Polymer-Amphiphile Interactions: An Overview

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Abstract

Interactions between the polymers and amphiphiles in aqueous solutions have generated considerable interest among researchers because of the widespread applications, relatively complex behavior and improved physicochemical properties of the mixtures. Numerous studies on the surfactant-polymer systems have been carried out in recent years and the number of scientific reports has considerably increased. Various applications of polymers in different areas and many works concerning the amphiphiles are being published every year. Usually, the mixed systems containing polymers and amphiphiles show solution properties different from those of individual solutions due to interaction between the components. The present review article mainly focuses on the behaviour of polymers in aqueous solutions, in the absence or presence of amphiphiles, such as surfactants, drugs, etc. It also summarizes effect of the nature of amphiphiles on aggregation properties of polymers in aqueous solution, and interaction of conventional as well as gemini surfactants with polymers.

1. Introduction

Interaction of the polymer with amphiphile is very much significant in various pharmaceutical as well as medical industries in view of their importance in industrial products like the detergents, cosmetics, pesticides, among others. Net charge on the molecules determines the nature of interactions. Other important factors, which play important role, are length of the hydrophobic tail of the amphiphile and the temperature. Interaction of ionic surfactants with water-soluble polymers has been investigated by several researchers by different methods. Mixtures of the amphiphile and polymer can improve the properties of the system: surfactants are generally added to control the dispersions, flocculation and wetting properties of suspensions whereas polymers are mainly added to meet rheological requirement. Usually, the techniques which are employed to investigate the surfactant behavior are also applied for the study of polymer-amphiphile interaction. In some cases there may not be any interaction, though sometimes the interaction can be very strong.

Presently the research work focuses on systems with mixed interfacial films made of either two surfactants or surfactants combined with polymers. These mixtures can have an effect on the solubilization efficiency. Polymer-amphiphile interactions are of great importance in living systems as well [1]. Effect of the addition of polymer, to surfactant systems, has been reviewed by Scottmann [2]. He has suggested that the increase of solubilization capacity occurs because of the adsorption of polymer at surfactant membranes in dilute microemulsions. The most favorable monolayer curvature and flexibility can independently be controlled by the mixed short-chain surfactant and long-chain block copolymer systems.

2. Polymers

Monomers assemble to form the long chain giant molecules called polymers. Silk, rubber, proteins, carbohydrates, DNA etc. are the natural polymers whereas polyurethane, polystyrene, polyvinyl chloride etc. are the synthetic polymers. Polymers constitute the basis for plastics, adhesives, fiber

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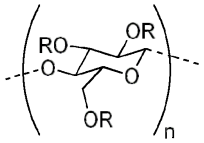
etc. and can be classified according to their use, such as thickening agents, resinous powders, humectants. Polymers are used in pharmaceuticals in various ways, like gelling and viscosity increasing agents, filling materials, suspending agents, tablet binders, film formers and extended release materials [3]. Extensive research on the physical and chemical properties along with modification of the structures of both polymer as well as micellar aggregates has been done by many workers [4–6].

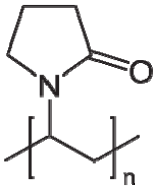
$$[-CH_2-CH_2-O]_x-[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O]_y-[CH_2-CH_2-O-]_x \quad (1)$$

Amphiphilic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers (1) are known as Pluronics. These polymers are highly surface active compounds and form micelles, above the critical micelle concentration (cmc) in water. Amphiphilic copolymers have widespread applications in emulsification, solubilization and controlled release, and product formulation in industries ranging from agriculture to pharmaceuticals. Formation of the triblock copolymer micelles is temperature dependent and a small increase in temperature causes notable decrease of the cmc. The PEO–PPO–PEO triblock polymers interact with the ionic surfactants [7–11]. Hydroxypropyl methyl cellulose (HPMC) is a pharmaceutically important polymer (2) containing both the hydrophobic and hydrophilic structural units [12–15]. In formulations, it either serves as a part of regulating system, as a neutral substance to provide adequate flow properties, or as an adsorbent for the drug.



$$R = H \text{ or } CH_3 \text{ or } CH_2CH(OH)CH_3 \quad (2)$$

Biopolymers frequently have disordered hydrophobic and hydrophilic sequences which make them quite interesting. Gelatin is a denatured protein and does not interact with surfactants as the folded proteins do [16], it interacts in a simple manner like the polymer. Hydrophobic and electrostatic forces play important role in the interaction of polymers with surfactants when both the components are ionic in nature. Polyvinylpyrrolidone (PVP) is an amphiphilic polymer (3) soluble in aqueous and nonaqueous solvents [17]. Its highly polar amide group is responsible for its hydrophilic character while hydrophobicity is attributable to the nonpolar methylene and methine groups present in the ring and along its chain.



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3. Amphiphiles

Conventional surfactants are amphiphilic molecules comprising a hydrophilic polar head group and a hydrophobic hydrocarbon chain whereas gemini surfactants consist of two hydrophobic chains, two polar head groups covalently linked through a spacer [18, 19]. Schematic representation of the conventional and gemini surfactants are shown in Fig. 1. Amphiphiles decrease the surface as well as interfacial tension at the interface. At a particular concentration, i.e., at the cmc they aggregate to form the micelles. Geminis, the double-chained surfactants, possess properties superior to those of the conventional surfactants [20, 21], and are widely used in various industrial and commercial applications. The main advantages of geminis as compared to the corresponding conventional surfactants are due to their unusual physicochemical properties like higher surface activity, lower cmc, better solubilizing power, low Krafft point, and better viscoelastic properties.

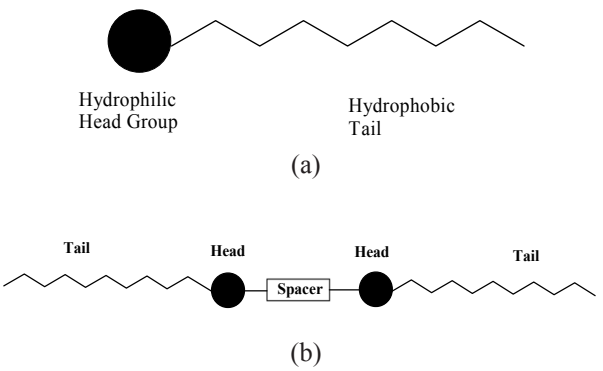


Fig. 1. Schematic illustration of the (a) conventional and (b) gemini surfactants.

