Liquid and solid foams / Mousses liquides et solides

Adsorption of soluble polymers at liquid interfaces and in foams

Adsorption de polymères solubles aux interfaces liquides et dans les mousses

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A B S T R A C T

We review some results from the literature describing the structure and dynamics of polymer molecules adsorbed at liquid interfaces as well as their behavior in foams. The first part describes theoretical and experimental results concerning the structure and dynamics of model polymer systems, i.e. homopolymers and copolymers. In the second part, we review experimental results concerning mixtures of polymers and surfactants that are widely used to stabilize foams. In such mixtures, the surfactants and the polymer molecules form complexes in the bulk solution and at liquid interfaces which help stabilizing the foams. We review the physicochemical parameters that influence the adsorption dynamics and the viscoelastic properties of the interfaces as well as the foam properties of such mixtures.

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R É S U M É

Nous passons en revue des résultats de la littérature décrivant la structure et la dynamique de molécules polymères adsorbées aux interfaces liquides ainsi que leur comportement dans les mousses. La première partie décrit des résultats théoriques et expérimentaux concernant la structure et la dynamique de systèmes polymères modèles, c'est-à-dire des homopolymères et des copolymères. Dans une seconde partie, nous rapportons des résultats expérimentaux ayant trait à des mélanges de polymères et de surfactants qui sont couramment utilisés pour stabiliser les mousses. Dans de tels mélanges, les surfactants et les molécules polymères forment des complexes au sein de la solution et aux interfaces liquides, qui concourent à la stabilisation des mousses. Nous énumérons les paramètres physicochimiques qui influencent la dynamique de l'adsorption et les propriétés viscoélastiques des interfaces, ainsi que les propriétés moussantes de tels mélanges.

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1. Introduction

Polymers, also named macromolecules, are long molecules, composed of a large number of repeat units, which show exceptional interfacial properties in comparison to small molecules such as surfactants. Polymer molecules adsorb slowly and almost irreversibly to solid or liquid interfaces while surfactants rapidly exchange between the interface and the bulk solution. Although the attraction energy of one monomer with an interface is of the order of kT, the thermal energy, the desorption energy of a polymer chain composed of a large number of monomers is much larger than kT. Hence, the probability for the chain to desorb from the interface is very low. Upon adsorption, some sections of the long chains, known as the *trains*, adsorb at the interface, while other segments form *loops* or *tails* extending into the bulk phase. In the case where the polymer molecules are adsorbed on solid colloidal particles, the loops provide a steric protection against the flocculation of the particles. In the case of liquid–air interfaces and more specifically bubbles in a foam or drops in an emulsion, it can therefore be expected that the loops can provide protection against bubble or drop coalescence. Surprisingly, the link between the dynamics of polymer molecules at liquid interfaces and their ability to stabilize aqueous foams remains largely unexplored.

In the first part of this article, we review the interfacial properties of soluble homopolymers and amphiphilic copolymers adsorbing at liquid interfaces from an aqueous solutions. We choose to focus on polymer systems spontaneously adsorbing at liquid interfaces from a solution and we exclude from this review the case of spread Langmuir monolayers, which nevertheless is a very active field of research. We will briefly review the main results concerning the structure of adsorbed layers of neutral homopolymers, which was well described theoretically in the 1980s and 1990s, using numerical simulations as well as scaling laws and mean-field calculations [1–3] and was reviewed in a book [4]. Concerning amphiphilic copolymers, their structure was also described theoretically. However, there are very few experimental studies dedicated to their structure and their interfacial dynamics, which remain poorly understood. We will focus on the mechanisms and physicochemical parameters that control their adsorption dynamics as well as the elasticity and viscosity of the adsorbed monolayers.

In the second part, we will review experimental results concerning the stabilization of foams using mixtures of polymers and surfactants. In such mixtures, the surfactants and the polymer associate in the solution and form complexes that adsorb at liquid interfaces in some conditions. We will review the physicochemical parameters controlling the structure of the adsorbed layers and the mechanisms that lead to increase the stability of foams with respect to pure surfactant solutions.

2. Adsorption and dynamics of homopolymers and block copolymers adsorbed at liquid interfaces

The structure of adsorbed polymer layers can be investigated by optical techniques such as ellipsometry, X-ray, and neutron reflectivity. Several techniques enable to investigate the interfacial dynamics of polymer adsorbed layers [5,6]. The Langmuir trough equipped with a Wilhelmy plate is a standard equipment to obtain the compression isotherm of polymer layers spread at an interface, i.e. the surface pressure, Π, in mN/m, as a function of the surface coverage, Γ, in mg/m². The surface pressure writes $\Pi = \gamma - \gamma_0$, with γ the surface tension of the polymer solution and γ_0 the surface tension of pure water. The pendant drop method enables to obtain the surface tension, γ, of polymer solutions by fitting the profile of a pendant drop of solution to the Laplace equation. When the area of the drop is made oscillate, the surface compression modulus, ε, in mN/m, can be obtained and writes $\varepsilon = \mathrm{d}\gamma / \mathrm{d}\ln A = \varepsilon' + \mathrm{i}\varepsilon''$, where ε' is the surface compression storage modulus and ε'' is the surface compression loss modulus. To obtain the surface compression elasticity at larger frequencies, techniques such as capillary waves can be used. The surface shear elasticity and viscosity of the polymer monolayers can be determined by measuring the displacement of a floating object at the interface when an external force is applied. In the case of micrometric particles, one can follow the Brownian motion of the particle due to the thermal energy; however, the mathematical analysis of such data is still debated [7,8].

