not always achieved. In the case of PESC from polyDADMAC (Figure 1), the PESC are still positively charged at $Z_s = Z_p$. This may be explained by the wide molar mass distribution of the polycation; i.e., at $Z_s = Z_p$, the smaller mass polymer chains are fully neutralized, whereas the larger ones still have “dangling” ends which are positively charged. Further, the surfactants also self-organize inside the PESC. Thereby, their charges are screened and they do not all bind to a cationic group along the polyelectrolyte. It can also be observed that the size of the PESC close to $Z_s = Z_p$ rapidly increases with Z_s to micron-sized species, which are the result of individual PESC entities aggregating and precipitating into a flocculated state. This occurs in spite of a net positive charge of the PESC which obviously is insufficient to prevent aggregation.

From the evolution of the ζ -potential and hydrodynamic diameter d_H with increasing Z_s , it follows from Figures 2 and 3 that polyDADMAC and PEI have a different behavior in complexation; the polyDADMAC PESC exhibit almost identical trends for the measured size and ζ -potential regardless of the size of the EO block in the SLES. The size and ζ -potential dependence on the relative amount of surfactant on the PESC made from PEI do vary with the EO block length; the larger the EO block, the earlier the onset of a decrease in ζ -potential and rise in PESC hydrodynamic radius.

These observations suggest that the inherent chain stiffness of polyDADMAC is a governing factor in the formation of the structure of the complex; the size of the surfactant EO block length hardly affects PESC structure development. For PEI, a flexible and branched polycation, it is clear that spatial restrictions govern the development of structure by the continued incorporation of surfactant molecules into the complexes' structure; a larger surfactant (longer EO block