When amphiphilic molecules are added to water their adsorption occurs at the air/water interface resulting in the decrease of cohesive interaction between solvent molecules and the surface tension of water is lowered gradually till the interface becomes completely saturated. After saturation, the molecules start to aggregate in the bulk solution without affecting the interface. Amphiphilic molecules normally assemble at the interface of water in an attempt to hinder the contact of nonpolar parts with the aqueous phase. This self-association results in a variety of phase structures. The self-aggregation behavior of the drugs and their interaction with macromolecules, because of their biological importance, are very exciting area of research and the field is more appealing for the amphiphilic drugs [22]. Therefore, it is important to understand the aggregation behavior of amphiphilic drugs in aqueous medium, particularly, in the presence of other materials. Many life processes need the presence of amphiphiles. Association between the amphiphiles is due to the hydrophobic interaction which is balanced by the hydration and electrostatic repulsive effects. Surfactant geometry plays a significant role for the shape of the aggregates, the formation and stability of which are the result of a delicate balance of opposing forces. When the amphiphile concentration exceeds the cmc, micelle formation takes place. Many workers have focused on properties of the micelles formed at the critical concentration. Mixed surfactants are the amphiphiles with wide practical applications. Surfactant mixtures have improved physicochemical properties than the single surfactant systems and have been widely studied [23–25]. Superiority of the mixed surfactant systems, as reported by many workers, is due to the synergistic interaction between various components present in the system. Distribution of surfactants between the aqueous and micellar phases along with the cmc play important role for the behavior of the binary surfactant solutions. The proper combination of surfactants helps to get tailor-made aggregate structure suitable for some particular use. The solutions having more than one type of surfactant are significant because of their better performance than the single surfactant systems in some applications. Khan and Marques [26] have reviewed the mixed surfactant systems with different charge, and have explained the adsorption of various surfactants on the hydrophilic and hydrophobic surfaces. Like surfactants, many drugs are amphiphilic in nature and form aggregates above a critical concentration. Phenothiazines and tricyclic antidepressants possess almost planar tricyclic ring system with a short hydrocarbon chain carrying a terminal, charged nitrogen atom. Presence of the alkylamine side chain makes them surfactant-like, which is evident by the self-association of these drugs [27]. These drugs, even though amphiphilic in nature, are not hydrophilic enough to be used without a carrier. Amongst various carriers, due to the commercial availability of a large number of viscosity grade pharmaceutically approved HPMC, its use is advantageous. Key features of the microbial biosynthesis of biosurfactants, their physicochemical and bioactive properties, and their application potential have been discussed [28]. Physicochemical behaviour of the biological amphiphiles like diminution of surface tension and emulsifying activities, and their potential for possible industrial applications have also been discussed. Studies on the interaction between polymers and drugs are necessary to understand the behavior of such systems. The system becomes more interesting when the drug is amphiphilic in nature.

4. Polymer-amphiphile interactions

Polymer-surfactant mixtures have wide use in domestic, industrial and technological applications. A mixture, in which the polymer and surfactant bear opposite charges, is of special interest because association in these systems is strong due to very strong force of electrical attractions. Review articles and books are available, covering systems with surfactants and polymers differing in ionic character, size and shape. Interaction between polymers and the oppositely charged amphiphiles depends upon a number of factors: (i) nature of hydrophobic part of the amphiphile, (ii) degree of solvation, (iii) degree of dissociation of amphiphile and (iv) solute-solvent interaction. Combinations of polymers and surfactants have applications in formulations of various household products, modern cosmetics, paints etc and, thus concern in fundamental investigations has been created for the study of interactions. These interactions are system-specific depending upon the temperature, external conditions (like pH, presence of additive etc.), molecular characteristics and charge of both the polymer and surfactant. Binding interaction between the amphiphile and polymer is a cooperative process. The polymer-surfactant combinations have superior properties such as surface activity, viscosity, wetting, foaming, solubilization, etc.

than the single component systems. Interaction of water soluble neutral polymers with the ionic surfactants mainly depends on the head-group as well as tail length of the surfactant, hydrophobicity and flexibility of the polymer. Minimization of the interfacial area between nonpolar parts of the polymer and the aqueous solvent, due to their association with the exposed nonpolar moieties of the surfactant molecules, is supposed to be the driving force responsible for the interaction. Polymers cause reduction of cmc of the amphiphile, particularly if it has the opposite charge. Interaction of surfactant with polymer starts above a critical aggregation concentration (cac) at which formation of polymer-supported micelles along the polymer chain takes place. cac is generally smaller than the cmc of the surfactant in polymer free solution. A further increase in the surfactant concentration gives rise to second break point (cmc), which is the saturation point of the polymer domain beyond which regular micelles of surfactants in solution coexist with aggregates supported on the polymer backbone. Addition of an amphiphile to a polymer solution stimulates binding among the components at a given amphiphile concentration (known as the cac) at which the interaction between amphiphile and polymer begins. Then formation of aggregates bound to the polymer and formation of free micelles, when the binding sites of polymer are saturated by the amphiphile monomers, occurs. There are also reports of the free micelle formation long before the polymer saturation [29, 30]. Usually, the cac does not depend on molecular weight of polymer, it depends on the nature of polymer and the polymer saturation concentration [30, 31]. The amphiphile-polymer interactions have many applications in various areas, but in the field of colloid chemistry it has become more important in view of their extensive industrial applications [32]. It is relatively easier to understand the cationic polymer–anionic surfactant and anionic polymer-cationic surfactant interactions due to Coulombic attractions. But for neutral polymers factors such as the nature of surfactant head group, nature of the polar groups embedded in the polymer backbone, polymer hydrophobicity are considered [33]. Interactions between the nonionic hydrophilic polymers and ionic surfactants have been studied extensively.