2.1. Homopolymers in good solvent

2.1.1. Structure

The structure of adsorbed polymer layers at solid or liquid interfaces was described in a series of seminal papers written in the 1980s and 1990s [1–3] and reviewed in the book of Fleer, Cohen-Stuart, Sheutjens, Cosgrove, and Vincent [4]. It results from a competition between the gain in enthalpy due to the monomer/surface attraction and the loss of translational and conformational entropy of the chains at the interface. In the case where the monomers are repelled by the interface, the polymer chains deplete the interface. In the case of a strong attraction of the monomers with the interface, flat layers are favored, where a large fraction of the monomers are adsorbed at the interface. When the attraction between the monomers and the interface is weak, the formation of large loops and tails extending into the solution is favored (Fig. 1).

For semi-dilute solutions, an adsorbed layer is composed of three regions with different density profiles (Fig. 2). The *proximal* region is situated close to the interface at a distance $z < D \sim a/\delta$, where a is the size of the monomers and δkT is the attraction between one monomer and the interface. The surface concentration $\phi_s = \phi(z=0) \sim a/D \sim \delta$. In this region, the short-range forces between a monomer and the wall are large. In the case of strong interaction between the monomers
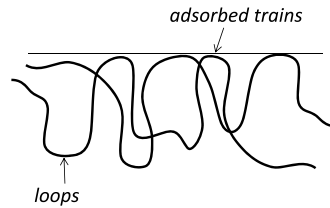
Fig. 1. Loops and tails formed by polymer layers adsorbed from solutions.
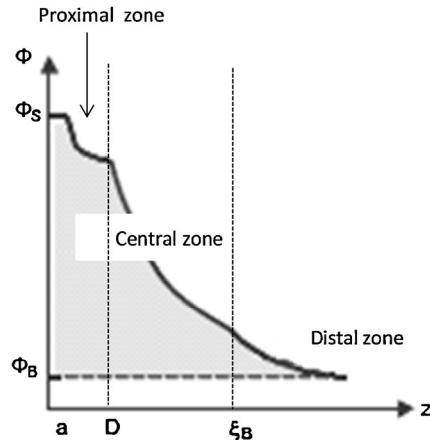

Fig. 2. Concentration profile of neutral homopolymer layers adsorbing at the air–water interface.

and the interface, i.e. $\delta = 1$, the size of the proximal zone is of the order of a. For $a < z < D$, the concentration profile scales as $\phi(z) \sim z^{-1/3}$.

In the *central* zone, $D < z < \zeta_b$, the structure of the layer is self-similar, meaning that its structure does not depend on the length scale. In this zone, the concentration profile writes $\phi \sim z^{-3/4}$. In this zone, the profile does not depend on the bulk concentration, c_B.

In the *distal* zone, $z > \zeta_b$, the concentration relaxes exponentially toward the bulk value, $\phi(z) \sim c_B \exp(-z/\zeta_b)$.

Bouchaud and Daoud [9] adapted these calculations to the case of dilute solutions and predicted the surface excess, $\Gamma = \int_0^z \varphi(z)\mathrm{d}z$, in mg/m^2, as a function of the bulk concentration, c_B. The surface excess increases with the polymer concentration up to a concentration ϕ_c. Above ϕ_c, the interface is saturated with monomers and has a self-similar structure. In practice, the concentration, ϕ_c, is of the order of a few micrograms per liter and it decreases with the molecular mass of the polymer molecules.

2.1.2. Surface tension and dynamic properties

Di Meglio et al. [10] found experimentally that the surface tension of a polymer solution may increase or decrease with the bulk concentration, depending on whether the polymer molecules are attracted or repelled by the interface, such as for PDMS, polydimethylsiloxane, in bromocyclohexane or PS, polystyrene in cyclohexane, respectively.

Manghi and Aubouy [11] showed theoretically that the surface tension of semi-dilute solutions increases with the molecular mass of the chains, because of a competition between the entropy, associated with a large distribution of loop sizes and the specific attraction of the chain ends with the interface, which may be surface active.

The dynamic properties of polymer adsorbed layers, such as their surface compression and shear elasticity, remain largely unexplored [12]. The existing studies report low compression elasticities for solutions of soluble polymers such as PEO, polyethylene oxide, or PVP, polyvinyl pirrolidone. The high compressibility of adsorbed polymer layers of soluble polymers is attributed to the fact that upon compression, monomers adsorbed in the 'trains' can rapidly desorb from the interface to form loops [12].

