



Self-assembled polyelectrolyte systems

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Abstract

Self-assembly of matter is of fundamental importance in different fields of science, including life sciences. It is a widely used term that describes the phenomena of self-organization. From the viewpoint of a colloid scientist it is limited, according to Shinoda's concept, to the requirements of amphiphilicity in solute-solvent interactions.

Starting from this concept different types of self-assembled polyelectrolyte systems have to be addressed. In the first part of this review, lyotropic liquid crystalline and hydrophobic polyelectrolytes, i.e. block polyelectrolytes, associating polyelectrolytes and polysoaps are discussed. In these cases the amphiphily is introduced into the hydrophilic polyelectrolyte chain by a partial rigidity (partial chain stiffness) or partial hydrophobicity (hydrophobic blocks or side chains).

Secondly, polyelectrolyte-surfactant systems are described. Here, self-assembly is created by interactions between the polyelectrolyte and the surfactant molecules. Polyelectrolyte-surfactant interactions in dilute or semi-dilute solutions, as well as in gels or the solid state are reviewed.

Lastly, self-assembly that is largely controlled by the surfactant component is discussed. In this case, polyelectrolytes can be considered as modifiers of surfactant based microemulsions, liquid crystals or foam films.

The aim of this review is to provide an overview of these different fields of self-assembled polyelectrolyte systems, illustrated by some selected examples. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Self-assembly; Associating polyelectrolytes; Block polyelectrolytes; Polysoaps; Polyelectrolyte-surfactant interactions; Polyelectrolyte gels; Microemulsions; Lamellar liquid crystals; Foams; Thin films

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1. Introduction

Polyelectrolyte (PEL) is the term used to classify macromolecules that have many charged or chargeable groups when dissolved in polar solvents, predominantly water [1]. The polyelectrolytes dissociate into a macroion and counterions in aqueous solution. One typical feature of polyelectrolytes is the extremely low activity coefficient of the counterion. If the charge density of the PEL is high enough a fraction of counterions is located in the vicinity or ‘at’ the surface of the macroion (condensed fraction of counterions) [2,3]). The physical background of the counterion–condensation effect is the competition between a gain in energy in the electrostatic interaction and a loss of entropy in the free energy. Another typical feature of polyelectrolytes is the high expansion or ‘stretching’ of the polyion chain due to the strong electrostatic repulsion between charged segments [4]. The abnormal viscosity behavior of the diluted salt-free PEL solution, i.e. the strong increase of the relative viscosity with decreasing polyelectrolyte concentration, has for many years been explained by the conformational change of the extended chain (empirically described by the Fuoss–Strauss law [5]). However, recently a series of papers has been published, showing a maximum viscosity at very low polyelectrolyte concentrations [6]. Extending the theory of dilute solutions of highly charged spherical particles [7] to solutions of rodlike polyelectrolytes, the maximum in the concentration dependence can be qualitatively described [8]. A quantitative description of the intrinsic viscosity of branched polyelectrolytes is given in Ref. [9]. Nonetheless, these features cannot be understood as a simple superposition of electrolyte and polymer properties. The interference between the polymer and electrolyte character has generated considerable interest in the field and opened new areas of application [1,10].

Polyelectrolytes and self-assembly. The self-assembly of matter is of interest as a fundamental prerequisite of life. According to Oparin’s approach [11], life originated via a spontaneous increase of molecular complexity and specificity. That is why biologists and biochemists proposed the polyelectrolyte RNA as one of the major macromolecules in living systems [12,13]. Another approach in investigating the origin of life starts from the self-assembly of phospholipids to lipid vesicles, considered as precursors of the living cell [14]. The ability of a solution to self-organize is now emerging as an approach to many new synthetic architectures, unique properties and commercial applications. Industrially important examples include micelles, bilayers, vesicles, bicontinuous structures as well as helical and folded polymers.

According to Shinoda’s concept of organized solutions there are no restriction on solvents and solute other than the requirement of amphiphilicity in solute–solvent interactions (Fig. 1) [15]. The conditions

Nomenclature

Polymers and monomers:

poly(ethylene glycol) PEG
 poly(propylene glycol) PPG
 poly(butadiene) PBD
 poly(vinylalcohol) PVA
 poly(acrylamide) PAM
 ethyl(hydroxyl)cellulose EHEC
 sodium carboxymethylcellulose NaCMC
 poly(sodium acrylate) NaPAA
 poly(acrylic acid) PAA
 poly(diallyldimethylammonium chloride)
 PDADMAC
 poly(sodium methacrylate) NaPMAA
 polystyrene PS
 poly(2-vinylpyridine) P2VP
 poly(4-vinylpyridine) P4VP
 poly(vinylpyrrolidone) PVP
 poly(allylamine hydrochloride) PAAN
 poly(L-lysine) P(Lys)
 poly(aspartic acid) P(Asp)
 β -benzyl L-aspartate-*N*-carboxyanhydride
 BLA-NCA
 acrylamide-*co*-acrylamidesulfonate *co*-AAS
 poly(sodium styrenesulfonate) NaPSS

carboxymethylchitin CMCh
 2-(dimethylamino) ethyl methacrylate
 DMAEMA
 maleic acid-*co*-styrene MA-*co*-St
 maleic acid-*co*-ethylene MA-*co*-E
 poly(L-glutamate) p(Glu)
 tetrahydropyranyl methacrylate THPMA
N-methyl-*N*-vinylacetamide NMVA
 Surfactants
 didodecylammonium bromide DDAB
 dodecylbenzenedimethylammonium
 chloride DBDAC
 dodecyltrimethylammonium bromide DTAB
 hexadecyltrimethylammonium bromide HTAB
 sodium di-2-ethylhexylsulfosuccinate AOT
 sodium dodecyl sulfate SDS
 tetradecyltrimethylammonium bromide TDAB
 dodecylpyridinium chloride DoPyCl
 dodecyltrimethylammonium chloride DTAC
 cetyltrimethylammonium chloride CTAB
 dodecylammonium chloride DoA
 acethylphenylpoly(ethylene glycol)
 Triton X-100
n-dodecyl pentaoxyethylene glycol ether C₁₂E₅

that define an organized solution according to Shinoda are:

1. Low solute solubility.
2. Swelling of solvent by solute phase.
3. Solute in a liquid or liquid crystalline state.
4. High molecular or aggregate weight of solute species.

This knowledge allows for two routes to create self-assembled polyelectrolyte systems. In the first route the amphiphily comes directly from the polyelectrolyte. This requires that the polyelectrolyte is a semi-rigid one (this requires defined solvent concentrations) or it has to be modified hydrophobically. One possible way to accomplish this is to incorporate hydrophobic side-chains or hydrophobic blocks into the main chain. The first class of such modified polyelectrolytes is named associating polyelectrolytes or polysoaps and the second block polyelectrolytes. Well-defined supramolecular polyelectrolyte structures can be induced by hydrogen bonding.

In the second route, the amphiphily is initiated predominantly by surfactant molecules.

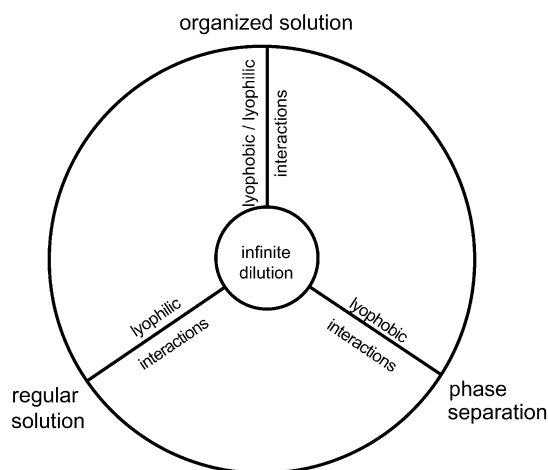


Fig. 1. Scheme of solute–solvent interactions leading to three idealized solution types.

In those cases, we have to differentiate between self-assembled surfactant–polyelectrolyte systems and polyelectrolytes in self-assembled surfactant systems. In this review, we will only look at selected examples of these topics.

2. Self-assembled polyelectrolytes

2.1. Lyotropic liquid crystalline polyelectrolytes

Semirigid or semiflexible polyelectrolytes, which are highly extended compared to conventional random coiling polymers, still possess a significant flexibility and may also impart liquid crystallinity to their solutions. Ionically modified polysaccharides as well as nucleic acids (DNA, RNA) in the double-helical conformation are typical examples. The possibility of polyelectrolytes to form ordered structures in dilute systems has been reported by several authors [16–19]. Ise et al. [18] found a single broad peak by X-ray and neutron scattering experiments, from which the Bragg spacing between the macroions was calculated. This spacing was found to be shorter than the average spacing and was attributed to the paracrystalline-distorted ordered structure of polyelectrolytes in solution. Less attention has been paid to the molecular arrangements of polyelectrolytes in highly concentrated aqueous solutions. However, it is well known that xanthans reveal a viscosity maximum in the concentration range of 3–8 wt%. The reason for this abnormal viscosity behavior is attributed to the formation of a liquid crystalline phase resulting from the formation of a semicrystalline helical structure.

Hatakeyama et al. [20–23] have systematically studied the molecular behavior of water–polyelectrolyte systems by means of differential scanning calorimetry (DSC), nuclear magnetic resonance spectroscopy (NMR) and polarizing microscopy in highly concentrated solutions. The polyelectrolytes used are cellulose sulfate, carboxymethylcellulose, lignosulfonate, xanthan and poly(styrene sulfonate). DSC heating curves of the concentrated polymer solutions (25–70 wt%) show a dependence on the type



Fig. 2. Polarized micrograph of a concentrated (30 wt%) aqueous sodium carboxymethylcellulose solution.

of polyelectrolyte. One endothermic peak present in the DSC curves is attributed to the melting of free water, and the other peak to the transition to the isotropic liquid state.

Using polarized light microscopy the authors assume that various kinds of polyelectrolytes, such as Li-, Na-, K-, Mg- and Ca-salts of carboxymethylcellulose, Na-cellulose sulfate, Li-, Na-, K- and Ca-salts of xanthan, sodium lignosulfonate and sodium poly(styrene sulfonate), form a liquid crystalline phase with an appropriate amount of water.

Our investigations of concentrated sodium carboxymethylcellulose–water systems show characteristic textures in polarized light (Fig. 2), but a second endothermic peak, identifying the transition from an assumed liquid crystalline state according to Ref. [23], disappears in the DSC curve. The DSC heating curve of Na-poly(styrene sulfonate)–water as well as Na-poly(styrene sulfonate-*co*-maleate)–water systems (30–70 wt% polymer) reveal two distinct endothermic peaks. By polarizing microscopy the formation of spherulites can be identified (Fig. 3). These observations are in agreement with our

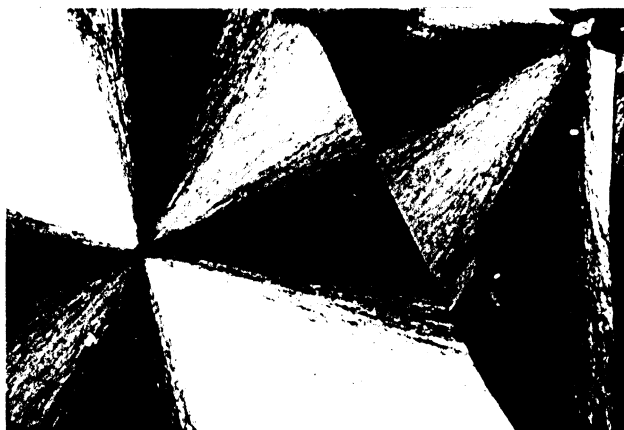


Fig. 3. Polarized micrograph of a concentrated (42 wt%) aqueous sodium poly(styrenesulfonate-*co*-maleate) solution at 8°C.