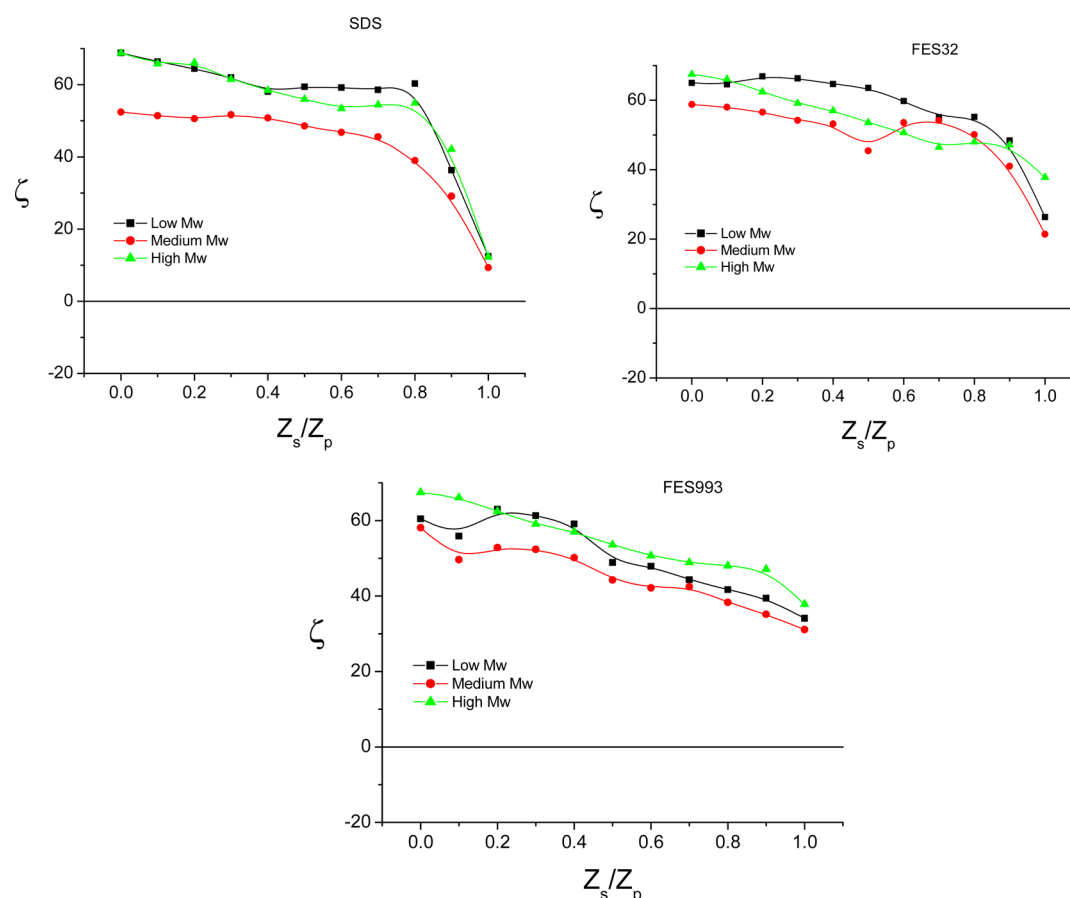


Figure 4. Influence of the molar mass of polyDADMAC (at 1 mM) on the ζ -potential (ζ in mV) of PESC respectively with SDS, FES32, and FES993, as a function of stoichiometry at pH 4 in 5 mM acetic acid buffer.

length) leads to larger PESC sizes, earlier onset of overlap between surfactant molecules on different PESC, and a stronger decrease in ζ -potential.

In order to investigate the influence of the molar mass of polyDADMAC in more detail, three stock solutions were tested with polyDADMAC of different molar masses. The ζ -potential seems to follow the same trend for SDS, FES32 (EO)₄, and FES993 (EO)₁₁, regardless of the molar mass, as is shown in Figure 4. Also, the size seems fairly independent of the molar mass of the polyDADMAC species involved, as shown in Figure 5. A remarkable observation is that at the highest molar mass the onset of the formation of larger sized aggregates does not appear at 1:1 charge neutralization, $Z_p = Z_s$, for the FES surfactants. This supports the idea that the surfactants are more preferentially present near the center of the PESC than near the outside because such an effect is expected to be stronger for larger (higher molar mass) polyelectrolytes.

The tendency of surfactant molecules to assemble into micelles can be characterized by their critical micelle concentration (CMC), which is the lowest concentration at which micelles exist. The CMC values of the studied surfactants in water are listed in Table 2. As is well-known, the CMC decreases with increasing EO chain length.

The interaction of surfactants with polyelectrolytes shows a very similar behavior to the formation of micelles. Also, here a minimum concentration exists above which surfactant molecules will start interacting with the polyelectrolyte, termed the critical aggregation concentration (CAC). Next to similarities

between micellization and PESC formation, there is also a major difference which is the fact that PESC formation results in entropic gain by the release of the counterions of both the surfactant and the polyelectrolyte. It is therefore commonly observed that the CAC value of a given surfactant is 1–3 orders of magnitude smaller than the CMC in the absence of the polyelectrolyte.^{6,35,36} The CAC for a given polyelectrolyte–surfactant combination depends on a large number of parameters, including the surfactant's alkyl chain length, polymer concentration, and ionic strength, but also on the structural properties of the coassembled structures. By adaptation of the model system used here, while keeping the ionic strength and pH constant with a constant surfactant geometry (only varying the EO block size), the determination of the CAC would possibly contribute to understanding the influence of the EO block and its possible restrictions to PESC formation for the two model polycations. Two commonly used methods to determine CAC values, (surface) tensiometry³⁶ and fluorimetry,³⁷ were also employed here.

In surface tensiometry, where the surface tension of a liquid–gas interface is determined, a KSV Sigma-70 Wilhelmy-plate-type instrument was used and the surface tension of a 1 mM polycation solution was measured during a manual titration with the surfactants studied here. As can be judged from the data depicted in Figure 6, most of our results yielded multiple, some less obvious, inflection points. This can be understood by the fact that we used nonpurified, industrial grade surfactants where some compositional variation is expected. Given this compositional variation, it is reasonable to assume that