2.2. Homopolymers in bad solvent

Johner and Joanny [13] studied theoretically the adsorption of polymers that are in bad solvent conditions. They showed that the adsorption polymer coils is very similar to a wetting situation. When the polymer globule wets the interface, it spreads and forms a flat pancake at the interface. At low concentrations, the adsorbed chains form a 2D layer which is in a bad or good solvent depending on the interactions between the monomers. When the 2D solution is in bad solvent, a demixing transition is predicted between a dilute phase and a concentrated phase. At larger concentrations, the adsorbed layer becomes continuous and its thickness increases.

PNiPAM, poly(*N*-isopropylacrylamide), is a good example of surface-active polymer that undergoes a coil-to-globule transition when the temperature is raised above 32 °C, which corresponds to the Lower Critical Solubility Temperature, LCST. The PNiPAM chains are in good solvent conditions in water below 32 °C and in bad solvent conditions above 32 °C. Jean et al. [14–16] investigated the adsorption of PNiPAM at the air–water interface using surface tension and X-ray reflectivity as a function of temperature. When the temperature rises, denser and thicker layers are obtained. The authors also studied thin-liquid films made from PNiPAM solutions. Between 24 and 27 °C, the thickness of the thin films is around 1500 Å, i.e. larger than the radius of gyration of the chains in solution and larger than the thickness measured by neutron reflectivity (110 Å). From these results, the authors conclude that the tails, which cannot be detected by reflectivity experiments, extend much further in the solution than the detected loops. The stability of the 1500-Å-thick films is therefore due to the entropic repulsion between the tails. Above the LCST, the thin liquid films become unstable [14] and contain micrometric aggregates. This behavior may be interpreted as the demixing transition predicted by Joanny. However, above the LCST, the surface tension of the PNiPAM solutions depends very weakly on the polymer concentration, showing that the interface is probably saturated with NiPAM units.

The compression and shear elasticities of PNiPAM layers increase with temperature as the layers become more dense and thicker [15,17]. The moduli are orders of magnitude larger than what is measured for more hydrophilic polymers such as PEO and PVP, probably because the layers are denser and more entangled.

2.3. Neutral and charged amphiphilic copolymers

We now review studies concerning amphiphilic polymers, which contain both hydrophilic and hydrophobic moieties (Fig. 3). The hydrophobic moieties can either be part of the backbone or grafted as a pendant group. Bloc copolymers are composed of alternate hydrophilic and hydrophobic blocks, while for random copolymers the hydrophobic moieties are randomly distributed on the backbone. In the case of grafted moieties, let us mention two specific cases: the comb polymers, where the size of the pendant group is of the order of the length of the backbone and the polysoaps, for which each monomer is grafted with a pendant group. Lastly, for telechelic polymers, the hydrophobic moieties are situated at both chain ends.

Pancake and quasi-brush regimes The hydrophobic moieties, which provide surface activity properties to the polymers, adsorb at the liquid/air or liquid/liquid interface and form a flat pancake, while the rest of the chain remains mostly swollen in the aqueous phase (Fig. 4). In a series of papers [18–21], Daoud described theoretically surface transitions for layers of block copolymers as a function of surface coverage, Γ. In the dilute regime, the chains are far from each other, the hydrophilic blocks form 3D coils swollen in the liquid phase, while the hydrophobic blocks form 2D pancakes at the interface. For higher surface coverage, as the chains start overlapping—but not the blocks—, a first 2D semi-dilute regime is expected. For higher surface coverage, on the gas side, we encounter successively a 2D semi-dilute regime where the hydrophobic pancakes overlap, then a quasi-melt when the pancakes are expulsed in the gas phase and lastly a quasi-brush extending into the gas phase [22]. On the liquid side, when the hydrophilic blocks overlap, the coils stretch in the direction perpendicular to the interface and form a quasi-brush in the solution. For random copolymers [23], a brush structure is also expected between the hydrophobic anchors.

Surface pressure and surface compressibility of the layers Daoud derived the free energy of the block copolymer layers and deduced scaling laws predicting the surface pressure, Π, as a function of the surface coverage, Γ,

$$\Pi \sim k\Gamma^y \tag{1}$$

In good solvent conditions, the exponent $y = 3$ for purely 2D semi-dilute regimes, while in the case of semi-brushes forming in the liquid or in the gas phase, $y = 1$. In the quasi-melt, $y = 0$. In θ and bad solvent conditions, these exponents are modified, as shown in Table 1.

These scaling laws can be tested experimentally by two different methods. The standard method consists in spreading the polymer layer at the air–water interface in a Langmuir trough and compressing it using barriers. The surface pressure can then be measured using a Wilhelmy plate. Aghie-Beguin and Daoud [18] proposed a second method using the pendant-drop
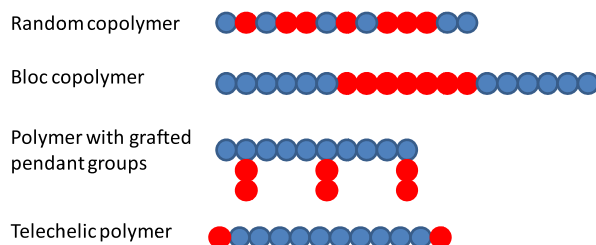