The process leading to polymer-amphiphile aggregates is a multistage complex mechanism. Association between the polyelectrolyte and surfactant starts at very low concentration range and strongly depends on charge density of the polyelectrolyte. At a low surfactant concentration, interaction of surfactant molecules with the polymer is mainly due to strong electrostatic attraction between the opposite charges. Other driving forces acting in this association are the hydrophobic interactions between surfactant tails and the polymer backbone, which is hydrophobic. At a very high surfactant concentration numerous chains of polyelectrolyte are able to perform complexation with many charged micelles. When the surfactant is added to an aqueous polymer solution, no interaction is noticed up to cac. At [surfactant] ≥ cac, the surfactant starts to get adsorbed to the polymer chains in a cooperative manner in the form of small clusters. The adsorbed clusters increase in size with both the polymer and surfactant concentrations up to a certain limit. The number of cluster binding sites on the polymer increases strongly as the adsorption begins and continues until the entire polymer gets saturated. When more surfactant is added, normal micelles begin to form at the cmc. Surfactants play important role either alone or with the assistance of polymers. Water-soluble polymers having polar groups, like hydroxyl, carboxylic acid, or ether groups, are capable of taking part in hydrogen bonding. As the temperature rises, hydrogen bonding is weakened and polymer solubility becomes less. Ultimately, phase separation may occur.

Polymer conjugation is a well-known technique which is useful for the improvement of therapeutic properties of various drugs. Higher stability due to extended half-life, aqueous solubility and lower immunogenicity can be expected from polymer conjugated drugs [34]. These are very helpful for the specific targeting to tissues or cells. Synthetic polymers are utilized to get a broad and united picture of the interaction as this show a discrepancy in the nature and degree of substitution [35].

Surfactant molecules adsorb at the colloidal interface, but the polymer-surfactant complexation occurs in the bulk phase without being adsorbed at the interface. The repulsive force between the colloidal droplets is not appreciably altered by the complexes. When polymer is preadsorbed at the colloidal interface, the interaction causes remarkable changes in repulsive forces due to the conformational change of polymers at the interface and appreciable enhancement of stability of the colloid. There may be competition between the surfactant, polymer and the complex for adsorption.

Technical interest in optimizing the use of mixtures and scientific interest in understanding the physicochemical properties determine the high per-

formance of some mixtures of the amphiphilic drug with polymer. The physicochemical characteristic of these systems can be dealt with the study of interaction mechanism in aqueous medium. Also, the side effects of drugs can be reduced by the addition of some other components, such as polymers, which increase the solubility of drugs or limit the area of contact between drug and mucous membrane.

Stability and solubility are two important characteristics of the successful solution formulations. Many problems, like solubilization in body fluids and interaction with barrier membranes in the organism, occur with respect to their formulation to reach their final targets. The effect of micelles for solubilization and absorption of nonpolar solutes are quite well-documented. Polymer-amphiphile interactions depend on concentration of the solution, and also molecular structure of both the constituents. The concern of various factors for the effectiveness and safety of therapy are very important for the successful drug delivery [36].

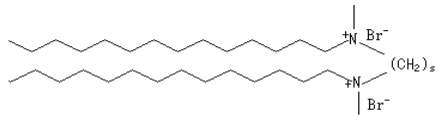
Polymer-amphiphile interactions are of various types: electrostatic interactions (when the polymer and amphiphile are oppositely charged), and hydrophobic interactions among the hydrophobic parts of the polymer and amphiphile [37]. Polymer-amphiphile interaction is akin to the surfactant-surfactant interaction in micelles in many ways: the presence of oppositely charged compounds increases the interaction although the main attractive forces are hydrophobic interactions. The same mechanism and entropy balance take place during the micelle formation, in presence of the polymer also. Addition of a polymer can either remove a surfactant from the surface or increase its adsorption to it. The water insoluble polymers can be solubilized in presence of the surfactants.

Interaction of drugs with polymers (the most often used carrier) is a very important aspect and plays an important role in drug delivery formulations [38–42]. A variety of drug molecules, such as antihistamines, antidepressants, tranquilizers, local anesthetics, and nonsteroidal anti-inflammatory drugs (NSAIDs) are known to be amphiphilic in nature and form ordinary micelles or micelle-like associations above the cmc [43–47]. These drugs may interact with polymers in surfactant-like manner, i.e., there may exist cac, cmc or psp (polymer saturation point) [48]. The cac, the start of aggregation, is either near or well below the cmc of pure amphiphile [49] while the cmc is assigned to saturation of polymer domains by the monomers and/or micelle-like aggregates [24, 50–53]. Above cmc, formation of normal micelles takes place. Both hydrophobic and electrostatic forces play important roles in the interaction of polymers and amphiphiles when either both or one of the entities are ionic in nature. The knowledge of cac is important as the interaction of amphiphilic drug with polymer starts at this concentration.

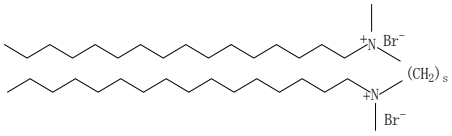
Banipal and Sood [54] studied the interactions of two triblock polymers, F68 ($EO_{76}PO_{29}EO_{76}$) and P123 (EO_{19}-$PO_{69}EO_{19}$), with conventional cationic surfactants such as dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB) and dicationic gemini surfactants namely dimethylene bis(alkyldimethyl ammonium bromide (m-2-m, m = 10, 12, 14). They have compared the effect of the number of EO and PO blocks, in triblock polymers, on various physicochemical parameters of the mixed micelles. The large number of PO blocks caused the poor solubility of P123 in the aqueous phase although there was a possibility that these blocks might create greater steric hindrance in the mixed state. The micelles of SDS (sodium dodecyl sulphate), SDBS (sodium dodecyl benzene sulfonate), CTAB, TTAB and CPC (cetylpyridinium chloride) in water as well as in the aqueous solutions of polyethylene oxide (PEO) was studied by Banipal et al. [55]. Aromatic ring in the head group of surfactant caused the decrease in its interaction with PEO, while increase in hydrophobicity in the tail was the reason of stronger interactions with it. Strong affinity of the anionic surfactants, for these polymers, than the cationics has been explained on the basis of electrostatic and nonelectrostatic interactions between the surfactant and polymer.