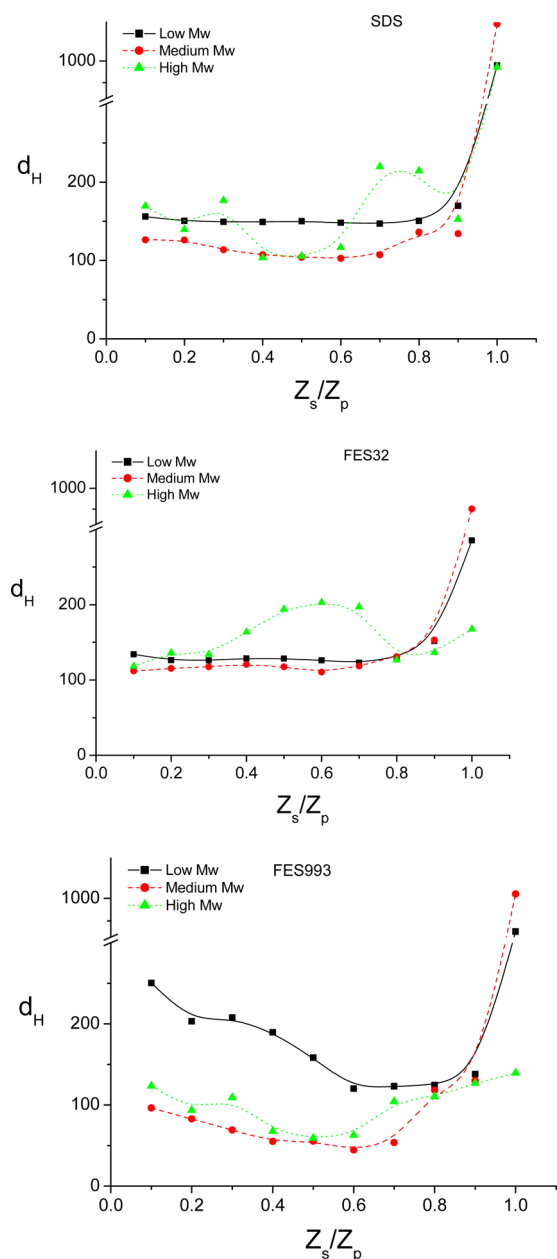


Figure 5. Influence of the molar mass of polyDADMAC (at 1 mM) on the hydrodynamic radius (d_H in nm) of PESC respectively with SDS, FES32, and FES993, as a function of stoichiometry at pH 4 in 5 mM acetic acid buffer.

aggregation of surfactants onto polyelectrolytes takes place within a concentration range rather than a discrete concentration. This made the localization of the position of the CAC and its determination ambiguous.

It was decided to use fluorescence of an added Nile red probe molecule as a second, independent, method to determine CAC values. Nile red shows a marked increase in fluorescence intensity, and a typical shift in emission wavelength, when it is transferred from a polar into an apolar environment.³⁷ The onset of PESC formation in an aqueous solution can therefore be determined by monitoring emission intensity and wavelength as a function of the surfactant concentration. For this, individual samples of PESC were prepared (at 1.00 mM polycation) to which the surfactants were added in a wide concentration range. From each individual sample spectrum,

Table 2. Estimated Apparent CAC for PEI and polyDADMAC

PEI	CMC ^a (mM)	CAC (μ M)	CMC/CAC
SDS (0 EO)	8.4	10	8.4×10^2
FES27 (2 EO)	1.0	2.6	3.9×10^2
FES32 (4 EO)	0.47	3.1	1.5×10^2
FES993 (11 EO)	0.29	1.4	2.1×10^2 ^b
FES77 (30 EO)	0.19	2.8	0.7×10^2
polyDADMAC	CMC ^a (mM)	CAC (μ M)	CMC/CAC
SDS (0 EO)	8.4	1.7	49×10^2
FES27 (2 EO)	1.0	2.6	3.9×10^2
FES32 (4 EO)	0.47	7.8	0.6×10^2
FES993 (11 EO)	0.29	2.9	1.0×10^2 ^b
FES77 (30 EO)	0.19	8.0	0.2×10^2

^aData from suppliers. ^bPrecipitation observed during the fluorescence experiments.

