

# A Brief Review of Polymer/Surfactant Interaction

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This brief review of polymer-surfactant interaction opens by describing how polymers behave in solution. Then we survey the literature on the interaction of nonionic polymers with surfactants, and the interaction of polyelectrolytes with ionic surfactants of opposite charge. After a brief discussion of polymer adsorption at interfaces, we consider the implications of these interactions on the design of shampoo products.

## **Polymers in Dilute and Semi-dilute Solution**

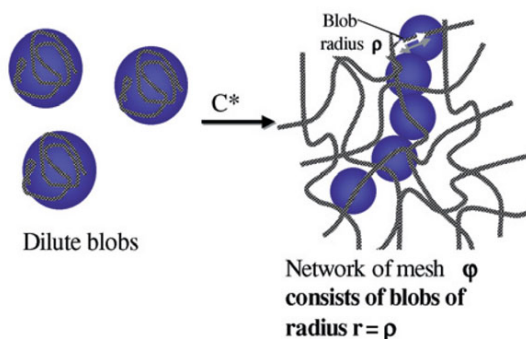
Polymer-surfactant interaction in personal care compositions usually occurs in aqueous media. In order to understand the concepts of this type of polymer-surfactant interaction, it is first necessary to grasp how typical polymers behave in solution. The condition for a polymer molecule to dissolve is that the polymer-solvent interaction is greater than both polymer-polymer and solvent-solvent interactions. If this condition is achieved the polymer will dissolve and, depending upon the concentration, a dilute solution or semi-dilute solution will be formed.

A dissolved polymer can occupy many times the volume of the polymer molecule itself—that is, a polymer swells when it is dissolved and the volume inside the swollen polymer contains solvent. It is not unusual for a dissolved polymer to be swollen to a thousand times its original size. In a dilute solution each dissolved polymer molecule will be isolated. If the polymer concentration is increased, eventually there comes a point when the entire space is filled with swollen polymer molecules and above this concentration the polymer can only occupy the solution if the molecules entangle and thread through each other's domains.

The concentration of the onset of entanglement is called the “critical overlap concentration” ( $C^*$ ). Above the critical overlap concentration the system is in the semi-dilute regime. When polymers phase-separate from solution, they usually do so in the semi-dilute or concentrated condition and therefore they are in an entangled state.

Polymer scientists gain conceptual understanding of the process of separation by introducing the concept of correlation length. The correlation length is known more colloquially as the “blob size.” In dilute solution, the blob size is the size of the entire polymer molecule and in semi-dilute solution the blob size becomes the distance between entanglement points ([Figure 1](#)).

Figure 1. Blobs in dilute to semi-dilute solutions

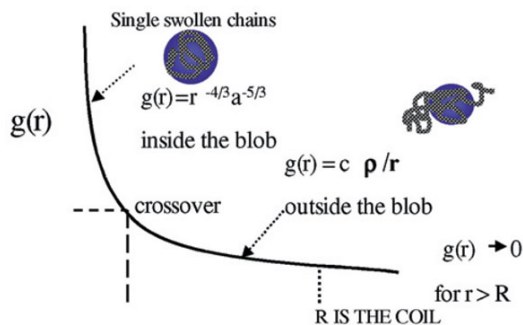


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The blob size decreases as polymer concentration increases even in dilute solution. This is depicted in **Figure 2** in which  $g(r)$  represents the blob size and the horizontal axis represents polymer concentration.

Figure 2. The decrease in blob size as the polymer concentration increases

The blob size decreases as polymer concentration increases even in dilute solution; here,  $g(r)$  represents the blob size and the horizontal axis represents polymer concentration.



### Interaction of Nonionic Polymers with Surfactants

The field of polymer surfactant interaction owes a great deal to Suji Saito, whose early work formed the basis of much of the formal research that has been conducted subsequently. In 1952 he observed that the water-insoluble hydrophobic polymer polyvinyl acetate completely dissolved in micellar sodium dodecyl sulfate solution.<sup>1</sup> This was intriguing because the polymer molecules were substantially too large to fit into the micelle and therefore the existing theories of solubilization could not explain this phenomenon.

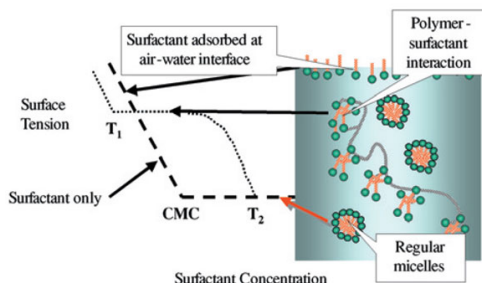
Based upon simple viscosity measurements, Saito and Sata proposed a model of micellar aggregates along the polymer chain. This “pearls on a string model” is now well accepted and has been validated by more sophisticated methods such as neutron scattering.<sup>1</sup>

In a 1957 publication, Saito extended this model to explain the sodium dodecyl sulfate-induced increase in the viscosities of aqueous solutions of the hydrophilic polymers methyl cellulose and poly(N-vinylpyrrolidone).<sup>2,3</sup> For these hydrophilic polymers, he explained that ionic repulsion between the “micellar pearls” caused expansion of the polymer chain, which in turn caused an increase of this viscosity. Today, we would refer to this as an increase in the ionic persistence length of the molecule—or an increase in “blob size.”