Almgren et al. [56] studied the interaction of SDS with PEO-PPO-PEO triblock copolymer, Pluronic F88, in water and observed that the non-micelle forming copolymer F88 induced the aggregation of SDS at a much lower concentration than cmc. Excess of SDS concentration led to the formation of SDS-rich micelles and the mixed surfactant system behaved like a charged polyelectrolyte with stronger solubilizing action [57]. Binding of SDS and TTAB to both unassociated and micellar F127 was investigated [58, 59]. Surface activity and solution behaviour of two block copolymers PEO-PPO-PEO viz. P123 and F127 in presence of the anionic SDS or cationic CPC surfactants, in the absence and presence of salts, has been reported. Addition of salts to P123 and F127 solutions caused a linear decrease in cloud points,

shifting of the micellization and micelle growth to lower temperatures. Both the surfactants (CPC and SDS) demicellized P123 as well as F127 [60]. Ali et al. [53] studied the interaction among two homologous cationic gemini surfactants, bis(hexadecyldimethylammonium)hexane dibromide (16-6-16), bis(tetradecyldimethylammonium)hexane dibromide (14-6-14), and their corresponding conventional counterparts (CTAB and TTAB) with the nonionic polymer PVP to see the effect of hydrophobicity and molecular architecture. PVP interacted strongly with the geminis than the conventional surfactants, and the surfactants with shorter hydrocarbon chain interacted weakly than those of longer hydrocarbon chain (Table 1). The degrees of micelle ionization along with the free energies associated with aggregation, micellization and transfer have been discussed.



14-s-14 (s=6) (4)



16-s-16 (s=6) (5)

Mata et al. [61] have reported the surface activity and solution behavior of Pluronic P105 (PEO–PPO–PEO), the anionic surfactant SDS, cationic DTAB and their binary mixtures in the absence and presence of NaBr. P105 interacted more strongly with SDS than DTAB. Addition of SDS or DTAB (below cmc) to micellar P105 showed demicellization for which SDS was more efficient. Patel et al. [62] examined the micellar behaviour of two amphiphilic polystyrene-poly(ethylene oxide) (PS-PEO) diblock copolymers, and their mixed micelles with the ionic surfactants, SDS and DTAB. Addition of surfactant reduced the micelle size, even though the micelles remained ellipsoid. Anionic surfactant SDS showed better effect than the cationic surfactant DTAB. Mixed micelles, along with the free surfactant micelles, were observed at high surfactant concentrations. Sharma et al. [63] investigated the micellization of Triton X-100 (TX-100), SDS and their mixtures at different mole fractions. They observed interaction of SDS with PEO and PEO–PPO–PEO block copolymer (P65: $EO_{19}PO_{30}EO_{19}$) whereas TX-100 did not show any interaction. In mixed micelles the interaction decreased with the increase of mole fraction of TX-100. Insertion of SDS molecule into the TX-100 micelle changed the surface charge density and caused intermicelle repulsion.

Bahadur et al. [64] studied the interaction of poly(4-vinylpyridine-N-oxide) (PVPNO) with SDS in water. Having a high dipole, the polymer behaves as a hydrophilic nonionic macromolecule in water. The polymer began to interact with SDS at a concentration below the cmc like the other nonionic polymer-surfactant systems (e.g., PEO-SDS). They observed interaction between uncharged polymers like poly(ethy1ene oxide) (PEO), poly-(propylene oxide) (PPO), PVP, poly(viny1 methyl ether) (PVME), poly(viny1 alcohol) (PVA), and ionic surfactants like SDS, alkyltrimethylammonium salts. SDS formed polymer-bound aggregates (smaller than the normal micelles) at concentrations less than the cmc. The interaction started at surfactant concentrations far below the cmc and both the monomeric surfactant as well as its aggregates could bind to the polyelectrolyte.

Table 1
Effect of PVP on critical aggregation concentration (cac) and critical micelle concentration (cmc) of cationic surfactants at 30 °C [Ref. 53].

% PVP (w/v)	TTAB		14-6-14		CTAB		16-6-16	
	10^3 cac mol dm^{-3}	10^3 cmc mol dm^{-3}	10^4 cac mol dm^{-3}	10^4 cmc mol dm^{-3}	10^3 cac mol dm^{-3}	10^3 cmc mol dm^{-3}	10^4 cac mol dm^{-3}	10^4 cmc mol dm^{-3}
0.00	-	3.0	-	0.75	-	0.95	-	0.55
0.02	3.07	7.70	0.85	1.67	0.96	2.64	0.67	1.31
0.04	2.76	7.92	0.68	1.60	0.83	2.82	0.66	1.43
0.06	2.52	8.19	0.66	1.62	0.80	3.20	0.64	1.53
0.08	2.40	8.77	0.66	1.71	0.77	3.38	0.60	1.59
0.10	2.23	9.25	0.60	1.73	0.75	3.67	0.58	1.61
0.15	2.03	9.38	0.60	1.74	0.73	3.87	0.49	1.66

Adsorption at an interface depends upon the competition between complex formation in the bulk and at interface. There are numerous studies on the associative nature of polymers in bulk solutions [65–76]. Philip et al. [77] have reported that the interaction between a neutral polymer (PVA), an ionic surfactant (SDS) and colloid can lead to three different states which depends upon the sequence of adsorption of polymer and surfactant on the colloidal interface. Their findings provide the right conditions at which the polymer-surfactant complexation can increase the stability of the colloidal suspension considerably and the role of sequential adsorption of polymer, surfactant and colloid on repulsive forces.

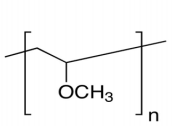
Although the production of ultrafine fibres with the use of electrospinning has been known since long back, it got attention only in the last few decades [78, 79]. Tin et al. [80] have reported a work where they have illustrated the electrospinning of polystyrene nanofibres with small amount of cationic surfactants (DTAB or TBAC-tetrabutylammonium chloride) in the polymer solution. Interaction of polystyrene with DTAB created thinner fibres than the system without interaction.