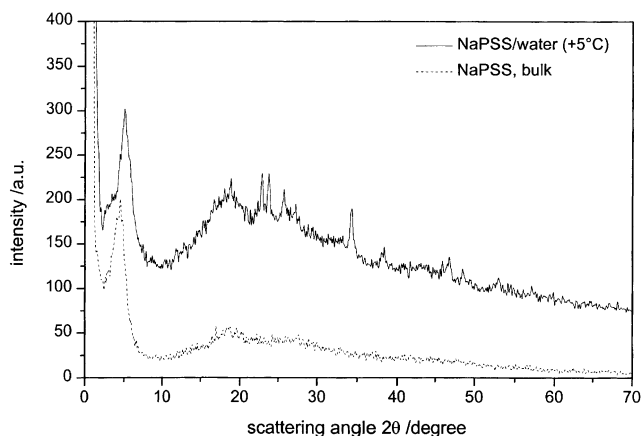


Fig. 4. Wide angle X-ray diffractogram of a concentrated (42 wt%) aqueous sodium poly(styrenesulfonate-*co*-maleate) solution at 5°C.

wide-angle X-ray scattering (WAXS) data, which exhibit semi-crystalline scattering patterns (Fig. 4). However, spherulitic behavior is often observed in the field of natural and synthetic polymers. For example, chitosan oligomers [24] or chitosan blends containing poly(ethylene oxide) are able to crystallize in the form of spherulites [25].

Another approach to liquid crystalline polyelectrolytes starts from the idea of polymerizing liquid crystalline ionic monomers. Kurihara et al. [26] described the preparation of helical polyelectrolyte networks with carboxylate groups as ionic species by polymerization of liquid crystalline monomers at the induced cholesteric phase. In Ref. [27], the polymerization in the cholesteric phase was induced by the addition of chiral molecules in the hydrogen-bonding nematic monomers resulting in helical polyelectrolyte networks.

Gray et al. [28] developed a method for cross-linking an amphiphilic polarizable mesogen mixed with a reactive hydrophilic precursor. With retention of microstructure the mixture is subsequently photopolymerized, forming a heavily cross-linked network around the precursor solution. This approach yields polyelectrolyte networks possessing hexagonally packed hydrophilic channels that are approximately 2 nm in diameter. The Na⁺ counterions associated with the carboxylate headgroups reside within these channels with an interchannel spacing of approximately 4 nm. Such polymers can be used as source materials for generating semiconductor (e.g. CdS) nanoparticles in situ [29], or for assembling transition-metal and lanthanide ions [30].

Turning to *biological* polyelectrolytes we have to differ between reversible and irreversible self-assembly. If one can take a structure from a cell or from a part of a living thing and dissolve it in solution so that it has recovered its function, it will be an example for 'biological self-assembly'. A textbook example for this type of reversible self-assembly is the tobacco mosaic virus, this consists of one kind of globular protein wound in a helix about an RNA strand [31,32]. In general, globular proteins without chemical cross-links bridging side groups are completely reversible. Those with chemical cross-links, e.g. disulfide bonds, may be irreversible. Triple-stranded collagen molecules, formed by the assembly of three larger procollagen molecules, will be a good example for an irreversible process [31,32]. A deeper insight into this special class of 'biological self-assembled' polyelectrolytes will not be discussed in this review.

2.2. Hydrophobic polyelectrolytes

Hydrophobic polyelectrolytes can be classified according to their chain-architecture as block copolymers, hydrophobically modified polyelectrolytes (or so called associating polyelectrolytes) and poly-soaps. Sometimes it is difficult to put a sharp borderline between these categories.

2.2.1. Block polyelectrolytes

The simplest type of block copolymers is a diblock copolymer consisting of two covalently bound blocks, A and B. A diblock polyelectrolyte, consisting of a hydrophilic A-block (polyelectrolyte-block) and a hydrophobic B-block in water takes on a ‘tadpole’-like conformation, because water is good for the swollen polyelectrolyte block and is poor for the collapsed block B. Several B-blocks prefer to aggregate together into a micelle core, which is stabilized by the hydrophilic polyelectrolyte-based corona (Fig. 5). This ability to form different self-assembled structures, e.g. micelles, above a critical concentration (cmc) in aqueous solutions parallels surfactant behavior. The size of diblock polyelectrolyte micelles in aqueous solution results from a balance between the surface tension of the hydrophobic core and the electrostatic repulsion with the charged corona [33,34]. With poor solvent conditions, a partial chain collapse can be expected [35,36]. What makes the block polyelectrolytes unique is the very large driving force and/or the ability to control the driving force by regulating the hydrophilic/hydrophobic balance through a variation of the molecular parameters of the two blocks. This special feature of charged diblock copolymers opens the possibility to *design* the morphology by varying the ionic strength and/or the pH of the aqueous solution. Recent experiments show a large number of different micellar morphologies, e.g. spherical or cylindrical micelles and vesicles, induced by the addition of salt or change in pH [37–40]. Using scaling arguments, Netz was able to propose a complete scaling diagram

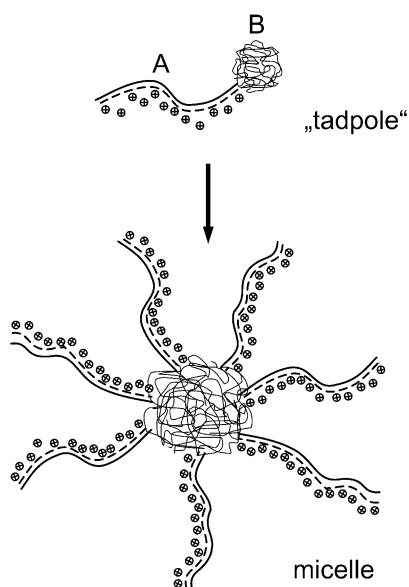


Fig. 5. Micelle formation of tadpole diblock copolymers in aqueous medium. A: anionic polyelectrolyte block. B: hydrophobic block.

obtained by comparing the free energies of different morphologies [41]. Based on this concept a change from spherical to cylindrical micelles can be brought about by increasing the ionic strength. At intermediate salt concentrations cylindrical, spherical and bilayer morphologies coexist, but bilayers are favored at high salt concentrations. The micellization phase diagram correlates well with experimental findings in Refs. [37,38,40].

The self-assembly of block copolymers often leads to well-defined patterns with topologically or chemically distinct regions. If the diblock copolymer is spread onto the aqueous surface of a Langmuir film balance distinct aggregates (termed surface micelles) can be visualized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The interfacial behavior of amphiphilic polyelectrolytes based on polystyrene (PS) poly(4-vinylpyridine) (P4VP) AB diblocks, (PS)₂₆₀ (P4VP)₂₄₀, has been systematically investigated by Eisenberg et al. [42–44]. The AB blocks were synthesized by sequential anionic polymerization, with *n*-butyllithium as an initiator, in THF, and fully quaternized with decyl iodide [42]. Depending on the block length, the surface micelles of the block copolymers can be small circles, ribbons, or lamellae of varying dimensions. The morphology is primarily controlled by the interactions between the polymer blocks and the air/water interface. X-ray reflectivity measurements of the diblock polyelectrolyte monolayers are consistent with the plateau being associated with water expulsion from the P4VP⁺ layer [45]. It can be assumed from the surface micelle core and its corona that each chain is anchored to the water surface.

The films of PS–P2VP diblock copolymers coated onto solid substrates (e.g. mica) show ordered periodic structures consisting of PS-based circular aggregates which are hexagonally packed into domains on top of the film. Generally, the segregation between P2VP- and PS-blocks strongly depends on the P2VP interactions with the solid substrates [46]. In Ref. [47], an example is given where the pattern formed from PS–P2VP serves as a self-assembled lithographic mask. Metal colloid formation in micelles of amphiphilic block copolymers is a promising new direction in modern material science for making colloid particles [48,49]. In Ref. [50] different ways of forming nanoparticles in ordered block copolymer micelles are reviewed. An example for the formation of gold particles in PS–P4VP block polyelectrolytes is given in reference [51].

Armes et al. used the technique of group-transfer polymerization [52] to prepare diblock copolymers based on 2-(dimethylamino) ethyl methacrylate (DMAEMA) [53]. Well-defined zwitterionic DMAEMA-based block copolymers can be synthesized using 2-tetrahydropyranyl methacrylate (THPMA) as the protected monomer component [54]. After removing the protecting group by acid hydrolysis essentially monodisperse DMAEMA–methacrylic acid zwitterionic block copolymers result with polydispersities comparable to those of the protected precursor blocks ($M_w/M_n = 1.18–1.24$). The isoelectric points of the zwitterionic species vary with the block copolymer composition. These block copolymers reveal a temperature controlled reversible aggregation and near monodisperse micellar aggregates in the order of 200–800 nm were formed [54]. Potential applications for these new zwitterionic block copolymers are pigment dispersions and protein separation [55,56].

Poly(ethylene glycol), PEG, based diblock copolymers with biodegradable poly(amino acid) segments, i.e. poly(L-lysine), P(Lys), as the polycation and poly(aspartic acid), P(Asp), as the polyanion, are discussed in a separate section. A specific feature of these copolymers is that both blocks A and B are water soluble. This type of block copolymer can be synthesized using *N*-carboxyanhydride polymerization [57]. The primary amine at the end of the α -methoxy- ω -aminopoly(ethylene glycol) chain, used as an initiator, attacks exclusively the carbonyl carbon of the β -benzyl L-aspartate–*N*-carboxyanhydride (BLA–NCA) ring to initiate the polymerization. As primary aliphatic amines are more nucleophilic than

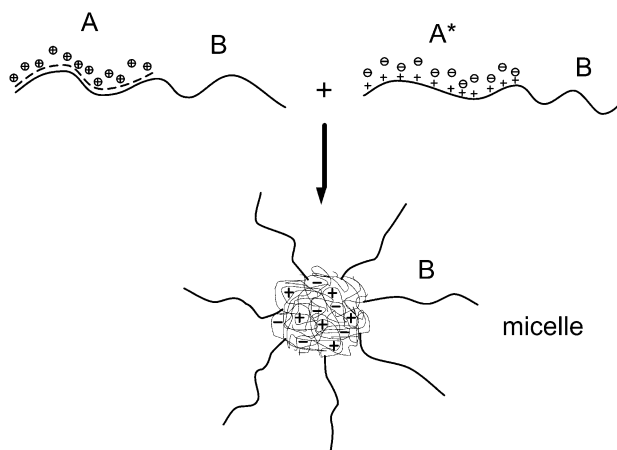


Fig. 6. Micelle formation between oppositely charged block copolymers in water. A: anionic block. A*: cationic block. B: nonionic water soluble block.

the active chain ends, all initiator molecules (i.e. PEG molecules) were incorporated into the growing chain to obtain a block copolymer of PEG and protected poly(amino acid). Mixing of the oppositely charged block copolymers PEG-P(Lys) and PEG-P(Asp) in an aqueous solution leads to the spontaneous formation of polyelectrolyte complex micelles via largely electrostatic interactions [58]. These micelles, with number average diameters of 30 nm and a polydispersity of 1.07, may have a corona of hydrophilic PEG segments which surround the stoichiometric, thermodynamically stable polyelectrolyte complex of anionic and cationic segments [59]. The micelles (Fig. 6) may have potential utility as vehicles for charged compounds in the field of drug delivery.