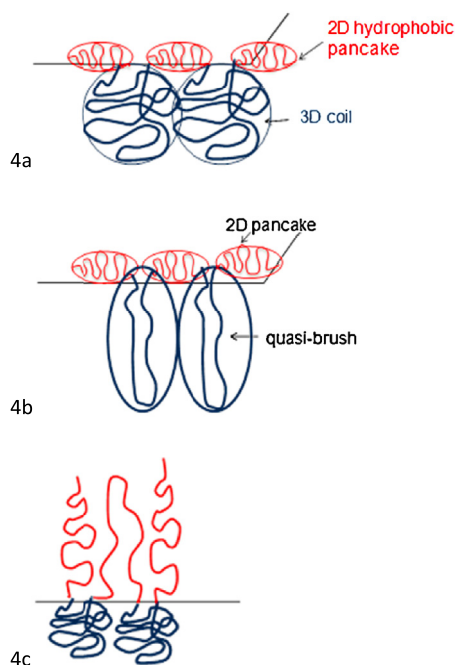**Fig. 3.** (Color online.) Families of synthetic amphiphilic polymers.

Fig. 4. (Color online.) Schematic drawing of the conformation of amphiphilic block copolymers adsorbed at the liquid–gas interface. (a) At low surface coverage, the hydrophobic parts form flat pancakes and the hydrophilic blocks form 3D coils swollen in water. (b) When the surface coverage increases, in the case where the 3D coils are larger than the hydrophobic parts, the 3D coils may overlap and form a brush stretching into the aqueous phase. (c) In the case where the hydrophobic blocks are larger than the hydrophilic blocks, the pancakes may overlap and lead to the formation of brush extending into the gas phase (adapted from Refs. [18–21]).

Table 1
Values of the exponents of the power laws, $\Pi \sim k\Gamma^y$, as a function of regimes and solvent conditions.

Conditions	Exponent	
	2D regime	3D quasi-brush
Poor solvent	∞	0 (melt)
θ solvent	8	1
Good solvent	3	1

experiment. A pendant drop of polymer solution is formed at the tip of the syringe. During the adsorption process, the area of the drop is continuously made oscillate. From the oscillations, one can obtain the surface elasticity $\varepsilon = \frac{d\pi}{d\ln A} = \frac{-d\pi}{d\ln \Gamma}$. During the adsorption kinetics, the surface coverage increases, hence the surface pressure increases, hence one can obtain ε as a function of Π. From Eq. (1), the exponent y writes $y = \frac{d\ln \pi}{d\ln \Gamma} = \frac{\varepsilon}{\pi}$, it is therefore equal to the slope of the curves $\varepsilon(\Pi)$. This method is based on the assumption that the surface excess remains constant during an oscillation.

Daoud's group tested eight triblock copolymers, either PEO–PPO–PEO or PPO–PEO–PPO, with varying degrees of hydrophobicity (PPO stands for polypropyleneoxide). For all the eight copolymers, they found the first 2D semi-dilute regime with $y = 3$. At larger surface pressures, the elasticity presents either a maximum or a plateau for the polymers with moderate hydrophobicity. These results were not satisfactorily described by the model.

The Miller [24] and Langevin [25,26] groups also reported maxima of the surface compression elasticity or plateaus in the surface pressure for solutions of PEO–PPO–PEO copolymers. Combining their surface pressure and ellipsometric measurements, Munoz et al. [26] concluded that, for the highest surface pressures, the PEO monomers form a brush in the liquid and the PPO block is ejected in the air.

For diblock copolymers, such as PEO–PS [27,28], the surface pressure shows only one plateau with the surface coverage followed by a steep increase at high compressions. Unlike for PPO–PEO–PPO triblocks, there is no report of a second maximum of the elasticity, which can be attributed to the fact that the PS blocks stick strongly to the interface and keep their 2D pancake conformation. These authors compared these static measurements with dynamic compression measurements obtained at frequencies up to 500 Hz. Qualitatively the results depend weakly on the oscillating frequency. The main reason is that the exchange of monomers between the interface and the liquid are fast and the surface compression/dilatation stress can be relaxed by squeezing trains and loops out of the surface upon compression. Using evanescent wave light scattering, Stocco and Sigel studied the diffusion coefficient of PI–PEO (polyisopren/PEO) diblocks at the air–water interface [29]. They
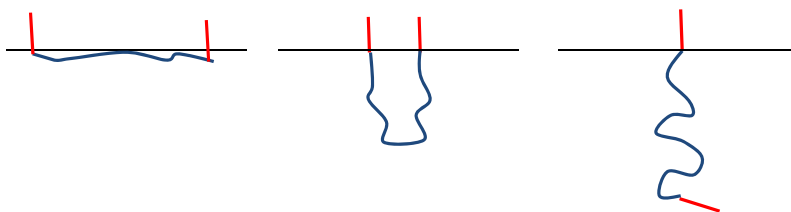
Fig. 5. (Color online.) Compression of telechelic PEO adsorbed at the air–water interface in a Langmuir trough. Upon compression, the PEO part can desorb into the water. At larger compressions, the hydrophobic moiety may also desorb.

found that the diffusion coefficient decreases at relatively high surface concentrations, possibly because of the aggregation of PI moieties.

