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## What conjugated polyelectrolytes tell us about aggregation in polyelectrolyte/surfactant systems

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### ABSTRACT

The interaction between conjugated polyelectrolytes (CPEs) and surfactants in aqueous solutions is reviewed, based on results from absorption and fluorescence spectroscopy, NMR, dynamic light scattering (DLS), small angle X-ray (SAXS) and neutron (SANS) scattering, electrical conductivity and molecular dynamics simulations. It is shown that the conjugated polyelectrolytes frequently form aggregates (clusters) in water, but these can be broken up by the addition of co-solvents or surfactants. With oppositely charged surfactants, both enhancement and quenching of fluorescence are observed, depending on the nature of the CPE. These interactions start at very low surfactant concentrations, and, in some cases, associative phase separation is observed. However, there is little evidence for the “pearl necklace” structures observed with surfactants and nonconjugated polyelectrolytes. This may be related to the greater chain rigidity of the CPEs. Associative interactions are also seen with CPEs and non-ionic surfactants, which efficiently break-up the CPE aggregates to form mixed systems with greatly enhanced fluorescence. The relevance of these results to both the nanostructuring of conjugated polyelectrolytes and to our general understanding of polyelectrolyte–surfactant systems will be discussed.

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### 1. Introduction

Conjugated organic polymers are important materials for electronic and optoelectronic applications in field effect transistors, bulk heterojunction photovoltaic cells, and light emitting devices, particularly light emitting diodes (LEDs) or electrochemical cells [1]. In addition, the high delocalisation on the pi-conjugated backbone facilitates electronic energy migration and leads to the possibility of amplified fluorescence quenching or enhancement, which makes them attractive systems for sensing various chemical and biological systems [2]. Conjugated polymers have the advantages as advanced semiconducting materials of easily tunable electronic properties, through appropriate synthetic modification, and low-cost processing using solvent-based methodologies. Particularly important for this are techniques, such as ink-jet and screen printing, for thin-film device preparation [3], and it is now possible to mass produce optoelectronic devices from these materials using reel-to-reel printing.

It was recognized over two decades ago that the introduction of ionic groups into conjugated polymers would enhance their solubility in water or other polar solvents [4,5]. Since then, a number of conjugated polyelectrolytes (CPEs) have been synthesized, and their behaviour

and applications reviewed [6]. Luminescent CPEs and the corresponding oligoelectrolytes have emerged as important materials with applications in areas such as charge transport layers in optoelectronic devices, optical sensors and biomedical imaging agents [7]. They combine the luminescence properties of conjugated polymers with the characteristics of polyelectrolytes, such as solubility in water and polar solvents. In addition, they show interesting aggregation behaviour with surfactants. The charges of these CPEs provide possibilities for self-assembly through electrostatic interactions with surfactants, which can be exploited both in optoelectronic devices [8], and optical platforms for highly sensitive chemical and biological sensors [9]. We will consider the behaviour of negatively and positively charged CPEs having fluorene, thiophene, phenylenevinylene and aryleneethynylene units on their backbone and their interactions with both ionic and neutral surfactants. Results on these will be presented from studies using fluorescence and absorption spectroscopy, electrical conductivity, NMR, small angle X-ray (SAXS) and neutron (SANS) scattering and molecular dynamics simulations. The high sensitivity of their fluorescence is particularly important because it provides possibilities of studying polyelectrolyte–surfactant interactions at very low concentrations. In this review, we will focus both on what these interactions tell us about polyelectrolyte–surfactant behaviour in solution, and on how this may be used to modulate and control nanostructure and properties using self-association.

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## 2. General considerations on polyelectrolyte–surfactant interactions

Polyelectrolyte–surfactant systems are involved in a wide range of applications, including personal and domestic care products, paints, pharmaceutical formulations, and biomedical uses, such as DNA compaction for gene transfection. These have been extensively reviewed [10–16], and there is now a general consensus of the consequences of the interactions between charged polymers and surfactants in solution. Frequently phase separation is observed, and can be associative or segregative. In the former case, mixed polyelectrolyte–surfactant aggregates are formed, while with segregating systems, separate polyelectrolyte structures and surfactant micelles are present. The behaviour observed depends upon the balance between the various attractive and repulsive forces present. Electrostatic and hydrophobic interactions are suggested to be particularly important attractive interactions [17]. However, effects, such as the entropy change following replacement of counter ions by surfactants may also be involved [18], and there is increasing evidence for the importance of loss of hydration water as a driving force for binding of oppositely charged species to polyelectrolytes [19]. In addition, although no clear example has yet been reported, it is likely that hydrogen bonding may also play a role, particularly with nonionic surfactants.

The high sensitivity of fluorescence makes this an excellent method for studying polyelectrolyte–surfactant interactions [20]. This has normally been achieved through the addition of an external fluorescent probe to the system. However, an external probe may affect the phase behaviour, and also only provides limited information on what happens at low surfactant and polyelectrolyte concentrations. In contrast, many conjugated polyelectrolytes are, intrinsically, strongly luminescent, and can report on the behaviour at very low (nanomolar) concentrations. This can provide information on the initial stages of the aggregation process.

We will provide an overview of the interactions between conjugated polyelectrolytes and surfactants (both ionic and neutral) in aqueous solutions. This will be discussed on the basis of the techniques used to study them. We will then show how this can help in understanding polyelectrolyte–surfactant interactions in general. We will also address the limitations of this approach. These come, in particular, because the strong electron delocalization in CPEs implies fairly rigid polymer backbones. Although some theoretical and experimental studies have been reported on the effect of chain rigidity on polyelectrolyte–surfactant interactions (see, for example, [15,21]), we believe that this is an area where further studies are needed.