The formation of ionic graft copolymers, where methoxy poly(ethylene oxide) was grafted onto a poly(acrylic acid) backbone was described by Gramain [60]. However, block polyelectrolytes can also be obtained by polymer analogous reactions. A classical example is the sulfonation of polystyrene blocks according to Vink [61].

To form a network of micelles, triblock (or multiblock) copolymers with more than one collapsed block per chain are needed. BAB triblocks with collapsed end blocks can form loops [62] or stay in open configurations [63]. In selective solvents they form flowerlike micelles and reorganize at higher concentrations into clusters of micelles connected by bridges [64]. The amphiphilic block copolymers are important in interface and particle stabilization and in structure-controlled nanomaterial formation [50].

2.2.2. Associating polyelectrolytes

Polymers based on a hydrophilic backbone, to which some small amounts (typically less than 2%) of very hydrophobic groups (e.g. long alkyl chains) have been attached, will be named hydrophobically modified water-soluble polymers or associating polymers (Fig. 7). The interesting feature of this special type of water-soluble polymer is their ability to produce highly viscous aqueous solutions above a threshold polymer concentration. This viscosity enhancement is due to the strong tendency of the hydrophobic side chains to form intermolecular aggregates [65–69], presumably of a micellar type, which can act as reversible cross-links between the polymer chains. The remarkable rheological

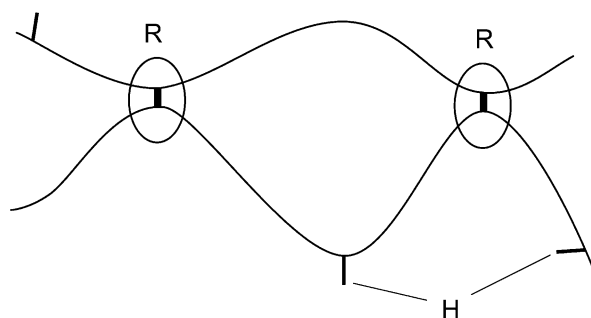


Fig. 7. A simple model of an associative polymer. H: hydrophobic side chain. R: reversible bonds.

properties of these polymers lead to many industrial applications such as paint formulations, cosmetics, paper coating and enhanced oil recovery [70].

If the hydrophilic backbone chain is an ionic one, such hydrophobically modified polymers are called associating polyelectrolytes. The molar incorporation rate of the hydrophobic groups can be higher for ionic polymers, up to 10%. Hydrophobically modified poly(sodium acrylates) can be obtained from commercially available poly(acrylic acid) by forming amide bonds with alkylamines as described in Ref. [71]. Perfluorinated analogues can be synthesized using the same procedure [72]. Both series of modified polyacrylates display the same general trends, which are typical for associating polymers: the higher the content of the hydrophobic groups or the longer the hydrophobic chains, the lower the critical polymer concentration and the more pronounced the sharpness of the viscosity increase. The molecular mechanism responsible for the viscosity enhancement, supported by small angle X-ray scattering (SAXS) and fluorescence spectroscopic measurements [73], can be explained by a micellar type aggregation. At low polymer concentrations the viscosity decreases upon addition of salt due to screening of the electrostatic repulsions. In contrast to this classical polyelectrolyte-behavior, at higher polymer concentrations and with the addition of salt the viscosity of associating polyelectrolytes can be enhanced by several orders of magnitude. In that case, the salting out effect becomes dominant, and leads us to enhanced hydrophobic association. However, because of the more hydrophobic nature of the perfluorinated groups, aggregation properties of these associating polymers are enhanced. By mixing a hydrophobically modified polymer, i.e. an octadecyl side group modified poly(acrylate), with another hydrophobic polymer, i.e. poly(*N*-isopropylacrylamide), the viscosity is enhanced several orders of magnitude [74]. Hydrophobically modified synthetic polyelectrolytes can be applied as very efficient viscosifiers, they can be used for stabilizing colloidal dispersions of highly hydrophobic particles [75] and vesicles [76].

Several reports [77–79] have been devoted to the study of hydrophobically modified nonionic water soluble polysaccharides and only a few have dealt with ionic ones. However, the hydrophobically modified polysaccharide chitosan can be considered as a characteristic example of an associating ionic polysaccharide, which has been studied recently by Nyström et al. [80–82]. Chitosan having a degree of deacetylation of 84% was modified by the reaction of C12-aldehyde to the extent of 2.5, 5, and 10% [80–82]. The linear and non-linear viscoelasticity of the hydrophobically modified samples can be affected much more by factors, such as pH, temperature and polymer concentration. The dynamic light scattering results from semi-dilute solutions revealed that the association effects are promoted by increasing the hydrophobicity.

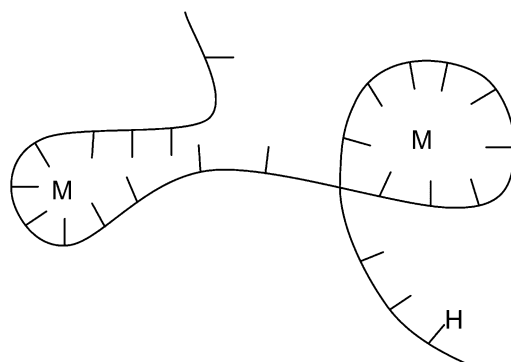


Fig. 8. A simple model of a polysoap. H: hydrophobic side chain. M: microdomain.

2.2.3. Polysoaps

A number of studies have been dedicated to polymers that can form hydrophobic microdomains in aqueous solution [83–85]. The hydrophobic polyelectrolytes, that have ionizable and hydrophobic groups, have been known to form local micelles in water (compare Fig. 8). Such polysoap behavior is known for different types of hydrophobic polyelectrolytes.

Poly(methacrylic acid) and its derivatives show a compact-globule form at acid pH and the pH-induced reversible globule-to-coil transition. The globule form has been considered to be the result of the hydrophobic interactions between the methyl groups. The abnormal pK_a versus α (degree of ionization) curve of poly(methacrylic acid), in contrast to poly(acrylic acid), indicates the pH-induced globule-to-coil transition [1,86], reflected by a sharp change of the intrinsic viscosity [87].

For alternating copolymers of maleic acid and alkylvinylether with longer side chains than butyl (four to eight carbon atoms in the alkyl groups) a similar pH-induced conformational transition to the globule form was observed [88]. Thus they behave as polysoaps at low pH and as polyelectrolytes at high pH. In an intermediate pH-region they exhibit a transition between the two conformations, which can be detected by potentiometry, viscometry, calorimetry and fluorescence probing [89–91]. Those copolymers whose alkyl group contains from one to three carbon atoms behave as typical polyelectrolytes over the whole pH-range, and those that have more than nine carbon atoms behave as typical polysoaps [89]. Hydrophobic polyelectrolytes carrying both a sulfonic and a carboxylic acid moiety with pendant chromophores can be obtained by reacting the corresponding poly(maleic anhydride-*co*-alkyl vinyl ethers) with 2-aminoethanesulfonic acid [92]. The hydrophobic polyelectrolytes with a perfectly alternating distribution of chromophores along the backbone form large aggregates in water in which the polymer chains are entangled. The aggregates that form are highly ordered. Anthony and Zana [93] studied the effect of polyelectrolyte hydrophobicity with regard to the association of cationic surfactants.

In general, the transition from polyelectrolyte to polysoap can be demonstrated by the results found with a series of P4VP derivatives, obtained by quaternization with *n*-dodecylbromide and the remainder with ethyl bromide [94,95]. Up to a dodecyl content of 6.7% the viscosity shows typical polyelectrolyte behavior. Above 13.6%, the viscosity is dramatically decreased. These abnormally low intrinsic viscosities indicate a high degree of compactness of the polysoap molecules. Weak compactness may be attributed to intramolecular contraction and intermolecular association due to hydrophobic interactions between the dodecyl groups. The sharp change of the

viscosity from 6.7 to 13.6% indicates a critical intramolecular micelle composition in analogy to the cmc of low molecular surfactants.

3. Self-assembled polyelectrolyte–surfactant systems

The interaction of polyelectrolytes with oppositely charged colloidal particles is an important phenomenon in biological systems, such as immobilization of enzymes in polyelectrolyte complexes [96] or nonspecific association of DNA with basic proteins [97]. PELs are also of special interest for commercial processes that include water treatment by colloidal flocculation [98], flocculation of cellulosic fibers in paper making [99] or recovery of mineral suspensions [100]. The interaction of polyelectrolytes with surfactants shows intriguing phenomena that are interesting and important from the viewpoints of academic research, as well as industrial applications. A lot of knowledge has been accumulated and has already been documented in review articles [101,102].

The present article is focused on polyelectrolyte–surfactant systems, where the nature of polyelectrolyte–surfactant complexes will be discussed in dilute solutions as well as in the solid state. It has to be realized that dilute solutions are important for an understanding of the concentrated systems, since a concentrated polyelectrolyte–surfactant aqueous mixture can be regarded as a system where polymer–surfactant complexes known to be present in dilute solution, interact with each other. Attention needs to be focused on the small size of the polymer-bound surfactant aggregates, which can be considered as small self-assembled structures.

Research on solid-state polyelectrolyte–surfactant complexes has multiplied, not only because of their importance in fundamental polymer physics/biophysics but also because of their potential application to pharmaceuticals, engineering, and food sciences [103–106]. Many useful properties of these complexes result from the highly ordered structures formed by the self-assembly of surfactant molecules inside the aggregates.

3.1. Polyelectrolyte–surfactant interactions in diluted systems

Most of the experimental papers on polymer–surfactant interactions in the past two decades have dealt with either interactions between polyelectrolytes and oppositely charged surfactants, or the association of nonionic polymers with ionic surfactant micelles [107,108]. In the former case electrostatic forces dominate the interaction, and hydrophobic forces play only a secondary role. The binding of ionic surfactants to the oppositely charged polyelectrolyte is a process of discharging, and is more favorable than binding to a neutral polymer. Compared to the uncharged polymer, the formation of surfactant–polyelectrolyte complexes is conceptually more straightforward since there are well-defined binding sites on the polyelectrolyte.

The properties of the polyelectrolytes are of obvious importance for the interactions with surfactants. These factors include chemical composition, linear charge density, location of the charges, and backbone flexibility of the polymers. The linear charge density of the polyelectrolyte can be correlated to the distance between adjacent charges along the polymer backbone.

A number of methods have been employed to study the interaction between polyelectrolytes and surfactants in solution. One of the basic approaches used to obtain information in the range below the cmc (critical micelle concentration of the surfactant) is the determination and analysis of the binding

isotherm. The experimental determination of the binding isotherm requires a procedure to separate surfactant ions into bound and free species. Equilibrium dialysis is a frequently used method, where the amounts of surfactant in a polymer solution and in the polymer free equilibrium solution are determined after dialysis equilibrium has been established.