Dispersion polymerizations of methyl methacrylate (MMA) were carried out with different types of organic peroxides, as radical initiator, in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) in supercritical carbon dioxide [81]. Micron-sized, relatively monodisperse poly(-MMA) particles were prepared by using benzoyl peroxide. Because of the interaction between ionic surfactant and block copolymer, formation of polyelectrolyte type complex in aqueous solution was observed. Complex formation between the polymers and surfactants in water has been critically studied for wide varieties of applications of mixed systems [82–85]. The most common system investigated is the interaction between a nonionic polymer, PEO, with the ionic surfactants in aqueous media. Interaction between poly(ethylene oxide)-polystyrene-poly(ethylene oxide) (PEO-PS-PEO) triblock copolymers with cationic (CPB, cetylpyridinium bromide) and anionic (SDBS) surfactants was investigated. The polymer-surfactant interaction was dominated by hydrophobic interaction and thus was dependent on the molecular characteristics of copolymers and surfactants [86].

Abuin and Scaiano [87] have reported the use of photochemical probes in order to characterize polyelectrolyte-surfactant aggregates. They examined various photochemical processes in the aggregates of poly(styrenesulfonate) and DTAB. They have suggested that up to 50% coverage the surfactant was almost quantitatively associated with the polymer. Formation of the relatively nonpolar aggregates occurred with concurrent coiling of the polyelectrolyte chain.

Interaction between the water-soluble nonionic polymers and ionic surfactants has become a field of extensive research in recent years [84,88]. These studies generally deal with the action of anionic surfactants although the cationic species interact relatively weakly with the nonionic polymers. However, if a hydrophobic polymer is used, a more prominent interaction is noticed. Carlsson et al. [89] measured the self-diffusion behavior of dodecyltrimethylammonium ions (DTA^+) in aqueous solutions of ethyl(hydroxyethy1)cellulose (EHEC). They analyzed the experimental data by means of a simple two-site model and obtained the amounts of free and bound DTA^+ ions in the polymer solution. Temperature-induced conformational changes occur in polymer, i.e., the polymer molecules become increasingly more hydrophobic with the increase of temperature.

Drastic reduction of viscosity and transition from a non-Newtonian to Newtonian fluid are caused by breaking down of the long rod-shaped micelles in the viscoelastic system to small and spherical micelles surrounded by a nonionic polymer, PVME (6). Interaction of surfactant with polymer and the resulting association structure significantly affect many properties of the system, the rheological properties in particular. Investigations on the polymer-surfactant interaction have shown that the morphology and rheological properties of surfactant solutions can substantially be changed and controlled by the addition of polymer [90].



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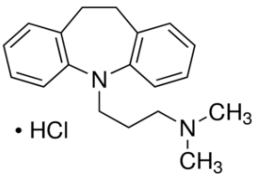

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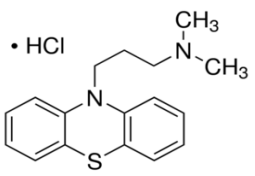

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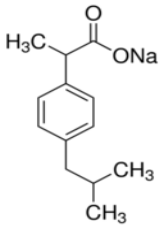

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While examining the effect of two cationic drugs, imipramine hydrochloride (IMP, 7) and promazine hydrochloride (PMZ, 8), and one anionic drug, sodium salt of ibuprofen (IBF, 9), on the clouding behavior of a nonionic polymer, HPMC, Khan et al. [14] observed that the disruption of water structure became very prominent at lower concentrations of the drugs for fixed salt concentrations. Above the cloud point (CP), the solutions spontaneously and reversibly separated into two distinct phases: one phase was polymer-rich and the other polymer-lean. Variation in the CP of HPMC solution in presence of the amphiphilic drug (IMP, PMZ or IBF) and the effect of additives (inorganic salts) on the CP of HPMC were examined. Stronger interaction of cationic drugs with the polymer than the anionic IBF was found. The CP values of HPMC decreased linearly with the increase of salt concentration in the presence of IMP and PMZ, whereas in their absence the effect was negligible. The authors [91] have also reported interaction of the non-steroidal anti-inflammatory drug, IBF, with various biocompatible polymers viz. PVP, polyethylene glycol (PEG), HPMC, hydroxyethyl cellulose (HEC), sodium carboxymethyl cellulose (NaCMC), dextran sulphate (DxS), hydroxyethyl cellulose ethoxylate (HECEQ). Because of its amphiphilic nature, the drug interacted with the polymers in a similar manner to that of the surfactants. The anionic IBF interacted with cationic and nonionic polymers more strongly as compared to the anionic polymers. The cac decreased while cmc increased on increasing polymer concentration in all the cases, and the decrease in cac on increasing the polymer concentration was much sharp in case of cationic and nonionic polymers than the anionic polymers due to the possible repulsion between the anionic-anionic pair (of drug and polymer) – hydrophobicity played an important role in the polymer-amphiphile interaction and dominated the repulsion between the same charges. Interaction of the cationic amphiphilic drug, IMP, with a denatured protein, gelatin, was studied. The drug interacted with gelatin in a surfactant like manner. The gelatin-IMP complex was highly surface-active. The decrease in cac on increasing the gelatin concentration (Table 2) indicated strong interaction between gelatin and IMP. The random coil content of gelatin increased with increasing the drug concentration [92].

Veggeland and Nilsson [93] carried out the self-diffusion NMR studies for a systematic investigation of the polymer-surfactant interactions,

Table 2
Critical aggregation concentration (cac) and critical micelle concentration (cmc) of IMP in presence of gelatin at 25 °C [Ref. 92]

% gelatin (w/v)	cac (mol dm^{-3})	cmc (mol dm^{-3})
0	-	0.046
0.02	0.022	0.052
0.05	0.015	0.051
0.1	0.014	0.059
0.2	0.014	0.064
0.4	0.013	0.07

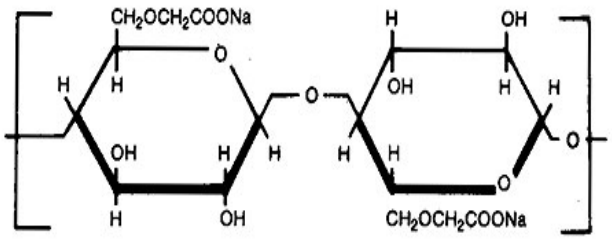
also to examine the association of PEO with anionic ethoxylated surfactants and to verify the aggregate structures in different phases. Diffusion of the components was influenced by size, shape and interactions of the surfactant aggregates. Hydrophilic part of the surfactant was increased by inserting the EO groups. Association between the ethoxylated sulfonates and PEO decreased when ethoxylation degree of the surfactant increased. When the number of EO groups was more than three, no association was noticed.