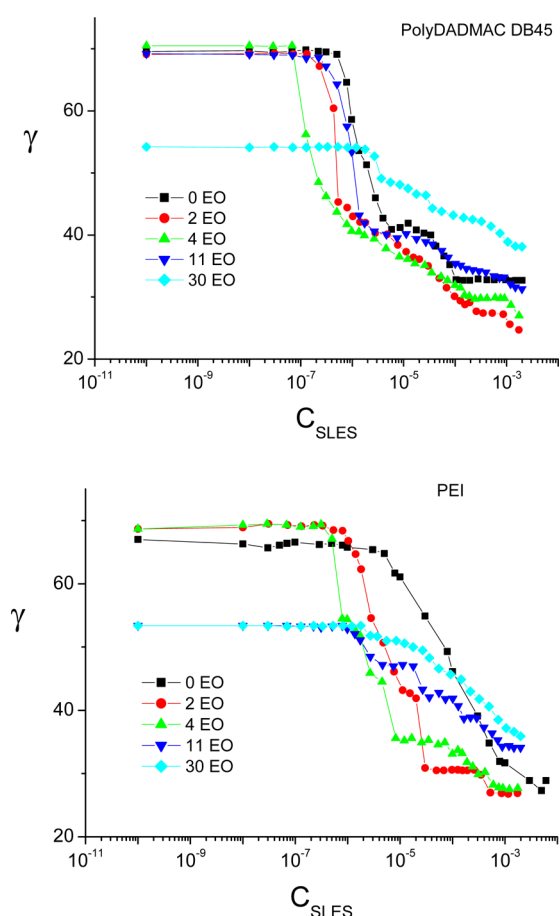


Figure 6. Surface tension (γ in mN/m) dependence on the concentration of added SLES to polyDADMAC (medium molar weight DB45) and PEI at pH 4 in 5 mM acetic acid buffer.

the emission wavelength maximum, λ_{\max} , and intensity, I_{em} , were determined. Plotting λ_{\max} and I_{em} as a function of surfactant concentration provides similar curves for the tested surfactants. Figure 7 provides an example of the curves obtained for FES77 for both polycations.

The resulting curves, as shown in Figure 7, do not always give a single value for the transition concentration. The cause of the latter observation may again be the compositional polydispersity of the investigated surfactants; hence, only an estimate of the CAC values is provided.

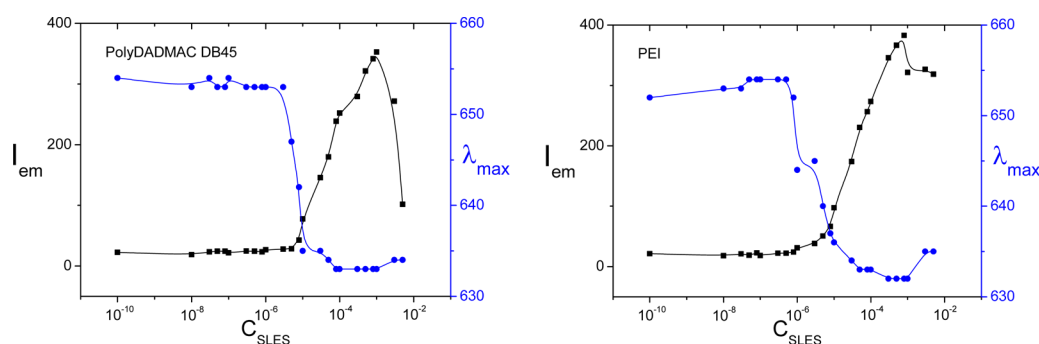


Figure 7. Emission wavelength maximum (I_{em} in au) and emission peak position (λ_{max} in nm) versus the concentration of added SLES for PESC with FES77. Left panel: polyDADMAC DB45. Right panel: PEI.

However, when combining the three data sets of concentration dependence of the surface tension, wavelength maxima, and emission intensities, it seems possible to indicate the possible locations of the CAC values for the PESC studied. Table 2 gives an overview of the CAC estimates based on the comparison of surface tensiometry and fluorescence data. Given the fact that the CAC depends on the ionic strength, ionic composition, and pH, it is noted that the reported CAC values should be considered “apparent” CAC values. Finally, the CAC values were manually selected, rather than calculated; it is therefore not possible to include standard deviations on the presented data, and they should be considered estimates at best.