Various types of spectroscopic methods allow in-situ determination of the two states of surfactant molecules, but systems in which such methods are applicable are limited. Viscosity and surface tension measurements are indirect methods yielding more qualitative results.

Surfactant selective electrodes have been developed and these have led to great progress in the study of polyelectrolyte–surfactant interaction [109,110]. The polyelectrolyte–surfactant binding isotherms permit one to extract association constants and cooperativity parameters. Analysis of these parameters yields insight into how they are influenced by variables such as surfactant chain length, polyelectrolyte linear charge density, and ionic strength.

The binding of surfactants to polyelectrolytes of opposite charge has been reported to be a highly cooperative process in which the cooperative binding range is restricted to the early stage of binding. It is known that the presence of polyelectrolyte induces aggregation of the oppositely charged surfactant [111]. As in the case of self-assembly, the aggregation starts in a narrow concentration range (critical aggregation concentration (cac)), which is usually a few orders of magnitude below the cmc of the free surfactant [108]. In a series of papers, Hansson and Almgren [112–115] have shown that the surfactant aggregates formed in polyelectrolyte solutions are similar to free micelles (Fig. 9). The influence of the charge density of the polyelectrolytes, NaCMC and NaPAA, on the binding isotherm, as well as on the surfactant's aggregation number, was studied by Hansson and Almgren [115]. They reported the binding of alkyltrimethylammonium bromide to a series of NaCMC of different linear charge densities by using a surfactant selective electrode together with time-resolved fluorescence quenching measurements. They found that an increase in linear charge density gives rise to a stronger interaction, but the aggregation number for dodecyltrimethylammonium bromide (DTAB) in solutions of NaCMC and NaPAA was

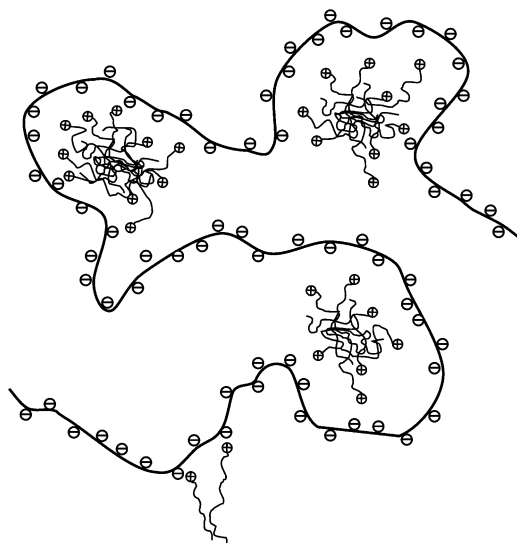


Fig. 9. Polyelectrolyte–surfactant complexes in diluted systems — necklace model.

about the same as those for the corresponding free micelles. However, the difference in flexibility between NaPAA and NaCMC had no influence on the DTA⁺ aggregation number.

Wei and Hudson [116] studied the binding of sodium dodecyl sulfate (SDS) to chitosan with various degrees of acetylation, where the polymer charge density decreases. They obtained the same initial binding constant (K) for each of the systems, which they interpreted as indicating that the contribution of the charge density variation may not be high enough to influence the effective potential at the polymer surface. A similar dependence on the linear charge density of the polyelectrolyte was also reported by Malovikova et al. [117] who studied the binding of alkylpyridinium chloride to a series of pectinates with different degrees of esterification. However, investigations of polyelectrolytes with a similar charge density showed that binding parameters can still vary significantly. Hayakawa et al. investigated the binding of different carboxylic polyelectrolytes (NaCMC, NaPAA, alginates, and pectates) to dodecyl- and tetradecyltrimethylammonium bromide [108,109]. Although the charge density of NaCMC, alginate, and pectate differ only slightly, the cooperativity parameter (u) is very much higher for the pectate and alginate system, even higher than for NaPAA, a polymer with a much smaller linear charge separation. Since the cooperative effect in the binding of surfactants by linear polymers is considered to be caused by the hydrophobic interactions between bound surfactants, one may expect this effect to be sensitive to the neighboring charge-to-charge distance on the polymer. It seems clear from these observations that the detailed structure properties of the polymer play an important role in the surfactants binding behavior. Apparently, other influences such as hydrophobic character, flexibility, and detailed local structure of the polymer can also strongly influence both the binding constant and the cooperative parameter.

The influence of the charge density of cationic and anionic copolymers in preformed soluble polyelectrolyte complexes carrying negative charges on the interaction of such complexes with the cationic surfactant dodecylpyridinium chloride (DoPyCl) was investigated by Kosmella et al. [118,119]. The studies investigated the problem of whether preferential binding phenomena occur in the aqueous pseudo-quaternary system polyanion, polycation, cationic surfactant. The results clearly showed that binding is cooperative for all systems investigated but its strength was found to be dependent on the charge density of the polyelectrolyte in the preformed complexes. The values of the binding constants indicate that the binding interaction between the complexes and the surfactant plays a minor role. The cationic surfactant molecules give preference to the free polyanion molecules in solution. Data given by static light scattering measurements on primary complex aggregates were explained by a diminished polymer chain accessibility in the presence of polyelectrolyte complexes [118].

Added salt always reduces the binding affinity between surfactants and oppositely charged polyelectrolytes. A linear relationship between the binding affinity and the salt concentration has been reported for various systems [110,117,120]. While added salt decreases the binding affinity, it increases the cooperativity of the interaction. The cooperativity is achieved via side-by-side molecular interaction of n -alkyl chains in local molecule arrangements, i.e. micellar aggregates. The addition of low molecular salt favors the formation of polymer segments because polymer chain expansion is suppressed.

The effect of polymer hydrophobicity on cationic surfactant binding in combination with time-resolved fluorescence quenching has been studied on two polyelectrolytes of differing hydrophobicity [alternating copolymers of poly(maleic acid-*co*-alkyl vinyl ether)] by Anthony and Zana [93,121]. The constant for dodecyltrimethylammonium chloride (DTAC) binding to the polyelectrolytes increased while the cooperativity parameter decreased as the copolymer hydrophobicity was increased. The binding is not cooperative but noncooperative or even anticooperative. The binding isotherms show

no critical aggregation concentration. The surfactant partitions between the aqueous phase and the hydrophobic microdomains of the polymer, which can be considered as a pseudophase. For very hydrophobic polyelectrolytes, where the majority of repeat units are involved in microdomains, the surfactant aggregation number is proportional to the surfactant concentration. In contrast, hydrophilic polyelectrolytes bind surfactants cooperatively above the cac, and the surfactant aggregation number is nearly independent of the surfactant concentration.

Shimizu et al. [122] reported a number of binding isotherms of dodecylpyridinium chloride to various alternating copolymers of maleic acid with styrene (MA-co-St) and with ethylene (MA-co-E) differing in their hydrophobicity. For the MA-co-St system they obtained a two-step binding process, while binding to MA-co-E occurs in a single step. For the more hydrophobic MA-co-St system they found the first binding shifts to a lower concentration region with increasing size of the hydrophobic side chains on the copolymer, while the binding is still cooperative. The position of the second-step binding appears to be independent of the nature of the hydrophobic side chain.

Beznan et al. [123] studied binding isotherms in combination with flow microcalorimetry on poly(styrenesulfonate)-pyridinium surfactant systems differing in their alkyl chain length. The results showed that higher local, and therefore higher total, surfactant concentrations were needed for strong binding of surfactants with shorter chain length. The observed cac's are well below the cmc of the surfactant, and were characterized by highly exothermic and surfactant independent enthalpies of binding. Furthermore, the measured enthalpies of binding (9 kJ mol^{-1}) are more exothermic than the corresponding enthalpies of micellization. The enthalpies of binding are not only determined by the aggregation of the hydrocarbon chain of the bound surfactant but also by the counterion-polyion-solvent interactions taking place in a hydrophobic environment by the bound aggregates.

Interactions of surfactants with biopolymers, e.g. proteins, exhibit several similarities to the interaction of surfactants with synthetic polymers because they are amphoteric polyelectrolytes. Surfactants are well known for their ability to denature proteins, i.e. uncoiling or unfolding of the secondary and tertiary structure without rupture of the covalent links of the primary structure. The binding of charged surfactants to protein can be viewed as taking place in two distinct stages. At first, the surfactant bind to the specific site on the protein surface, so called high-energy binding region, where electrostatic and hydrophobic interactions are involved. In the second stage of binding, the protein unfolds to expose its hydrophobic interior and hence further potential binding sites. The binding of cationic surfactants to biopolymers of low charge density occurs via a combination of noncooperative and cooperative binding [108].

The structures of protein-surfactant complexes have been investigated using photochemical techniques such as fluorescence life time studies or by NMR and SAXS measurements. Mel'nikov et al. [124,125] made a direct fluorescence microscopic observation of DNA in CTAB solutions, where a globule-coil transition was seen with increasing cationic surfactant concentration.

Shirahama et al. [126] measured the conformational changes in the anionic polypeptide/cationic surfactant system of sodium poly(L-glutamate), P(Glu) and several cationic surfactant solutions, where the surfactants differ in their head groups (dodecylpyridinium chloride (DoPyCl), dodecylammonium chloride (DoA), and DTAC). By using the combination of binding isotherms and circular dichroism they wanted to obtain additional information permitting a detailed picture of the secondary structure in polypeptides. Typical α -helix CD spectra were found of P(Glu) in DoA solutions, but neither DoPyCl nor DTAC is effective at inducing the α -helix. The authors contribute these differences to the steric

hindrance of the surfactant head group, which may inhibit the formation of organized conformation of the polypeptide.

A review of the models presented for polymer–surfactant complexes is given by Shirahama in Ref. [127]. For example, Cabane and Duplessix proposed a model based on NMR and neutron scattering studies [128]. They also suggest the term ‘necklace’ for the initial ionic binding sites along the polymer chain, micelle-like aggregates are clustered with increasing surfactant concentration. It is noted that the aggregate sizes are always smaller than the micellar aggregation number under the same solvent conditions. This may be due to the fact that the amphiphilic polymer chains are meandering through the methylene groups adjacent to the ionic groups of aggregated surfactants. The polymer chain protects these methylene groups from the aqueous solvent. This process seems to favor smaller aggregation numbers.

3.2. Polyelectrolyte–micelle complexes

Above the cmc, polyelectrolytes most often interact with oppositely charged surfactants so strongly that irreversible macroscopic phase separation usually occurs. This, at one time, inhibited studies on polyelectrolytes with oppositely charged surfactant micelles. Dubin et al. [129] showed that such strong electrostatic interactions can be attenuated by ‘diluting’ the surface charge of ionic surfactant micelles with nonionic surfactants. This results in the formation of soluble polyelectrolyte–micelle complexes. Consequently, it became possible to identify a critical micellar surface charge necessary for complex formation and its square-root dependence on ionic strength [130,131].

Many experimental approaches have been used to study polymer–surfactant interactions, but relatively few techniques can be utilized to identify and to clarify the dynamics of polyelectrolyte–micelle association. Valuable information can be derived from static and dynamic light scattering experiments. But soluble complexes can only be detected by quasielastic light scattering if their lifetime is sufficiently long and the scattering intensity of the complexes is large compared with those of the micelles and polymers from which they are formed. Fluorescence measurements have been used to study polymer–surfactant interactions because of their inherent sensitivity. Recently, Dubin et al. [132,133] examined the quenching of a pyrene labeled polyanion. The quenching arises from polyanion interaction with cationic micelles and interactions with mixed micelles of a cationic and nonionic surfactant. Based on a kinetic model for polymer–micelle association, Dubin et al. calculated the binding constant and association constant from fluorescence quenching data. The binding is strongly dominated by the electrostatic forces, although they found that micelles preferentially bind to pyrene sites, so that complex formation results from electrostatic and hydrophobic forces.