Ghoreishi et al. [30, 94] reported the presence of strong electrostatic attractive force between SDS and the cationic polymers, such as dendrimers and methylvinylimidazole/vinylpyrrolidone/vinyl acrylic acid copolymers. The interaction is generally accepted as an ion-exchange process where the electrostatic forces of interaction are reinforced by aggregation of alkyl chains of the bound surfactant molecules. The current understanding on the interaction between a fully ionized polyelectrolyte such as poly(acrylic acid) and a cationic surfactant is that the polymer chains induce formation of micelles on them. Surfactant unimers get attracted to the charged sites of the polymer backbone prior to the formation of micelles caused by the polymer-induced micellization process. Wang and Tam [95] examined the interactions of a cationic surfactant (DTAB) with the anionic polyelectrolytes – poly(acrylic acid) (PAA) and methacrylic acid/ethyl acrylate copolymers (MAA/EA copolymers). Addition of salt shielded electrostatic attraction between the surfactant and oppositely charged polymer making it unfavorable for the polymer-induced micellization of the surfactant to occur.

Investigation on the interaction of water soluble nonionic polymers with surfactants has been the subject of large interest over the years [96]. In

many formulations containing surfactants, polymers are used to enhance the performance (such as in adjusting rheological properties), and it is also interesting from a basic scientific point of view. Pettersson et al. [97] studied the interaction between the nonionic polymer PEO and surfactants of various types (SDS, DTAB, octyl β-D-glucoside, potassium laurate). While the anionic surfactant (SDS) interacted with PEO at room temperature [98], cationic and nonionic surfactants required higher temperatures to bind to PEO [99]. The mutual interaction led to surfactant self assembly at a lower concentration than the cmc. Their results support the accepted picture of the aggregation process in the SDS-PEO system and indicates that a maximum of two SDS micelles are formed on the PEO (molecular weight = 20 000) used by them.

Interaction among a cationic copolymer (acrylamide-trimethylaminoethyl acrylate) and an anionic perfluorinated surfactant (lithium perfluorooctanoate) was studied by Proietti et al. [100]. They detected a complete saturation of the cationic charges of the polymer and proposed two mechanisms of flocculation – polymer bridging and electrostatic patch attraction. Khan et al. [101] have reported that the interaction of the cationic amphiphilic drugs, IMP and PMT, with several cationic, nonionic and anionic polymers (PVP, PEG, HPMC, HEC, NaCMC, HECEQ) in water was dependent on the nature of the polymers. Due to the occurrence of many stabilizing effects, molecular interactions between the drugs and polymers are associated with a significant change of thermodynamic parameters. The anionic polymer NaCMC (10) interacted strongly with the drugs as compared to the nonionic and cationic polymers due to possible electrostatic attraction between the anion–cation pair of the drugs and polymer. Strength of interactions between the drugs IMP/PMT and the polymers was dependent on the nature and concentration of the latter. Recently, it has been reported that the anionic IBF interacted more strongly with the cationic polymers than the nonionic ones whereas the anionic polymers showed least interaction [102]. Influence of six polymers viz. HEC, HPMC, PEG, PVP, NaCMC and DxS on solution properties of the amphiphilic drug IBF has been reported by Khan et al. [15]. Amongst the polymers used by them, only HPMC showed clouding behavior. Value of the free energy of clouding obtained by them indicated that the process was energetically less favorable on increasing the polymer concentration.



(10)

Study of interactions of water-soluble polymers with surfactants in aqueous solutions has long been important because of their numerous industrial applications in pharmaceuticals and biomedicine, detergents, enhanced oil recovery, and food and mineral processing. It was expected that the conformational changes of polymer chains might possibly take place as a result of polymer surfactant interactions [103]. Sardar et al. [13] have reported the effect of a series of additives (salts) on the CP of aqueous solution of a nonionic polymer, HPMC. In presence of additives, CP of HPMC decreased almost linearly on increasing their molar concentration (salting out effect) either by dehydration or by enhancing the structuring of water. Trivalent and divalent anions showed higher efficiencies than monovalent anions at much lower molar concentrations. Interaction of two gemini surfactants (16-s-16, s = 5, 6), and their conventional counterpart, CTAB, with polyvinylpyrrolidones (PVP K15 and PVP K90), NaCMC and HPMC was studied by Sardar et al. [104–106]. The authors have suggested that there is no PVP-CTAB complex formation if molecular weight of PVP < 15.000. Both PVP K15 and PVP K90 interacted with the gemini surfactants, and the cac and cmc did not depend on the polymer molecular weight. Addition of PVP lowered aggregation number in all the systems due to the adsorption of PVP chain in the micelle palisade layer. cac and cmc values of the surfactants, at different weight percentages of NaCMC, are given in Table 3. Electrostatic and hydrophobic interactions were thought to play dominant role in the CTAB + NaCMC and gemini + NaCMC systems implying that the geminis interacted strongly with NaCMC than CTAB due to the presence of two polar head groups and two alkyl chains. The gemini surfactant with shorter spacer chain interacted more strongly than that with longer spacer and the conventional counterpart. Interaction of the nonionic polymer (HPMC) with CTAB, 16-5-16 and 16-6-16 is illustrated in Fig. 2. HPMC interacted strongly with the

geminis than the conventional surfactant, CTAB. Formation of polymer-surfactant micelles took place at surfactant concentration higher than the cmc of micelle without polymer (Table 3).

Effect of various additives (surfactants) on the phase behavior of nonionic cellulose ether, HPMC, was also studied [107]. Various factors, such as chain length, charge on the head group, counterion, etc., affected the CP of HPMC. Polymers interacted more strongly with the anionic surfactants than the cationics [108, 109]. In case of alkyltrimethylammonium bromides, surfactants with a longer alkyl chain (CTAB and TTAB) influenced the CP much more than that with a shorter alkyl chain (DTAB).

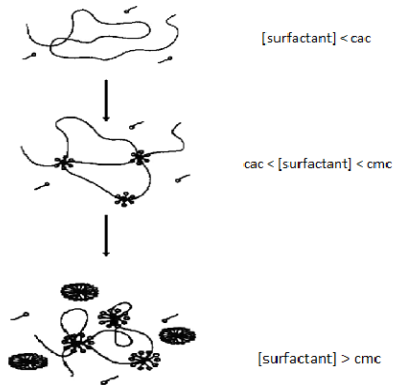


Fig. 2. Conformation of HPMC and surfactant complexes [Ref. 106].