In the literature, there are other systems which present a maximum of the compression elasticity. Barentin observed a plateau in the surface pressure isotherm, hence a maximum of the elasticity, for Langmuir monolayers of telechelic PEO spread at the air–water interface. The authors also attributed this behavior to a mushroom-to-brush transition [30,31]. At low surface concentrations, the chains lie flat at the interface and the surface pressure is the same as the one predicted by scaling laws for a 2D semi-dilute regime, $\Pi \sim \Gamma^3$. At larger compressions, the PEO monomers desorb from the interface and form a 'brush', anchored by the two hydrophobic moieties. A second maximum of the elasticity can be observed at larger surface coverage, when the hydrophobic anchors desorb from the interface (Fig. 5). The desorption time writes $\tau_{des} \sim \exp(nE/kT)$, where n is the number of carbon atoms of the hydrophobic chain end and E is the desorption energy of a –CH$_2$– unit. After desorption of the hydrophobic moiety from the interface, it can be rapidly expulsed from the brush because of the gradient of chemical potential between the brush and the solution. The expulsion event, derived by Wittmer [32], is much shorter than the desorption; hence the relaxation dynamics of the layer is controlled by the desorption dynamics. The authors confirmed experimentally that the relaxation of the surface pressure after a strong compression depends on the number of carbon of the hydrophobic moiety.

Experimentally, it was found that the architecture of polymers statistically grafted with hydrophobic pendant groups influences the surface tension of the solutions. The surface tension presents a minimum with the number of grafting groups on the chains, which is attributed to a competition between the gain in enthalpy obtained upon adsorption of the pendant groups and the loss of entropy of the chains and anchors as they adsorb at the interface [33]. Consequently, as the grafting density increases, flat conformations are favored, but for the largest grafting densities, the flat conformation becomes entropically unfavored and the chains form loops extending in the solution. Also, when the hydrophobicity of the pendant groups increases or when the polymer concentration increases, micelles form in the bulk solution, leading to an increase in the surface tension [33,34]. To determine the thickness of the layers, ellipsometry and X-ray reflectivity are often used, but they are only sensitive to the proximal zone close to the interface and do not detect the formation of the largest loops. To circumvent this issue, Millet et al. combined X-ray measurements at a single air–water interface as well as for a vertical thin-liquid film to study the adsorption of hydrophobically modified polyacrylic acid polymers in their neutral acidic form, PAAH and in their charged PAANa form [35–38]. The total thickness of the thin liquid films can be easily measured and was found to be set by the size of the largest loops and tails. For concentrations exceeding the Critical Aggregation Concentration, CAC, the polymer chains form a physical gel inside the film due to intermolecular associations, leading to an increase in the film thickness and a strong decrease in the drainage velocity. Below the CAC, the thickness of the PAAH layer is of the order of 210 Å and does not depend on the molecular weight. The authors concluded that all the hydrophobic anchors are adsorbed and that a stretched brush is formed between the anchors, whose thickness does not depend on the length of the chains. The thickness of the layer results from a balance between the osmotic pressure of the neutral monomers and the adsorption energy of the anchors. In the case of the charged PAANa, the layers are thicker, around 450 Å. For the charged chains, the anchors do not all adsorb at the interface and the chains form large dangling loops whose size is of the order of the radius of gyration of the chains in bulk solution. In the latter case, the thickness depends on the molecular weight and is therefore controlled by a balance between the adsorption energy of the anchors and the osmotic pressure of the counterions, which is much larger than for the neutral case.

2.3.1. Adsorption kinetics

The adsorption kinetics of polymer at interfaces is usually slow. We provide below several examples of energy barriers that slow down the adsorption process of polymers at interfaces.