A review article concerning ^2H NMR studies of polyelectrolytes interacting with deuterio-labeled surfactants in different surfactant self-assembled architectures like micelles, monolayers and bilayer membranes was published by Macdonald [134]. In the case of phase-separated anionic polyelectrolyte–cationic surfactant micelle complexes, the authors illustrate the ability of ^2H NMR to provide information on molecular order and dynamics. For example, Monte Carlo simulations on ^2H NMR spectra suggest that greater polyelectrolyte chain flexibility produces more compact polyelectrolyte–surfactant complexes [135]. In other words, the differences in packing density within the phase-separated polyelectrolyte–surfactant micelle complexes arises from differences between the flexibility of the polyelectrolytes involved. The molecular motion amongst surfactants within the polyelectrolyte–surfactant micelle complexes were investigated by temperature-dependent NMR measurements [136].

Swanson-Vethamuthu et al. [137] carried out Cryo-TEM on samples containing polyelectrolyte–micelle complexes, formed by combining poly(diallyldimethylammonium chloride) (PDADMAC) as a strong cationic polyelectrolyte with oppositely charged mixed micelles of SDS and nonionic Triton X-100. Microscopic observations are largely consistent with conclusions of earlier light scattering studies on such systems. Complexation appears, presumably, within the domains of polymer chains involving the formation of micelle-rich regions. The complexes are highly ordered and quite dense, but Cryo-TEM reveals no particular organization of the micelles in these complexes. At polymer concentrations above 0.4 g l^{-1} , clusters with dimensions of 50 nm are observed. With increasing polymer concentration the dimensions of aggregates continue to grow indicating the involvement of many polymer chains.

The fundamental question, whether micelle structure is or is not preserved upon binding is still ambiguous with respect to the complexes of charged polymers with oppositely charged surfactants. Abuin and Scaiano [138] found $N/N_0 \cong 0.1$ (where N and N_0 are the aggregation numbers for complexed and uncomplexed micelles, respectively) for poly(sodium styrenesulfonate)–DTAB. Almgren et al. [139] found for a system in which $N/N_0 \cong 0.5$ little effect of poly(sodium acrylate) on the aggregation number of DTAB [18].

3.3. Surfactants in polyelectrolyte gels

Research studies on polymer gels have increased, because water-equilibrated polyelectrolyte–surfactant complexes have potential use in biology. The ability of the gels to absorb large amounts of water (up to several hundred times its own weight) is utilized in many commercial products.

Polymer gels are made of linear polymers, cross-linked to make a network in which water and ions can penetrate. Surfactant binding to polyelectrolyte gels can be compared to polyelectrolyte–surfactant interactions in solution, but the binding is less cooperative [140,141]. This effect is ascribed to the interruption of binding at the cross-linking sites resulting in a limited interaction. Okuzaki and Osada [140] showed a decreasing cooperative nature of the system DoPyCl and poly(2-acrylamido-2-methylpropanesulfonic acid) in dependence on the increasing degree of cross-linking. For the complexes formed, they proposed a cubic structure identified by SAXS.

Kabanov et al. [142] proposed a lamellar structure for NaPAA gel– C_n TAB complexes. The authors demonstrate that the lamellar thickness increases with increasing hydrocarbon chain length in surfactant homologues. By analyzing SAXS diffraction data they represent the complex structure as a system of surfactant lamellae inserted into an oppositely charged network.

By using high resolution SAXS, Chu et al. [143] investigated the effect of hydrophobic character in terms of the surfactant alkyl chain length and the hydrophobicity of the polyelectrolyte chain for the system NaPAA, NaPMAA and C_n TAB. The complexes showed highly ordered cubic structures at $10 \leq n \leq 16$. The longer the surfactant alkyl chain, the lower the charge density and the hydrophobicity of the polyelectrolyte chains drives the formation of highly ordered structures inside the resulting complexes. To examine the flexibility effect of polyelectrolyte chains on the nanostructured polyelectrolyte–surfactant complexes, the authors also chose NaPSS. The 2D hexagonal structures observed for this water-equilibrated system were different from the layered structures found in the corresponding solid-state complexes [144].

The influence of charge density was studied using the interaction of slightly cross-linked anionic polyelectrolyte copolymer gels with oppositely charged surfactants [145]. The resulting complexes show

very rich, highly ordered cubic nanostructures. The charge density variation of the polyelectrolyte chains can induce a phase structure transition of the formed complexes. When the charge density is decreased, the structures inside the complexes become less ordered. The structural elements in these aggregates were shown to be spherical and/or cylindrical micelles. These micelles are formed by the self-assembly of the surfactant molecules inside the complexes, driven by electrostatic and hydrophobic interactions.

Structural studies of a cross-linked PAA gel interacting with the cationic surfactant dodecyltrimethylammonium bromide using time-resolved fluorescence quenching have been reported [146]. Hansson investigated the transition of the gel from the highly water-swollen state at low surfactant contents to the collapsed state. In addition, a model is presented, describing the volume changes induced by the formation of globular surfactant micelles in the covalently cross-linked network [147]. A statistical mechanical description of the volume transition of the gels and the influence of surfactants on the volume phase transition is given by Tanaka et al. [148].

Polyelectrolyte–surfactant complexes of polycationic gels and anionic surfactants have been studied by using SAXS [149]. Khokhlov et al. investigated the system of slightly cross-linked networks of PDADMAC and dodecylbenzenesulfonate in the presence of low molecular salt. Especially in the presence of large amounts of salt the complexes can be nonstoichiometric. The SAXS diffractograms indicate a more ordered structure for such nonstoichiometric complexes than that of the complexes prepared in the absence of salt.

PDADMAC–gel complexes with SDS and mixed *n*-alkyl sulfate surfactants are the focus of the SAXS research activities of Chu et al. [150,151]. It was reported that the mixed surfactants could form a multitude of crystalline structures gradually changing from cubic to hexagonal as the composition of the surfactant mixture was changed. For the PDADMAC–gel–SDS system it was found that the complexes exhibit a highly ordered hexagonal supramolecular structure. It is interesting to note that the polyelectrolyte–surfactant complexes do not form a highly ordered structure in the gel phase when the initial external SDS concentration is above the cmc.

3.4. Polyelectrolyte–surfactant complexes in the solid state

Solid-state polyelectrolyte–surfactant complexes have recently received interest as a new class of materials with unusual optical, electrical, and mechanical properties. Remarkably diverse mechanical properties ranging from elastomers to crystalline solids can be achieved. Control over the organization of synthetic supramolecular structures by tuning the assembly processes opens fascinating possibilities in manipulating properties of materials on the nanometer scale. Ober and Wegner [103] have reviewed the growing quantity of research in this fascinating field.

Stoichiometric polyelectrolyte–surfactant complexes are in general insoluble in water but soluble in organic solvents of low polarity. In the solid state, the 1:1 combination leads to the spontaneous formation of highly organized assemblies with lamellar structures [152,153]. Tirrell et al. [154,155] reported the solid state properties of the stoichiometric complexes formed by the synthetic polypeptide sodium poly(α ,L-glutamate) and the oppositely charged surfactants dodecyl and cetyltrimethylammonium bromide. They showed that the polymer chains in the complexes adopt an α -helical conformation in the solid state. With ^1H NMR, SAXS, and WAXS measurements two types of surfactant organization were observed: shorter disordered chains and longer chains crystallized in a hexagonal lattice. Generally, the complexes are organized in lamellae consisting of alternating layers of the polypeptide chains separated by bimolecular layers of surfactant.

Polyelectrolyte–lipid complexes were studied by Antonietti et al. [156]. Polyelectrolyte–lipid complexes were used as matrices for functional molecules to study biological membrane processes. In these studies the authors focused their experiments on the resulting superstructure of the complexes. The complexation of soybean–lecithin with PDADMAC results in a very well defined stack of bilayer lamellar order with a long period of $d = 5.09$ nm. The complexes can be isolated as free-standing films with properties of a rubbery material.

Other examples of different lamellar modifications were seen in a series of complexes between NaPSS and various alkyltrimethylammonium surfactants. All these complexes show, in addition to a principally lamellar structure, different interface undulations [153,157].

The structure and mechanical properties of new fluorinated surfactant-containing polymer complexes which form ordered colloidal structures were investigated by Thünemann et al. [158]. Films prepared from the complex exhibit a remarkably low critical surface tension and show lamellar repeat units. Moreover, the high solubility of oxygen in these films, combined with the high order and mobility inside the structure enables the construction of highly permeable and selective gas membranes.

Nuyken et al. [159] report on the structure of polyelectrolyte–surfactant complexes containing photo-labile diazosulfate chromophores by means of SAXS and WAXS measurements. The incorporation of functional groups might render these bilayered complexes ‘intelligent’, because the structure can selectively be changed. Polymers containing these chromophores were found to be suitable as photo-resins in offset printing techniques since upon radiation the water-soluble polymer is converted into a fully insoluble polymer accompanied by the loss of the sulfonato group [160].

Another way to change the structure inside the complexes is by the introduction of monomer surfactant thereby obtaining a mesoscopically structured material with improved mechanical, thermal, and solvent resistance. Dreja et al. [161] found that monomeric surfactants can be used to form polymerizable polyelectrolyte–surfactant complexes with controlled mesoscopic properties and internal order. The mesoscopic dimensions can be tuned by varying the length of the hydrophobic surfactant tails.

4. Polyelectrolytes in self-assembled surfactant systems

4.1. Polyelectrolytes in microemulsions

Microemulsions [162] are homogeneous, optically isotropic mixtures of water, oil and surfactant (and cosurfactants) that are thermodynamically stable. In systems made of nonionic surfactants the temperature controls structure and stability. The spontaneous curvature, H_0 , decreases with increasing temperature. This temperature dependence permits the formation of o/w (oil in water) spherical droplets at $T < \text{PIT}$ (phase inversion temperature), bicontinuous structures at $T \cong \text{PIT}$ and w/o inverse spherical droplets at $T > \text{PIT}$. Microemulsions containing ionic surfactants can be controlled similarly by varying the ionic strength and the concentration of cosurfactants. The described structures vary in size between 1 and 40 nm. The topology of the surfactant monolayer (spherical, cylindrical, planar, spongelike etc.) that divides oil and water domains, is dependent on geometric considerations (i.e. relation between the hydrophilic and hydrophobic part) and its bending elasticity [163] according to the Hookean equation [164] for the curvature free energy:

$$dG_c = (2\kappa(H - H_0)^2 + \bar{\kappa}K) dS \quad (1)$$

with the mean and Gaussian curvatures $H = (c_1 + c_2)$, and $K = c_1c_2$ (c_1 and c_2 are the two principle curvatures). Both constants κ and $\bar{\kappa}$ are the bending modulus and the saddle splay modulus and have a dimension of energy. While the bending modulus describes the flexibility of the monolayer, the saddle splay modulus is connected with the surfactant film topology. High quotients of the bending modulus to the thermal energy $k_B T$ describe rigid monolayers, like liquid crystalline phases, and quotients near one, i.e. the thermal energy $k_B T$ is comparable to the bending modulus, describes bicontinuous phases.