The anionic surfactant, SDS, was found to be more effective than DTAB (its cationic counterpart with the same alkyl chain), whereas nonionic surfactants showed no influence. Drummond et al. [110], in a comparative study of the interaction of surfactants (anionic, cationic and nonionic) with hydroxypropyl cellulose (HPC), have shown that the anionic surfactants display much stronger affinity for HPC than the cationic surfactants, while nonionic surfactants do not influence CP of the polymer.

Kaur et al. [111] have reported that interactions between the polymer, pluronic L64, with each of the twin tail cationic surfactants, didodecyldimethylammonium bromide, ditetradecyldimethylammonium bromide, dihexadecyldimethylammonium bromide, was nonideal and antagonistic in nature. Vesicles were formed by the pure twin tail cationic surfactants while the pure pluronic L64 formed spherical micelles. Transition of vesicles of pure surfactants to spherical mixed micelles was noticed on addition of pluronic L64.

Interactions of the anionic surfactant SDS with the nonionic polymers PEG, PVP and various PEG + PVP mixtures have been suggested to be due to the electrostatic as well as hydrophobic interactions in the SDS-PEG/PVP-water systems [112]. Negm et al. [113] studied the surface properties of the individual cationic surfactants, S-alkyl isothiouronium bromide (n = 10, 12, 14), and their mixture with the nonionic polymer, PVA, and have

Table 3
cac and cmc values for CTAB, 16-6-16 and 16-5-16 in solutions containing different weight percentages of NaCMC (or HPMC) at 298.15 K

Polymer (wt%)	CTAB		16-6-16		16-5-16		
	cac (mmol dm^{-3})	cmc (mmol dm^{-3})	cac (mmol dm^{-3})	cmc (mmol dm^{-3})	cac (mmol dm^{-3})	cmc (mmol dm^{-3})	
NaCMC							Ref. [105]
0.000	-	0.956	-	0.0429	-	0.0321	
0.001	0.209	0.962	0.0271	0.0620	0.0205	0.0579	
0.002	0.225	1.000	0.305	0.0654	0.0246	0.0603	
0.004	0.243	1.000	0.0405	0.0679	0.0263	0.0671	
0.006	0.327	1.040	0.0420	0.1080	0.0346	0.1060	
0.010	0.410	1.180	0.0838	0.1630	0.0604	0.1580	
HPMC							Ref. [106]
0.00	-	0.956	-	0.0429	-	0.0321	
0.05	0.508	1.320	0.0312	0.1195	0.0495	0.1495	
0.10	0.542	1.350	0.0312	0.1204	0.0495	0.1520	
0.20	0.560	1.500	0.0322	0.1204	0.0503	0.1554	
0.50	0.576	1.590	0.0329	0.1212	0.0520	0.1578	
1.00	0.610	1.950	0.0412	0.1387	0.0562	0.1779	

proposed that the mixed systems have improved surface properties over the individual cationic surfactants (Fig. 3). It was also suggested that at a particular concentration of the polymer-surfactant mixed systems there is good salvation of the polymer segments in the aqueous phase.

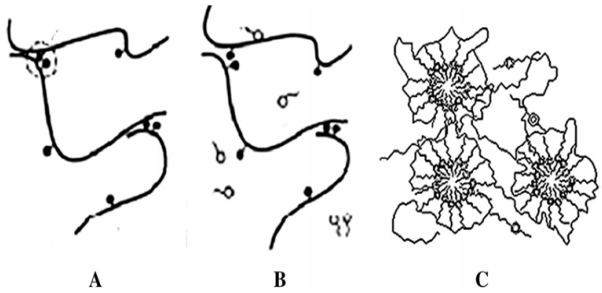


Fig. 3. Interaction of polymer with the surfactant molecules. (a) at low surfactant concentration, (b) at high concentration and (c) at cmc [Ref. 113].

Nambam and Philip [114] studied interaction of surfactants on the self-assembly of a PEO−PPO−PEO triblock copolymer (Pluronics-F108) with anionic (SDS), cationic (CTAB) and nonionic (nonylphenolethoxylate, NP9) surfactants in aqueous solution. They have suggested the formation of a soft solid-like microstructure by the aggregation of self-assembled triblock polymers and a strong electrostatic barrier imparted by the head group of SDS at the core–corona interface. The possible micellar conformation of pluronic in the absence and presence of anionic surfactant head groups, as illustrated by the authors, is shown Fig. 4. Temperature-induced micellization of octablock star copolymers, Tetronic® T904 [$(EO_{15}PO_{17})_2NCH_2CH_2N$ $(PO_{17}EO_{15})_2$] (11), was investigated [115] in aqueous salt solutions in which spontaneous micellization occurred with substantial enthalpy–entropy compensation of T904 micellization.