## 3. Optical properties and simulation studies

Marked changes have been detected in the optical properties of conjugated materials upon addition of surfactants, and have been termed surfactochromicity by Lavigne et al. [7]. Three different types of changes of the fluorescence properties of conjugated polymers have been observed upon addition of surfactants: a) enhancement of the emission quantum yield, b) quenching, sometimes accompanied by the appearance of new, red-shifted, bands in the emission spectrum [22] and c) a combination of these behaviours in which the surfactant can both, quench and increase, the conjugated polymer emission intensity, depending on its concentration [23]. From the point of view of applications, particularly in biosensory processes, an enhancement of the emission intensity of the conjugated material upon addition of surfactant is always desirable. However, a lot of information is also obtained about the nature of polymer–surfactant interaction, particularly at low surfactant concentration, from those systems in which polymer emission is quenched in the presence of the surfactant. Applications in the sensing field are found when further surfactant addition induces emission intensity recovery [23]. These differences in the surfactant modulation of the optical properties of conjugated materials are observed regardless of the charge of the polymer and surfactant. However, although, the interaction between conjugated polyelectrolytes with oppositely charged surfactants

is strong [7,24–27]; the interaction between non-ionic water soluble conjugate and non-ionic surfactants is also possible and leads to interesting surfactochromic effects [7].

### 3.1. Enhancement of the emission quantum yield

One of the first, and most cited, works showing that the interaction between conjugated polymers and appropriate surfactant can lead to a dramatic increase of the emission intensity of these materials (up to twenty-fold) was carried out by Chen et al. [24]. The fluorescence quantum yield of the anionic polymer poly(2,5-methoxy-propyloxysulfonate phenylenevinylene) (MPS-PPV) with an estimated molecular weight between 1 and  $5 \times 10^5$  (~1000 monomer repeat units) is enhanced by more than an order of magnitude upon addition of small amounts of the cationic surfactant dodecyltrimethylammonium bromide (DTA), even for surfactant:polymer ratio as low as 1:100 (surfactant molecules per repeat unit of the polymer). Structures of this and many of the other conjugated polyelectrolytes and surfactants are shown in Scheme 1.

Upon interaction with DTA, the emission spectra of the polymer–surfactant complex show a well-defined vibrational structure, the absorption spectrum is narrowed and red-shifted, and the fluorescence decay is monoexponential, with a reported lifetime of 1.2 ps, while in the absence of surfactants the decay is double exponential with lifetimes of 0.2 and 2.4 ps, suggesting that the nonradiative decay pathways are eliminated. The polymer–surfactant interaction is suggested to be led by the Coulombic attraction and favoured by entropy changes, due to the release of interfacial water molecules. The surfactant chains are assumed to be orientated along the polymer backbone to maximize the contact of the hydrophobic aliphatic chains and to reduce their contact with water molecules. This inhibits the folding of the polymer chains, reducing the conformational disorder and increasing the quantum yield. By reducing the chain folding, the number of kink defects that act as non-radiative recombination sites is diminished and the tendency of the polymer chains to self-associate is also decreased [24]. With conjugated polyelectrolytes, there are no signs of formation of surfactant micelles or pearl necklace structures in the low surfactant concentration range studied. This contrasts with the behaviour when surfactants interact with flexible nonconjugated polyelectrolytes [10].

Changes in conformation were also suggested to be responsible for the increase in fluorescence and blue-shift in the emission maxima of the water soluble poly(2-methoxy-5-[2'-ethylhexyloxy]-1,4-phenylenevinylene) (MEH-PPV) derivatives with polyacrylic acid (PAA) chains grafted onto their backbone ( $M_n$  from 104,700 to 998,000) upon addition of non-ionic (Triton-X-100) and cationic surfactants (alkyl trimethyl ammonium bromide,  $C_x$ TAB with  $x = 12, 14, 16$  and  $18$ ) for concentrations below the critical micelle concentration ( $cmc$ ). The polymer–surfactant interaction is suggested to expand the polymer coils, leading to a less effective energy transfer within a single chain from shorter chromophores to longer ones and to a depletion in the number of intra-chain inter-chromophore excitons [28].

We have observed similar spectroscopic changes with the anionic conjugated polymer poly(1,4-phenylene-[9,9-bis(4-phenoxybutyl)sulfonate])fluorene-2,7-diyl) (PBS-PFP, average molecular weight  $6500 \text{ g mol}^{-1}$ , ~9 monomers per chain) upon interaction with the non-ionic surfactant *n*-dodecyl pentaoxyethylene glycol ether ( $C_{12}E_5$ ) [22,29] and with several cationic surfactants: the amino acid glyceride conjugate, 1-*O*-(*L*-arginyl) 2,3-*O*-di-lauroyl-*sn*-glycerol dichlorhydrate (1212R, a mimic for the phospholipid lecithin) [30] and cationic gemini surfactants:  $\alpha,\omega$ -( $C_mH_{2m+1}N^+(CH_3)_2$ ) $_2$ ( $CH_2$ ) $_s$ ( $Br^-$ ) $_2$  (*m-s-m*;  $m = 12, s = 2, 3, 5, 6$  and  $12$ ) [31], Scheme 2.

The main photophysical changes observed upon addition of  $C_{12}E_5$  to PBS-PFP are summarized in Fig. 1. For surfactant concentrations above the  $cmc$ , both the PBS-PFP emission quantum yield ( $\phi_F$ ) and its lifetime dramatically increase, while the emission wavelength is blue shifted by around 13 nm. The absorbance in the maximum at about 381 nm also

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