Nonionic hydrophilic polymers in microemulsions. Similar to liquid crystalline phases and thin films in foams some topologies of microemulsions, like bicontinuous and inverse spherical structures, form a constrained environment for hydrophilic polymers. Beside the interactions of polymers in bulk solution the energetic and entropic contributions of polymer–surfactant monolayer interactions have to be considered. The effect of a nonadsorbing water-soluble polymer (dextran) onto a balanced nonionic microemulsion was studied for the system water/ $C_{12}E_5$ (*n*-dodecyl pentaoxyethylene glycol ether)/decane [163,165]. Dextran is partitioned between the bicontinuous microemulsion and the excess water phase. The partition coefficient decreases strongly with an increase in the end-to-end distance, of dextran. At similar values of pore size of the microstructure and end-to-end distance no polymer is found in the bicontinuous microemulsion. Dextran with a high molecular weight is confined to the excess water phase. The addition of dextran leads to an increase of the osmotic pressure and therefore the volume of the microemulsion decreases by expelling oil and water. This behavior is also characteristic for other polymers, such as water-soluble PEG and oil-soluble poly(isobutylene). Consequently, the observed effects are steric and do not depend on the chemical nature of the polymer. While ethyl(hydroxyl) cellulose (EHEC) shows the same behavior, a hydrophobically modified sample containing 6.5 hydrophobic side chains per molecule is partitioned strongly to the microemulsion phase [166]. The hydrophobically modified EHEC causes a strong asymmetric swelling of the microemulsion phase preferred with water and to a lesser degree with oil. Above a saturation concentration additional polymer is solubilized in the excess water phase causing a contraction of the microemulsion phase by the osmotic pressure. The adsorbed polymer also affects the spontaneous curvature resulting in a positive shift.

The influence of polymers on the size and interdroplet interactions in inverse ionic droplet microemulsions was discussed considered in Refs. [167,168,171–174]. The effect of three groups of polymers on the system (sodium di-2-ethylhexylsulfosuccinate (AOT)/decane/water/alcohol) was studied: (1) water-soluble polymers (PEG, PAM and PVA); (2) an oil-soluble poly(butadiene), PBD, and (3) poly(propylene glycol), PPG, that is distributed between the water and oil phase [167]. Addition of the water-soluble PEG, PAM, PVA and PPG decreases the attractive interactions between droplets, which also decrease with increasing molecular weight of PEG. Furthermore, the droplet size dependence on concentration and molecular weight of PEG is reduced. This correlation can be understood by visualizing the decrease in droplet size as being due to the decrease of the overlapping domain of the interface of two colliding droplets. However, the oil-soluble PBD increases the attractive interactions in a similar way as an increase of the oil chain length induces a growing of the droplet size [168,169]. This is due to the decreasing penetration of the oil in the interfacial film of the droplet and the increasing overlapping of the film upon collision of the droplets. For PPG both effects have to be considered but the former dominates. Further investigations [170] extend the AOT based system to other surfactant based microemulsions like the anionic SDS and the cationic hexadecyltrimethylammonium bromide (HTAB) and dodecylbenzenedimethylammonium chloride (DBDAC). However, dynamic light scattering measurements (DLS) indicate that the hydrodynamic radius increases in the presence of PEG [171]. The PEG induces a structural reorganization of the dispersed phase leading to larger droplets that include

the polymer chains. Nanosecond luminescence quenching experiments support the observed results. With low molecular weight PEG ($M_w < 1000$) the surfactant monolayer at the oil–water interface is only modified, i.e. an increase in the electrical conductivity is observed [172]. The structure of the microemulsion is altered at polymer chain lengths comparable or larger than the droplets. At higher polymer concentration a percolating structure is found.

The influence of PEG on the inverse microemulsion of anionic (AOT) and nonionic ($C_{12}E_5$) surfactants is compared in Ref. [175]. For polymers that are *smaller* than the droplet radius the phase behavior of the nonionic system remains unaffected with increasing polymer concentration. However, in the ionic system the droplet phase is broadened and shifted towards higher temperature. Furthermore, conductivity measurements reveal a shift of the percolation transition to higher temperatures with increasing polymer concentration. At the percolation boundary the theory [175,176] gives the expression for the elastic bending constant κ . This constant increases from the polymer-free case to the polymer-containing microemulsion. Therefore, it can be expected that the polymer adsorbs at the surfactant monolayer and makes the surfactant film more stiff. In contrast to the ionic system in the nonionic microemulsion a depletion effect should occur. The polymer is found in the droplet interior. If the polymers are *larger* than the droplet radius, the polymers cannot be dissolved in the nonionic microemulsion because of geometrical considerations. The addition of polymer causes a macroscopic phase separation for these systems. In the ionic microemulsion the high molecular weight polymers can be dissolved by attractive polymer/surfactant interactions. The dissolution induces the formation of droplet clusters of a size comparable to the polymer coil.

The phase behavior of the system AOT/water/isooctane modified by PEG is investigated in detail in Refs. [177,178]. The addition of PEG significantly affects the stability and the extent of the different microemulsion phases. Large amounts of PEG, replacing water by 17% PEG, can be solubilized in the microemulsion. The PEG-solubility depends on the size relation R_w/R_G (radius of water core/radius of gyration): for $R_w/R_G < 1$, the solubility in the L2 phase is extremely low and for $R_w/R_G > 1$, the solubility increases with R_w . PEG also enhances the efficiency of the surfactant to solubilize water in the inverse droplet microemulsion. The polymer stabilizes large droplets. The molar ratio of water to surfactant is increased from 55 (without PEG) to 150. The largest droplets contain up to 200 PEG (20 K) chains. An interesting feature is the modification of the hydrophilicity of AOT after the addition of PEG. At constant composition the polymer changes the sign of the spontaneous curvature of the surfactant film and causes an inversion of the microemulsion from the o/w to the w/o type. Furthermore, electrical conductivity and light scattering data indicate a decrease of attractive interactions between micelles in the presence of PEG.

Synthetic polyelectrolytes in microemulsions. Beside the interactions found in the system microemulsion-nonionic polymer, electrostatic forces have to be considered when polyelectrolytes are added. These forces dominate the behavior of polyelectrolyte–microemulsion systems and result in new properties. The effects produced by equally and oppositely charged systems can be subdivided in the next section as follows: (1) polyelectrolytes in nonionic microemulsions; (2) oppositely and (3) equally charged polyelectrolyte–microemulsion systems. Furthermore, we prefer to regard here bicontinuous and w/o microemulsions according to their constrained environment. The o/w (L1) phases are treated here only in some cases.

The influence of an anionic NaPAA and the corresponding hydrophobically modified polyelectrolyte containing octadecyl side chains, on the phase behavior of the nonionic system $C_{12}E_5$ /water/decane was reported in Ref. [179]. The NaPAA is found to be insoluble in the lamellar liquid crystalline and the

sponge (L3) microemulsion phase, because of the geometric relations. The unperturbed polyelectrolyte coil size is comparable or larger than the water domains in both phases. In the L1 phase, with only minor restrictions on the polymer conformations, the NaPAA is soluble. In contrast the hydrophobically modified NaPAA can be solubilized in all three diluted phases. It can be assumed that the hydrophobically modified polyelectrolyte is adsorbed at the surfactant bilayers. The nonionic bilayers will be charged and long-range electrostatic interactions occur. The temperature stability of the L3 phase becomes wider and a strong shift of the phase boundaries to higher temperatures results. Furthermore, a positive shift of the spontaneous curvature of the surfactant monolayer was observed, this induces a transition from the lamellar to the L1 phase at higher polymer concentrations. A similar behavior was observed by adding small amounts of ionic surfactant to a nonionic surfactant film [180]. In Ref. [181], the effects of hydrophobically modified NaPAA on a balanced microemulsion ($C_{12}E_5$ /water/decane) was studied in a similar way as reported for the hydrophobically modified EHEC [166]. With growing polymer concentration the water/oil ratio in the bicontinuous microemulsion increases until a saturation value of polymer adsorption is reached at the surfactant bilayer. Then excess polymer is partitioned into the water phase causing an osmotic pressure that reduces the water/oil ratio in the bicontinuous microemulsion again. The saturation value found for the polyelectrolyte was determined to be 0.2 mg of polymer per m^2 of the surfactant film and corresponds to that for EHEC [166]. The solubility of the hydrophobically modified NaPAA in the balanced nonionic system depends on the geometry of the confinement and the surfactant film topology [181]. While the polymer is readily soluble in the bicontinuous microemulsion, in the lamellar phase its solubility depends on the polymer and salt concentration. It seems that the polymer is less confined in the three-dimensional continuous water labyrinths of the microemulsion than in the flat topology of the lamellar phase. At higher ionic strength the solubility in the lamellar phase is improved due to screening of the electrostatic interactions. The addition of hydrophobically modified NaPAA above a certain polyelectrolyte concentration to droplet microemulsions, leads to the formation of viscoelastic gels [182]. Furthermore with increasing temperature a viscous microemulsion can be transformed to a viscoelastic gel, the transformation is attributed to a major change in the surfactant aggregate structure.

Strong interactions should be found between the oppositely charged polyelectrolyte (NaPAA; $M_w = 30\,000$) and the surfactant didodecylammonium bromide (DDAB) in the w/o droplet microemulsion (DDAB/cyclohexane/water) [183]. Additionally, a nondissociated PAA ($M_w = 450\,000$) was used. DDAB forms rodlike aggregates in the organic phase, which remains unchanged after addition of both polymers. This result was confirmed by several methods like SAXS, DLS, conductivity and viscosity measurements. A reasonable explanation is based on the adsorption of DDAB at NaPAA that leads to a neutral complex solubilized in the water core of the DDAB aggregates. With neutralization, NaPAA loses its stretched conformation and its size, which is now comparable to the size of the DDAB aggregates. PAA with its high molecular weight was also dissolved within the water pool without any structural changes of the single DDAB aggregates but the polymer chains connect the rodlike aggregates, strongly increasing the viscosity. DDAB forms a more rigid surfactant film. Therefore, the inversely charged system of a positively charged polyelectrolyte poly(allylamine hydrochloride), PAAN, ($M_w = 72\,600$) and an anionic surfactant (AOT) based w/o microemulsion (AOT/*n*-hexane/water) was studied in Ref. [184]. A decrease in the conductivity was found in the microemulsion containing PAAN in comparison to the pure microemulsion connected with a shift of the percolation boundary ($\phi > 0.1$). A possible explanation is a reduction in the ion mobility in the water pool by the polyelectrolyte. SAXS measurements show significant changes in the scattering curves, which allow the

determination of two radii R_1 and R_2 . R_1 corresponds to the droplet radius and R_2 can be related to a polymer coil. Both SAXS and conductivity measurements provide a structural picture of a droplet cluster connected by a polymer chain, called a pearl-necklace structure. The formation of long water channels can be precluded. The structure factor for the chain was expressed by the modified Ornstein–Zernike correlation function from which the spatial extent of the chain structure was estimated. The radius, R_2 , of the salt free system was near the end-to-end distance of an uncharged polymer chain whose degree of polymerization was the same as that of PAAN. PAAN behaves like an uncharged polymer due to the strong electrostatic interaction with AOT. Its size depends on the salt concentration of the coexisting aqueous phase. With increasing salt concentration the interactions between AOT and PAAN become smaller and an increase of R_2 is observed because the number of monomer units of PAAN decreases in the droplets. A larger number of droplets are necessary to solubilize the polymer chain leading to larger R_2 . The radius R_1 becomes correspondingly smaller.