Adsorption barrier due to exchange between micelles and unimers in the bulk solution Theodoly et al. investigated experimentally the adsorption kinetics of three types of block copolymers, among which one block is hydrophilic, PAA, and the second block has an increasing hydrophobicity, PAA–PDEGA, PAA–PBA and PAA–PS [39]. Using the pendant drop method, they found that for the most hydrophobic core, PS, the surface activity is very weak. Indeed, the frozen micelles do not adsorb at the interface and there are no free polymer molecules in the solution. In the case of PAA–PBA, the adsorption kinetics is controlled by the rate of unimer extraction from the micelles. Finally, for the most hydrophilic copolymer, PAA–PDEGA, the adsorption is controlled by the diffusion of the unimers in the solution (Fig. 6a).
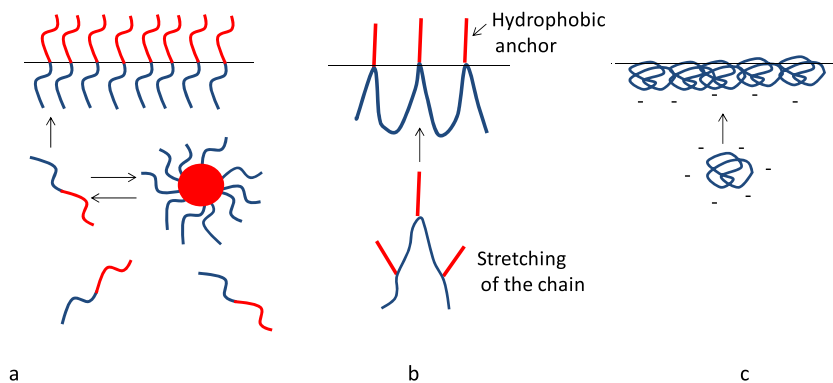
Fig. 6. (Color online.) Schematic drawing illustrating three types of energy barriers that slow down the adsorption kinetics of polymer molecules at interfaces. (a) The adsorption dynamics of amphiphilic diblock copolymers depends on the dynamics of exchange between the micelles and the unimers and on the diffusion of unimers from the bulk solution to the interface (drawing adapted from Ref. [39]). (b) Stretching of a chain approaching an interface covered with amphiphilic polymers adsorbed at early times and forming a quasi-brush (drawing adapted from Ref. [39]). (c) Electrostatic barrier obtained in the case of hydrophobic polyelectrolyte. The PS/PSS copolymers form a charged globule that is repelled by the layer of charged globules adsorbed at early times (drawing adapted from Ref. [41]).

Adsorption barrier due to diffusion–reptation of chains through the layer The kinetics of adsorption of telechelic [36] and diblock [37] polymers was described in two theoretical studies, which lead to very similar scaling laws. At short times, of the order of one second, the adsorption is limited by the diffusion of chains to the interface. For longer times, the adsorbed chains start overlapping at the interface and to stretch strongly in the direction perpendicular to the interface, forming a brush. The additional chains approaching the interface have to stretch and to diffuse by reptation through the brush already adsorbed (Fig. 6b). In this second regime, the adsorption of the chains slows down and the surface density increases logarithmically with time. This logarithmic law was verified experimentally by Millet et al. using polyacrylic acid polymers statistically grafted with hydrophobic anchors [35]. They found that the adsorption dynamics did not depend on the polymer concentration nor the salt concentration but only on the molecular mass, as predicted by Ligoure and Leibler [40].

Case of polyelectrolytes: adsorption barrier due to electrostatics In the case of charged polymers, known as polyelectrolytes, the first chains that adsorb at the interface induce a negative potential that slows down the adsorption of additional chains. Theodoly et al. observed that electrostatic effects also control the adsorption of random PS/PSS, polystyrene/polystyrene sulfonate copolymers at the air–water interface [41]. The authors found that the surface tension reaches a minimum with the degree of sulfonation. The surface tension of the PS/PSS with the highest degree of sulfonation remains equal to that of pure water. Highly charged polymers are not hydrophobic enough to be surface active. However, for sufficiently large polymer concentrations or salt concentrations, the surface tension decreases. For intermediate degrees of sulfonation, the polyelectrolyte is more surface active and the surface tension is lower than that of pure water. Unexpectedly, for the lowest degree of sulfonation, the surface tension is close to that of pure water, although the molecules are hydrophobic. In the bulk solution, the chains form hydrophobic globules that are surrounded by a cloud of counterions that is repelled by the interface (Fig. 6c). The addition of salt enables to screen the electrostatic interaction and to decrease the surface tension.

To probe the desorption dynamics of the PS/PSS layers, the same authors washed out the bulk solution either with pure water or with a salt solution. In these experiments, the adsorbed amount remains constant; however, a lower surface pressure is reached when the salt solution is used for the rinsing process. This result illustrates that the surface pressure originates from the electrostatic repulsions between the charged monomers at the interface and that it can be screened by the salt.

2.3.2. Surface shear viscosity

There are very few experimental studies concerning the shear properties of adsorbed polymer layers because the shear viscosity and elasticity are very low and therefore difficult to measure. Barentin et al. obtained the shear viscosity of telechelic PEO's by measuring the surface drag on a disk floating at the interface, but found surface viscosities of the order of 1 to 5 μN m s [42], which is of the same order of magnitude as for simple surfactant monolayers. This shows that the polymers are probably weakly entangled at the interface.

2.3.3. Thin liquid films and foams

In references [43,44], the stability of thin liquid films and foams made from triblock copolymers PEO–PPO–PEO with varying length for the PEO blocks is discussed. The authors report the disjoining pressure in the film as a function of their thickness, $\Pi(h)$, and find a steep repulsion between the two interfaces of the film, which is due to a brush-to-brush repulsion between the PEO brushes. For the polymers with the longest PEO blocks, the films are thicker and more stable over time, which correlates well with the fact that the foams made with these polymers are the most stable.
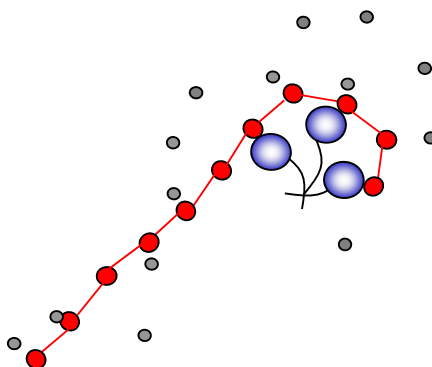
Fig. 7. (Color online.) Schematic drawing showing the complexation of a polyelectrolyte chain with oppositely charged surfactants. The chain collapses on the surfactants and the counterions of both the surfactants and the polyelectrolyte are released.