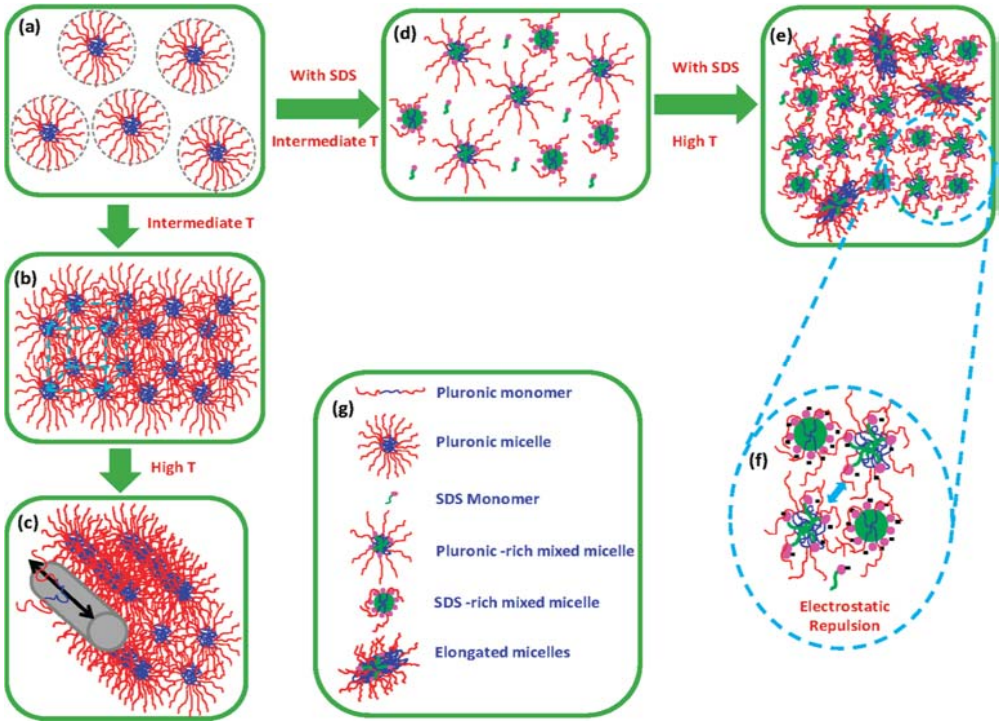
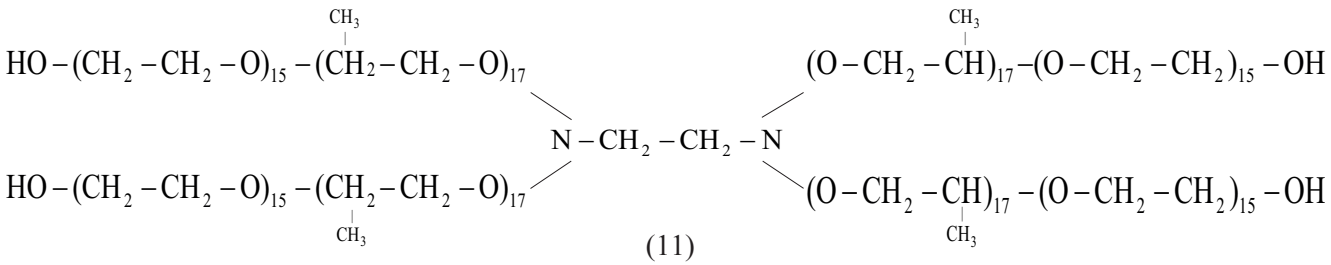


Fig. 4. Micellar aggregates of pluronics F108: (a) F108 at low temperature, (b) F108 at intermediate temperature, (c) F108 at high temperature, (d) F108 with SDS at intermediate temperature, (e) F108 with SDS at high temperature, (f) magnified view of the intermicellar clusters exhibiting electrostatic repulsion [Ref. 114].



(11)

Mixing behavior of benzalkonium chloride (BC) with different triblock polymers (TBP, P123/P105/L64/F127) was studied [116]. Penetration of TBP into the micelle of pure cationic surfactant, BC, brought about the improved micellar properties such as lower cmc values, synergistic interactions and spontaneous micellization due to the reduction of head group repulsions and increase of hydrophobicity of mixed micelles upon the incorporation of nonionic triblock polymer in it. Oikonomou et al. [117] synthesized a series of amphiphilic diblock copolymers, poly(sodium styrene sulfonate)-b-poly(methyl methacrylate), PSS-Na-b-PMMA, which formed micellar structures in water that was characterized by an increasing hydrophobic character and a decreasing size with the increase of the length of the PMMA block. The micelle-like structures change from surface inactive to surface active as the length of the PMMA block increased. Singh et al. [118] examined the interaction of cationic surfactant (CTAB), with pluronics F88 (EO_{103}-PO_{39}-EO_{103}) and P105 (EO_{37}-PO_{56}-EO_{37}) micelles and its effect on the localization of an anionic solute in the mixed micelles. They have suggested the formation of pluronic-CTAB supramolecular assemblies, in which the hydrophobic chains of CTAB occupy the hydrophobic core of the pluronic micelle whereas the positively charged head groups reside at the micellar core-corona interface (Fig. 5). The concentration of CTAB required to drag the probe molecule into the interior of the micelles was linearly correlated to thickness of the corona region of the respective micelles.

Kabir-ud-Din et al. [119] studied the adsorption and micellization of AMT in presence of PEG (of varying molecular weights from 400 to 35.000) of different chain lengths. They have suggested that the nature of interaction and microstructure of the aggregates depend upon the composition and chain length of the polymer. Addition of nonionic polymer PEGs reduced the overall cmc of AMT because of the amphiphilic nature of PEGs and decrease of the charge density near the micellar surface. PEGs, the nonionic polymers, function through weak non-specific (iondipole) and hydrophobic interactions with the drug. Aggregation behavior of triblock copolymer $EO_{76}PO_{30}EO_{76}$ (F68) with SDS and sodium bis(2-ethylhexyl)sulfonate (AOT) in aqueous solution has been reported by Li et al. [120]. F68/micellar SDS complexes were formed at the SDS concentrations above its cac, SDS interacted with F68 mainly through hydrophobic forces, polypropylene oxide (PPO) groups of F68 were solubilized into the SDS micellar cores and poly(ethylene oxide) (PEO) groups interacted with SDS micelles.

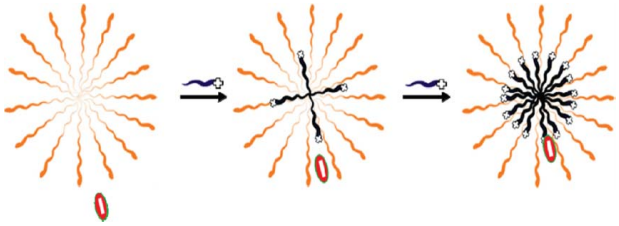


Fig. 5. Gradual changes in the location of an anionic solute with the addition of a cationic surfactant in a pluronic micelle [Ref. 118].

5. Conclusions

Because of the application of mixed polymer-surfactant solutions in various fields, these systems have attracted much interest in recent years. There is a considerable amount of literature on the topic of polymer-surfactant interaction, and we list only a few articles those are relevant to the present review. Review of the recent work makes it possible to suggest that the research is currently focusing on systems with mixed interfacial films made of either two surfactants or surfactants combined with polymers. This area will certainly be of great interest in the future.

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