In a Winsor II microemulsion (AOT/isooctane/water) the partition behavior of a positively charged polyelectrolyte (quarternized poly(vinylpyridine)) between the aqueous and the reverse micellar phase provides a deeper insight into the interactions between the surfactant and the polyelectrolyte and the structure of the resulting surfactant–polyelectrolyte complexes [185]. This complex is insoluble in pure isooctane and water phases. At a surfactant-to-cationic monomer concentration ratio ≥ 1.4 , the complex becomes soluble in the reverse micellar phase and is transferred quantitatively from the aqueous to the micellar phase. The ratio shifts to lower values from 1.4 to 1.1 when the counterion of AOT is changed from sodium to barium. Ultracentrifugation experiments indicate strong interactions between the AOT–polyelectrolyte complex and the reverse micelles. The authors suggest coexistence and a certain kind of aggregation between both. In comparison to polyelectrolytes, the transfer of amino acids and enzymes is characterized by their incorporation in the core and/or the shell of the reverse micelles.

Strong changes in the phase behavior of the quarternary system SDS/pentanol/xylene/water were induced by the addition of the oppositely charged PDADMAC [186]. High amounts, up to 20%, of the polyelectrolyte can be incorporated into the water-in-oil microemulsion. With increasing polymer concentration the area of the inverse microemulsion is reduced relative to higher water content, but the area is extended to an increased surfactant content. This can be rationalized only by the formation of polymer–surfactant complexes, which changes the composition of the microemulsion phase. The true SDS content forming the microemulsion has to be corrected by the term $m(\text{free SDS}) = m(\text{total amount of SDS}) - m(\text{complex bound SDS})$. These complexes are solubilized in the water core of the inverse micelles or they are incorporated into the surfactant film that leads to membrane stabilization. For both explanations experimental confirmations are available. Rheological measurements provide an indication for the formation of droplet clusters connected by polymer chains analogous to Ref. [184]. A strong shift of the percolation boundary was found by conductometric measurements and could be related to an enhanced membrane stability.

In comparison to the oppositely charged systems where large amounts of polyelectrolytes can be solubilized, in equally charged systems only small amounts of polymer can be incorporated [187]. Even with small amounts of charged polyelectrolytes the area of the inverse microemulsion decreases, e.g. NaPAA and NaCMC in the systems AOT/isooctane/water and SDS/pentanol/xylene/water. The phase behavior of such charged polymer–surfactant mixtures is discussed only in a few studies [188] and segregative phase separation was observed. This is analogous to the polyelectrolyte mixtures. Since the entropic counterion effect of ionic/nonionic and oppositely charged polymer mixtures is missing, such behavior can be rationalized.

Proteins in microemulsions. In this part only some general comments on proteins will be given, taking into account that a large number of review articles have appeared in the last few years [189–193]. Proteins can be treated as polyelectrolytes because of the relationship between the pK_a of the protein and pH of the surrounding solution. The solubilization of enzymes in reverse micellar solutions has two possible important applications. The reverse micelles with the enzyme solubilized inside the water core can be used as microreactors. In these microreactors it is possible to overcome incompatibility problems between polar enzymes and nonpolar substrates or products that can be dissolved in high concentrations in the continuous oil phase. Another advantage is that adjusting the water content can shift thermodynamic equilibria of reactions. Sometimes enzymes are found to be more active in these microreactors than in aqueous buffer solution. Enzymes found in nature are often present in heterogeneous, hydrophobic microenvironments (cells). The other important application is the liquid–liquid extraction of proteins in Winsor II microemulsions, i.e. between a w/o-microemulsion and an aqueous phase [193]. The distribution equilibrium is influenced by several factors like the pH, ionic strength, type of salt, concentration and nature of surfactant, and cosurfactant respectively, and the nature of oil and temperature. A protein of opposite charge favors its transfer into the reverse micellar phase. The charge of the protein depends on the pH of the solution and the isoelectric point of the protein (ribonuclease $pI = 7.8$; cytochrome $pI = 10.6$). This means proteins can be extracted from protein mixtures by adjusting the pH. Many proteins were solubilized completely at low salt concentration and no solubilization occurred at high ionic strength, which is important for the back transfer. The distribution behavior is also influenced by affinity ligands and the hydrophobicity of proteins. Increasing the temperature of a saturated microemulsion leads to a separate aqueous phase, concentrated by the enzyme. Enzymes can be recovered in this expelled phase at extremely high concentrations (up to 2000 times the initial concentration [193]).

Enzymes are very sensitive probes of changes in the microenvironment, which can be determined by measurements of the enzymes' activity. The activity varies for each enzyme relative to its dependence on the water content of the microemulsion [192]. Some lipases reach their optimum activity with traces of water in the organic solvent; other lipases need a significantly higher water content. At low water content the enzymes are in a frozen conformation as revealed by CD measurements. The first water molecules interact with ionizable groups that lead to a higher rigidity of the biomacromolecule. At about $w = 5$ (molar ratio of water-to-surfactant) the minimum enzyme activity is reached. Further addition of water hydrates the hydrogen-bonding sites. The activity-water content function is bell-shaped with its maximum near $w = 10$. It seems that the activity maximum corresponds to a structure in which the droplet radius is a bit larger than the radius of the enzyme [192]. The activity maximum is often connected with an enhanced activity compared with the bulk phase. In reverse micelles a shift in pH profiles is observed compared with the aqueous buffer solution [193]. The pH for the maximum activity of α -chymotrypsin in AOT/heptane shifts 1.5 pH units compared with that in the aqueous medium. Local influences of the charged interface layer around the enzyme, changes in the pK_a of ionizable groups due to dehydration and conformational changes in the enzyme can be the reason for the observed phenomenon.

The water-shell model gives a structural description of enzyme hosted reverse micelles. It is assumed that the enzyme is confined inside the water core and is protected by a water layer from the charged micelle interface. This model is restricted to hydrophilic proteins without large hydrophobic domains. More hydrophobic enzymes like lipases are adsorbed at the micelle interface and the hydrophobic domains are incorporated into the nonpolar part of the interface. Such a hydrophobic interface is

necessary for some lipases to open the lid covering the binding site [194]. After addition of enzymes to reverse micelles, the micelles that incorporate the enzyme grow in size at the expense of the empty ones [195], provided that the radius of the enzyme (R_E) is larger than the radius of the reverse micelle (R_M). An alternative model [196] proposes that no size effects should be observed after protein solubilization if $R_M \geq R_E$.

In the w/o-microemulsion based on AOT, lipase (*penicillium simplicissimum*) is located at the interface but does not strongly perturb the intermicellar interaction [197]. A decrease of the micellar radius was found at small lipase concentration (6×10^{-6} M) by SAXS. The influence of lipase (*pseudomonas cepacia*) on the structure of two microemulsions based on lecithin and AOT was examined [198]: The enzyme activity of the esterification of lauric acid and some alcohols was determined in both microemulsions. While esterification for lipase was not dependent on the chain length of the alcohols in the AOT based micelles, in lecithin based micelles a strong decrease of the esterification rate was found for the chain lengths from propanol to hexanol. The reason for this is the high solubility of propanol in water, while hexanol is soluble only in oil. Consequently, the interface of both micelles forms barriers of different strength for the diffusion of alcohols. In AOT based microemulsions, lipase decreases the number of individual micelles forming clusters and makes the interfaces less stiff and easier to penetrate. The microstructure of a lecithin microemulsion is based on a channel-like complex network of aqueous compartments. The lipase inhibits the communication between already existing compartments.

4.2. Polyelectrolytes in liquid crystalline systems

Lytotropic liquid crystalline phases, the most commonly encountered type of liquid crystals (LC), are formed upon the dissolution of amphiphilic molecules in a solvent. The amphiphilic molecules, e.g. surfactants, aggregate to micelles above the cmc and generate lyotropic liquid crystalline phases under certain conditions, i.e. at high surfactant concentrations. The lyotropic LC-phases can be lamellar, hexagonal or cubic are of significance as models for biological membranes, in cosmetics and in colloidal drug delivery systems. Polymers can modify the properties of thermotropic LC-phases, but our fundamental understanding of polymer-modified lyotropic liquid crystals is still rather limited. However, by manipulating with the inter-membrane interactions and the polymer–bilayer interactions the properties of the lamellar LC-phases can be modified significantly. The most appropriate ionic lamellar liquid crystalline model system, consisting of a long chain alcohol, SDS, and water [199] was used by several researches for systematically studying the influence of polymers.

Nonionic polymers in LC phases. Noncharged polymers, like PEG, were incorporated into lamellar AOT-water systems [200,201] as well as into lamellar structured lecithin films [202]. Generally, the polymers influence the interactions between the bilayers. The decrease of the compressibility modulus, determined by a surface force apparatus, indicates a softening of the bilayer interactions with increasing PEG-concentration. These findings can be rationalized in terms of a bridging mechanism [203]. The influence of noncharged polymers on structure formation in a nonionic surfactant based $L\alpha$ -phase has been reported [204]. The results indicate that the main reason for the phase separation in the concentrated aqueous $C_{10}E_6$ and $C_{13}E_7$ systems was depletion flocculation.

Polyelectrolytes in LC phases. It is also possible to incorporate ionic polymers into lamellar liquid crystalline systems. Radlinska et al. [205] added a post-sulfonated polystyrene, an anionic polyelectrolyte with a degree of sulfonation ranging from 30 to 90%, to the binary nonionic surfactant $C_{12}E_5$ /water system. Polyelectrolytes of low charge density, mimicking the hydrophobic/hydrophilic character

of proteins, are always embedded within the hydrophobic part of the lamellar phase and microscopic phase separation is observed. Macroscopic phase separation is observed by using highly charged, less hydrophobic polyelectrolytes. It is assumed that free water is necessary to facilitate changes of the interfacial curvature, which controls the transformation process.

The electrostatic part of interactions may play a much more important role by adding a polyelectrolyte to an electrostatically stabilized $L\alpha$ -phase. If the polyelectrolyte has the same charge as the ionically stabilized bilayer, repulsive forces have to be taken into account, and segregation phenomena can be expected. Our own experiments show indeed phenomena of macroscopic phase separation by adding NaPAA to the SDS/decanol/water system [206]. However, by decreasing the charge density, i.e. by turning to copolymers with *N*-methy-*N*-vinylacetamides, segregation can be 'suppressed' [207]. Surprisingly, the incorporation of NaCMC, with a degree of substitution of 1.7, is much easier. From the experimental results [208] it can be concluded that the NaCMC is incorporated on a supramolecular level and the formation of multi-vesicular structures become dominant.