3. Mixtures of polymers and surfactants at liquid interfaces and in foams

Mixtures of polymers or polyelectrolytes and surfactants are widely found in applications such as body care, cosmetics, oil recovery. Polyelectrolytes and polymers are usually used for their rheological properties, while the surfactants are used because of their ability to produce foams. When they are mixed, polymers and surfactants can interact and form complexes in the bulk solution. In the case of oppositely charged polyelectrolyte/surfactant mixtures, they also form amphiphilic complexes at interfaces, which can be efficient at improving the foam stability. Below we review the physicochemical parameters that control the interfacial behavior and the foam stability of these systems.

3.1. Bulk behavior

In oppositely charged polyelectrolytes/surfactant mixtures, the driving force for the complexation is the gain in entropy obtained when the counterions of the polyelectrolyte are released as the surfactants binds to the charged monomers. As the number of bound surfactant increases, the electric charge of the complexes decreases and hydrophobic interactions between the surfactant tails lead to a collapse of the polyelectrolyte chains around the surfactant micelles forming a pearl-and-necklace structure (Fig. 7). The collapse of the chains leads to a decrease in the viscosity of the solutions [45,46]. The phase diagram of such mixtures contains a precipitation zone [47,48], whose position and shape depends on physicochemical parameters such as polymer molecular weight, surfactant hydrophobicity, salt concentration.

3.2. Surface activity and surface rheology

Increasing the surfactant concentration for a given polyelectrolyte concentration The interfacial properties of oppositely charged polyelectrolyte/surfactant systems has been the object of several reviews [49–53]. An early study conducted by Goddard [54] on a cationic polymer and an anionic surfactant has shown that mixtures of polyelectrolyte surfactants of opposite charge present a lowering of the surface tension at surfactant concentrations much lower than the CMC of the pure surfactant. Similar results have been reported for other systems including anionic polyelectrolytes and cationic surfactants such as PAMPS/C_nTAB [55] systems or PSS/C_nTABs [56]. For PSS/C_nTAB surfactants, it was shown with potentiometric measurements that the decrease in the surface tension occurs for very low concentrations of free surfactants when all the monomers of the polyelectrolyte chains are bound with surfactants, meaning that the charge of the complexes is low [56].

Measurements of the interfacial viscoelastic properties of mixed polyelectrolytes–surfactants systems have shown that the addition of a polyelectrolyte to surfactant solutions enables to increase both the dynamic compression elasticity of the layers and the shear elasticity below the CMC of the surfactants [57–59], confirming that in this range of concentrations, mixed polyelectrolytes–surfactants layers are formed at the interface. Using linear and linear shear rheology measurements Espinosa and Langevin [59] measured two relaxation times for the DNA/C_{12}TAB layers. In the linear regime, the relaxation time deduced from the cross-over between G' and G'' is of the order of 10 s, showing that the polymer layers are not entangled and slide easily below the surfactant layer. In the non-linear regime, where fractures are observed, the relaxation time is of the order of 200 s and corresponds to the healing of the fractures.

In a narrow concentration zone below the CMC, such mixed layers were found to form very heterogeneous layers [58,60,61] using Brewster Angle Microscopy or AFM analysis of layers transferred on a solid surface From the study of thin-liquid films made from PAMPS/C_nTAB and PSS/C_nTAB in this range of concentration, it was observed that polymer/surfactant aggregates were trapped in the thin liquid films, bridging the two interfaces of the film and the drainage of the corresponding films was very slow [62,57]. The maximum in surface shear elasticity and in compression elasticity did not correlate with the presence of these aggregates, probably because they are very compressible and loosely connected at the interface.

For surfactant concentrations around the CMC, for a given polymer concentration, precipitation is usually observed and the surface tension either remains on a plateau or in some cases rises sharply [63], because there are fewer surfactants and polyelectrolyte molecules available to stabilize the interface. Accordingly, Monteux et al. found with ellipsometry [56] that the amount of adsorbed species at the air–water interface falls in the precipitation region.

Above the CMC of the surfactant, the surface tension usually returns to the one of the surfactant solutions alone, as the interface is only saturated by a monolayer of surfactant molecules. For PSS/C_{12}TAB, above the CMC an increase of the ellipsometric signal [57] was obtained because of a possible formation of mixed multilayers at the interface [64].

Physicochemical or formulation parameters controlling the interfacial behavior   Parameters such as polymer molecular weight [65], surfactant hydrophobicity [66] and polymer rigidity [67,68,59] can be varied to adjust the interfacial properties of the mixtures. Langevin's group investigated the influence of the rigidity of the polymer molecules on the shear properties and compression of the layers at large deformations. Rigid polymers such as DNA makes the most dense [68] and rigid [67] layers, but they are also more brittle [59]. For polymers of intermediate rigidity, such as carboxymethyl cellulose, the layers probably form loops, hence they are less dense and present a viscoelastic behavior. For very flexible polymers such as PAMPS, the layers have a purely viscous behavior in a shear deformation and were shown to be more compressible.