The apparent CAC values found here for both PEI and polyDADMAC are in the same range and seem independent of the type of surfactant, type of polyelectrolyte, or the combination. Disponil FES993 in combination with both polycations was close to the onset of precipitation in the fluorescence measurements; this may have been unnoticed in the surface tensiometry experiments. It may, however, very well explain the break in the trends observed in Table 2. The CACs observed for PEI are about 3 μ M and seem independent of the size of the EO block in the SLES surfactant. A similar observation can be made for polyDADMAC, where the CAC does not significantly change after the size of the EO block is larger than 2 units. Given the fact that the CMC decreases with a larger EO block size, and the near constant CAC, the CMC/CAC ratio decreases with increasing size of the EO block (an exception in the trend is FES993, most likely due to the above-mentioned reason). As the CMC value is the result of a thermodynamic balance between solvation and aggregation of hydrophobic regions, a similar trend in the CAC could be expected, which would have resulted in a nearly constant ratio. The fact that this is not seen suggests that the decrease in the CAC/CMC ratio with increasing EO block length is the direct result of the spatial restrictions in the incorporation of the larger SLES into the complexes.

The above-mentioned spatial restrictions may be the prime reason why SLES type surfactants with larger EO blocks are not the most suitable candidates for incorporation in dilution–deposition shampoos. For the purpose of capturing, encapsulating, and release of sparingly soluble solutes, it also seems that there are no additional advantages of using SLES with larger EO block sizes.

Overall, this study demonstrates that in fact the properties of the polycation, like chain stiffness and/or branching, are the most dominant factors in the development and properties of PESC containing SLES surfactants.

The PESC described in this study seem to have only limited stability at the concentration studied here. We observed that, at concentrations at and above 1 mM and equilibration times of 24 h, the PESC show visible precipitation. This is most likely caused by slow exchange of surfactant molecules between polycation chains causing the lower molecular mass polycations to become saturated ($Z_s/Z_p \approx 1$) and precipitate when $Z_s/Z_p \geq 0.8$. This severely limits the practical application of the described PESC, unless polycations with a low polydispersity can be used.

CONCLUSIONS

The formation of polyelectrolyte–surfactant complexes (PESC) has been demonstrated for two model polycations, polyDADMAC and branched poly(ethylenimine) (PEI), with a series of sodium lauryl ether sulfates of varying ethylene oxide (EO) block length. In case of polyDADMAC, having a stiff, linear backbone, no influence was seen of the surfactant EO block length on the development of the hydrodynamic radius of the complexes with increasing amount of surfactant in the PESC; below charge stoichiometry, all complexes were submicron-sized, and only near full stoichiometry, the complexes precipitated into macroscopic (micron-sized) particles. For PEI, with a flexible, branched backbone, the size of the EO block governs the hydrodynamic radius of the resulting PESC. Larger EO block lengths lead to unstable, aggregating, and flocculating PESC at lower amounts of surfactant. The ζ -potential of PESC made with polyDADMAC remain highly positive over a large range of Z_s/Z_p and only decreases when approaching charge stoichiometry ($Z_s/Z_p = 1$), in some cases while maintaining a positive charge. In the case of PESC made with PEI, the PESC’s positive charge decreases more gradually, which is more apparent when the EO block is larger.

PESC formation in the case of polyDADMAC is governed by the limited flexibility of the backbone, whereas spatial restrictions govern complex formation in the case of PEI. The influence of the molar mass of polyDADMAC on PESC formation is less obvious; for SLES with larger EO blocks, it seems that the lowest molar mass species may form PESC that involve multiple polyelectrolyte chains. The trend of ζ -potential versus stoichiometry is unaffected by the molar mass of the polyelectrolyte.

Critical aggregation concentrations (CACs) were estimated on the basis of the combination of three experimentally determined quantities: fluorescence emission intensity and peak wavelength of a Nile Red probe and surface tension. It was shown that CAC values are roughly 2 orders of magnitude

lower than the CMC of the surfactant species investigated. There is no clear trend in CAC values with respect to the number of EO groups present in the surfactant. The CMC/CAC ratio decreases with an increase of EO block size which suggests the inherent difficulty of larger surfactants to be incorporated into the PESC structure.

■ ASSOCIATED CONTENT

■ Supporting Information

Surface tensiometry results for the determination of the CMC of the SLES surfactants used in this study. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b02043.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank I. K. Voets (Eindhoven University of Technology) and the colleagues at the Colloids & Interfaces group at DSM DCT-ACES for useful discussions. Pierre Loison and Izabela Puzskarska are thanked for their contribution to the experimental work.

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