If the polyelectrolyte is a polycation, attractive forces between the SDS-bilayer and the polycation become plausible. Kosmella et al. [209] have shown that it is possible to incorporate a polycation, i.e. PDADMAC, without a macroscopic phase separation. SAXS-measurements indicate a non-swollen structure, independent of the water content, with an interlayer spacing of 4 nm. It can be assumed that the polymer is adsorbed flat onto the SDS headgroups of the individual bilayers. Electron micrographs clearly indicate the formation of compact onion-like structured multi-lamellar vesicles [208]. That means that the individual PDADMAC-modified bilayers of about 4 nm (in full agreement with the SAXS-measurements) form supramolecularly arranged spheres of the order of 2–50 μm . This behavior

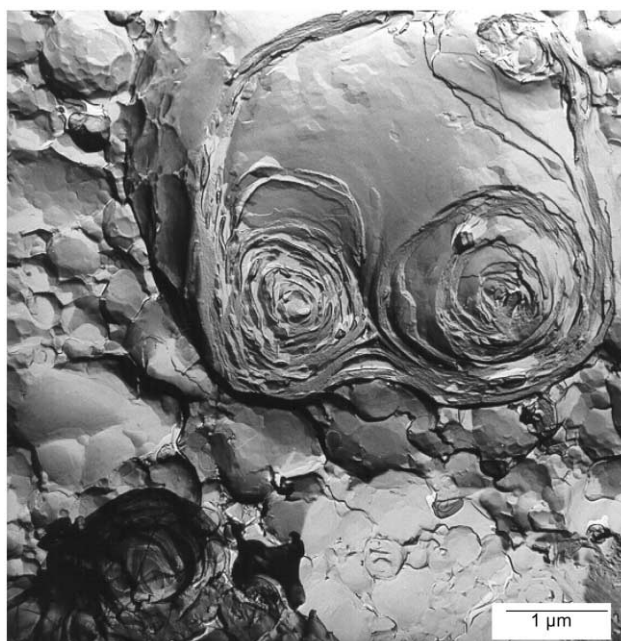


Fig. 10. Freeze-fracture electron micrograph of a lyotropic liquid crystalline system consisting of SDS, decanol, 50% water and 5% NaCMC/PDADMAC (ratio 1:1).

can be understood by the change of the curvature of the bilayer induced by the polyelectrolyte adsorption. The shape of these spheres can be influenced by the polymer concentration (up 20 wt%). EDX-measurements give evidence [208] that the individual shells of the onion-like spheres are PDADMAC-adsorbed lamellae. By decreasing the charge density of the polycation, two coexisting lamellar phases (i.e. a swelling and non-swelling $L\alpha$ -phase) are observed [210].

It should be mentioned, that the incorporation of two polymers is also possible. Examples are given in Ref. [206] for the PAA/PDADMAC system, in Ref. [211] for the PEG/DADMAC-NMVA-copolymers, and in Ref. [208] for the NaCMC/PDADMAC system. In the last case multi-vesicular vesicles become dominant, and can be clearly seen in freeze fracture electron micrographs (compare Fig. 10). The supramolecular ordering of the individual lamellae can now be understood on the basis of polymer–polymer interactions in contrast to polymer–bilayer interactions. Nevertheless, it is possible to design polymer-based liquid crystals via the strength of the polymer–surfactant interactions in order to construct multi-lamellar vesicles, multi-vesicular vesicles, as well as band-like structures on the supramolecular level.

4.3. Polyelectrolytes in foams (thin films)

Foam is a dispersion of a gas in a liquid and consists of thin films, which separate approaching gas bubbles. The stability of foams is best described in terms of the tendency of films to become thinner. At the point of rupture of the film the bubbles will coalesce and the foam will be destroyed. The stability of foams is very important for many industrial processes, i.e. in the froth flotation process for the separation of minerals, and in the food, the pharmaceutical and cosmetics industry. In some chemical processes it may be necessary to release products, and to destroy the foams. At this point it is necessary to discuss the most general system in the classification of thin films by Hunter [212], i.e. surfactant stabilized thin films and their interaction with polymers. The stability of this system results from the addition of intermolecular forces across the thin film, such as van der Waals forces, electrostatic forces and forces in overlapping interfaces (steric forces). Surfactant films, which are drawn out of solution, drain due to gravitational, capillary, and intermolecular forces until they attain an equilibrium thickness determined by the competition of these forces. A readily measurable parameter used to describe the film stability is the hydrostatic pressure in the interior of the film. It is called the disjoining pressure because the pressure opposes the approach of two gas bubbles. Aronson et al. [213] could show that high repulsive disjoining pressures in single foam films correlate with robust foam films.

Hydrophobic polymers such as poly(dimethylsiloxane) and PPG alone or in mixtures with nonpolar oils and hydrophobic solid particles are used as antifoaming agents [214]. The foam rupture mechanism is based on four basic steps: (1) the antifoam agents enter the aqueous thin film; (2) they adsorb at the first interface; (3) they bridge to the second interface; (4) and a high contact angle causes deformation leading to dewetting and rupture.

Nonionic polymers in foams. Hydrophilic noncharged polymers in foams are used to enhance their stability by impeding drainage through increased viscosity. Furthermore, these macromolecules should modify both the interface properties as well as the interactions between interfaces. Krichevsky et al. [215] have studied the influence of the modification of SDS stabilized thin films by PVP. SDS and PVP usually form polymer–surfactant complexes in the bulk phase and at the air–water interface. Thin films represent a constrained surrounding for polymers and it is worthwhile to describe how the polymer coils or the polymer networks are effected by the confinement. Two cases have to be considered [215]: (1) the

case of strongly attractive monomer-wall interactions, where the free energy of the polymers will be lowered by adsorbing onto the wall at the expense of losing configurational entropy; (2) repulsive or weakly attractive monomer-wall interactions, where the entropic contribution to the free energy dominates, and a depletion layer poor in polymer is formed near the wall. In the system SDS–PVP, depletion layers were formed despite the attractive interactions between both. A similar result was found for the system didodecyltrimethylammonium bromide–PVP. The monomer concentration, which is low in the depletion layer, increases towards the film interior. This is connected with a decreased effective viscosity compared to the one in the bulk solution. The formation of the depletion layer is accompanied by a squeezing of polymer chains remaining within the film, and results in a repulsive steric force between monolayer walls. Otherwise, the difference in polymer concentration between the film and bulk solution induces an osmotic pressure that leads to an attractive depletion force. This results in a decrease of the film thickness with increasing polymer concentration. In Ref. [216], changes of the hydrodynamic properties of SDS stabilized thin films modified by PEO were proved in relation to the Frankel law.

Polyelectrolytes in foams. Bergeron et al. [217] compared the qualities of thin films made of equally charged surfactant (AOT) and an acrylamide based polyelectrolyte (*co*-AAS; $x(\text{ionic monomer}) \sim 0.25$) as well as oppositely charged surfactant and polyelectrolyte (DTAB and *co*-AAS). *Co*-AAS is not surface active at the pure air-water interface.

Surface tension and disjoining pressure isotherms (dependent on the film thickness) show only small changes after addition of the equally charged polyelectrolyte to the AOT containing thin film and indicate that *co*-AAS is not present at the interface. Thus the interactions within the thin film are not substantially influenced. The small deviations in both the surface tension and disjoining pressure isotherms can be explained by the effect of *co*-AAS as a low molecular electrolyte.

Films made from solutions of oppositely charged surfactant and polyelectrolyte behave much differently. DTAB itself does not form a stable film. The addition of DTAB to aqueous solutions of *co*-AAS leads to the formation of very stable complexes. The surface tension will be strongly reduced by the adsorption of these complexes at the surface compared to the pure surfactant solution. The interpretation of the disjoining pressure experiments has to distinguish between surfactant concentrations below and above the *cac*. In the first case (0.05 mM DTAB) the isotherms contain branches that correspond to a discrete film-thickness transition from 125 to 75 nm. In thin liquid films this type of transition is termed film stratification. Bergeron [217] suggested that such force oscillations can be generated by the interplay between repulsive electrostatic forces and attractive polyelectrolyte bridging in very dilute polymer solutions (750 ppm). In the second case a dense polymer–surfactant layer is adsorbed at the interface. Depending on the rate of film formation, gel-like networks are formed that produce films with a very non-uniform thickness. Disjoining pressure isotherms could not be determined.

In Ref. [218], an extended concentration range of *co*-AAS (semi-dilute polyelectrolyte solutions) was studied at a surfactant content (DTAB) below the *cac*. With increasing polymer concentration additional branches in the disjoining pressure isotherms appear and for the branch with the smallest thickness, the film thickness decreases. The latter can be explained by the reduction of the electrostatic repulsion of the surface layers with increasing polyelectrolyte concentration. At a given polymer concentration the distance between the branches is equal and independent of the molecular weight of polymers. A relation between the oscillatory distance (d) and the polymer concentration (c) is given by the expression $d \sim c^{-1/2}$. Increasing the ionic strength causes the outer branches to disappear until one branch is left. The authors explain this as follows: the surfactant–polymer complexes are all situated at the interface and should not be present in the bulk solution (under the condition $c < c_{\text{cac}}$). The oscillatory forces are

associated with the polymer mesh structure. They found a remarkable agreement between the distance of branches in the disjoining pressure isotherms and the theoretical mesh size (i.e. the distance between overlapping points of two polymer chains). Furthermore, the mesh size is somewhat larger than the Debye length. These oscillatory forces are unique to polyelectrolytes and are not found with a noncharged polymer. They disappear when electrostatic forces are screened with low molecular weight electrolytes.

Klitzing et al. [219] compared thin films made of DTAB/*co*-AAS with films (DTAB/NaPSS) containing a more rigid polyelectrolyte with a higher charge density. In some cases the cationic surfactant DTAB was replaced by the nonionic one C₁₂E₅, leading to a replacement of the surfactant–polymer complexes through the pure nonionic surfactant at the interface. The anionic polyelectrolyte was now completely in the bulk solution. In this case the disjoining pressure isotherms do not show any change in the distance of branches. The jumps can be related to the polymer network formed in the bulk solution of the film that is not effected by changes at the surface. On the other side the film thickness for the branch with lowest thickness is reduced for the nonionic surfactant because the electrostatic term (repulsion) in the interaction of both interfaces is absent. The authors propose for the system DTAB/NaPSS (which is similar to DTAB/*co*-AAS [218]) that the measured oscillation period of the disjoining pressure isotherm is related to the mesh size, ξ , of the polyelectrolyte network with $\xi \sim c^{-1/2}$. The comparison between both polymers shows a lower jump size for the system DTAB/*co*-AAS than for DTAB/NaPSS at the same polyelectrolyte concentration. This can be explained by the lower charge density along the *co*-AAS chain that leads to a lower electrostatic repulsion between different chains and therefore to a smaller mesh size of the polymer network. For one structural proposal of the authors, to understand the disjoining pressure jumps, it is assumed that the layers of the network collapse one after another.

Microscopic foam films stabilized by adsorption layers of oppositely charged TDAB and carboxymethylchitin (CMCh) were investigated by Babak et al. [220]. The stability of the foam films was determined by τ^* (life-time before rupture) vs. CMCh concentration isotherms. The stability of the TDAB/CMCh complexes increases from $x(\text{TDAB/CMCh}) = 0$ to 0.1 and their maximum was found at a composition of $x(\text{TDAB/CMCh}) = 0.1$. The increased stability can again be explained by the formation of adsorption layers of these complexes at both interfaces and their mutual repulsion. The much higher stabilizing effect of the surfactant–polyelectrolyte complexes with regard to the pure CMCh is due to their higher adsorption free energy at the film interfaces. The surfactant chains bound to the CMCh act as anchors preventing the desorption of complexes. At compositions $x > 0.1$, additional surfactant does not adsorb at the interface and micelle-like structures are formed.

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