Studies concerning the influence of molecular weight [65] and surfactant hydrophobicity [66] on surface behavior of PSS/CTAB mixtures have shown that the adsorbed amount is correlated with the phase behavior. For the longest PSS chains or most hydrophobic surfactants (C_{12} and C_{14}TAB), the bulk phase diagram is characterized by a strong flocculation, which leads to a very large drop of adsorbed amount since most of the P/S complexes are in the solid phase. For intermediate surfactant hydrophobicity (C_{10}TAB) and polymer molecular mass, a maximum of adsorption is observed for intermediate surfactant concentrations.

Varying the polyelectrolyte concentration for a given surfactant concentration enables to vary the charge of the complexes [69,70]. Stable thin liquid films are obtained below and above the isoelectric point (IEP) of the complexes while no stable film can be obtained at the IEP although the surface coverage is the highest. At high salt concentration, the electrostatic barriers are screened and the adsorption dynamics was found to accelerate. Consequently, the compression elasticity to decrease because of faster adsorption/desorption dynamics of the P/S complexes at the interface [71], leading to a weak variation of the surface tension during area oscillation, hence small compression elasticities.

3.3. Foam stability

Surprisingly, even though the amount of data concerning the dynamics of polyelectrolytes/surfactants systems is quite significant, there are much fewer studies reporting their foaming properties.

In the case of strongly interacting systems of opposite charge, such as PSS/C_nTAB, the foam stability is increased for a ratio of surfactant-to-monomers concentration close to one, where the shear surface elasticity is maximal. However, the surface dilational elasticity, which shows a maximum at a lower ratio, does not seem to influence the foam stability. In the 'precipitation' zone, the foams were very unstable, and the hydrophobic aggregates probably act as antifoamers.

Recently, Tcholakova et al. [72] published a systematic study dealing with the foaminess and foam stability of several mixtures of polymers and surfactants. They studied strongly interacting systems of opposite charge, such as Sodium Dodecyl Sulfate, SDS and PVAm, polyvinylamine, and weakly interacting systems such as cationic surfactants and polymers (C_nTAB and polyvinylamine) or neutral surfactant $C_{12}O_{23}$ and cationic polymer PVAm. The authors found that for weakly interacting systems, both the foaminess (the amount of foam produced with a given volume of solution) and the foam stability are increased, whereas for strongly interacting systems, only the foam stability is improved with respect to the pure surfactant solutions, but the foaminess is reduced. The authors coupled their foam data with dynamic surface tension measurements as well as with thin liquid films observations. They concluded from these measurements that in the case of strongly interacting systems, there are fewer free surfactants in the solution, leading to a decrease in the foaminess; however, the presence of a polymer in the adsorbed layers leads to an increased stability. In the case of the weakly interacting systems, there is a larger quantity of free surfactants in the solution, which quickly adsorb at interfaces, leading to a good foaminess, and the adsorption of polymers also leads to an increase in the foam stability.

4. Conclusions and perspectives

In the first part of this article, we have reviewed theoretical and experimental results concerning the structure and adsorption dynamics of model systems such as homopolymer and copolymers. However, these layers remain quite compressible and easy to shear, as the exchange between adsorbed monomers and loops is very fast. Moreover, the adsorption is usually slow, because of electrostatic or steric energy barriers. These facts may explain why there are very few results concerning foams made with these systems. Mixtures of polymers and surfactants combine several advantages over copolymers. These systems form complexes in bulk solution, whose hydrophobicity and conformation can be easily tuned by varying the surfactant concentration or hydrophobicity. Therefore, the surface activity of these complexes can be easily controlled experimentally. The presence of free surfactants in the bulk solution, which can adsorb quickly to interfaces, enables to keep a good foaminess, while the formation of mixed P/S layers at the interface enables to obtain a better foam stability.

Proteins, which were not described in this review, are widely used for the stabilization of foams. It seems that their ability to denature and reorganize at liquid interfaces enables to combine a good foaminess and good foam stability. Proteins, in their native form, quickly adsorb at interfaces. The protein then unfold over time and form intermolecular linkage through hydrophobic moieties, which results in a rigid network [73] and even multilayers that are very efficient at stabilizing foams. Interfacial rheology is a very powerful tool to study structure and dynamics . . .

The use of polymer to modify the bulk rheology of the continuous phase and therefore modify the drainage flows is largely unexplored. Safouane et al. have used non-Newtonian polymers to modify the drainage velocity of the foams and observed non-expected behaviors, probably linked to the elongational viscosity [74]. Recently, Testouri et al. produced a foam using a microfluidic device where the continuous phase is gel [75]. Combining interesting bulk and interfacial rheological properties will probably be a strategy to improve the stability of foams made with polymer solutions.

Acknowledgements

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