The model was further advanced by Jones in a study of polyethylene oxide interaction with sodium dodecyl sulfate in aqueous solution.<sup>4</sup> Jones noted that in the presence of the polyethylene oxide the normal surface tension curve of the surfactant showed a premicellar breakpoint,  $T_1$ , followed by a slow descent to meet the normal micelle curve at higher concentrations,  $T_2$ , than the measured critical micelle concentration (CMC) of the surfactant. Jones described the  $T_1$  point as the lowest surfactant concentration at which interaction occurred between the surfactant and polymer and  $T_2$  as the surfactant concentration at which both the polymer and the air-water interface became “saturated” with surfactant and normal micelles first appeared (**Figure 3**).

**Figure 3. Polymer-surfactant interaction**

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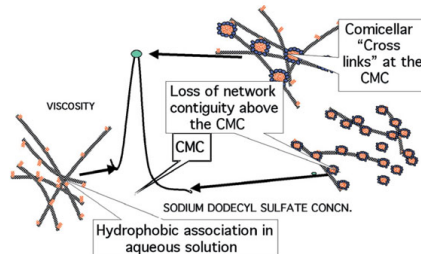


Jones’ concepts and methods are still used today to probe polymer-surfactant interactions. A careful NMR study by Professor Nagarajan of Penn State University showed that polyethylene oxide decorated the outside of surfactant spherical micelles, penetrating deeper than the micelle’s palisade layer and the polymer extended between many micelles to form the “pearls on a string.”<sup>5</sup>

Hydrophobically modified hydroxyethylcellulose is usually supplied as the hydrophilic polysaccharide backbone with less than one mole percent hydrophobic modification. The slight modification provides sufficient hydrophobic interaction between the chains to form a temporary network and to confer enhanced aqueous thickening properties on the molecule. It is interesting to note that the hydrophobically modified species phase separates from the unmodified species in aqueous solution. This is attributed to the fact that the hydrophobic associations form a network having a mesh size smaller than the unmodified polymer in solution;<sup>6</sup> that is, upon hydrophobic modification the blob size of the polymer becomes smaller. This example demonstrates the fact that similar polymers

with different blob sizes will not thermodynamically mix in solution. The network is not complete, however, because this polymer has a relatively stiff polysaccharide backbone and a number of the hydrophobes on the backbone will be sterically restricted from intermolecular hydrophobic association in aqueous solution. The addition of surfactant to solutions of this polymer, in the region of the CMC, causes a dramatic increase in viscosity followed by an equally spectacular decrease in viscosity to levels below that measured for the polymer solution in the absence of surfactant (**Figure 4**).

**Figure 4. Comicellization of polymer hydrophobes with surfactant hydrophobes (hydrophobically-modified hydroxyethyl cellulose)**  
 The addition of surfactant to solutions of this polymer, in the region of the CMC, causes a dramatic increase in viscosity followed by an equally spectacular decrease in viscosity to levels below that measured for the polymer solution in the absence of surfactant.



This behavior has been attributed to comicellization of the polymer hydrophobes with surfactant hydrophobes.<sup>7</sup> The comicellization is stoichiometric and when micelles first form, they link hydrophobes that were previously isolated, and as a consequence a better network of smaller blob size is formed and this results in an increase and the viscosity. As more surfactant micelles are introduced, a micelle concentration will be reached at which comicellization will not result in junction zones but rather in repulsion between polymer chains as they become effectively polyions. The loss of network structure results in the observed dramatic loss in the viscosity at concentrations immediately above the critical micelle concentration.

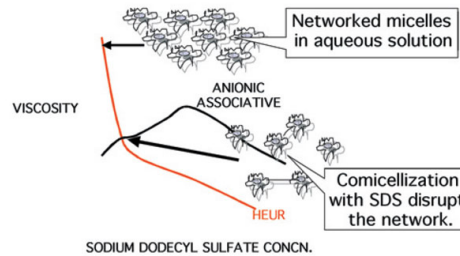
Similar behavior is observed for hydrophobically modified alkali swellable acrylate thickeners, as exemplified by acrylates/steareth-20 methacrylates copolymer, but in this case the viscosity increase is less dramatic. On the contrary, completely different behavior has been observed for hydrophobically modified ethoxylated urethane thickeners. These are block copolymers having a poly(ethylene oxide) chain end-capped with hydrophobes, or they consist of hydrophobes grafted to a poly(ethylene oxide) chain.

The flexibility of the polyethoxy chain allows these molecules to form micelles by themselves at very low concentrations. A network structure is formed by some of the polymers stretching from micelle to micelle. In this case, even small quantities of a low molecular weight surfactant comicellize with the polymer micelles and this results in

immediate breakdown of the network structure and loss of the viscosity even at surfactant concentrations well below the CMC (**Figure 5**).

**Figure 5. Effect of surfactant on low shear rheology**

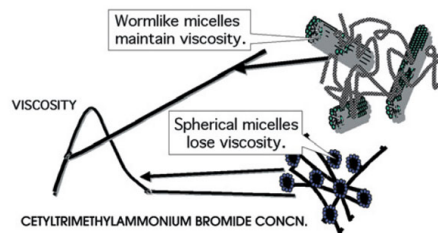
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Increase in the surfactant concentration, introduction of cosurfactants such as cocamidopropyl betaine, or increase in the ionic strength of the solution causes an increase in the micelle size. Spherical micelles become rod-like or they may even grow to become worm-like or branched micelles. These large micelles form exceptionally large junction zones and stoichiometric comicellization with hydrophobically-modified hydrophilic polymers results in a large increase in viscosity that can be maintained over a broad surfactant concentration range (**Figure 6**).<sup>8</sup>

**Figure 6. Interaction of hydrophobically-modified hydrophilic polymer (hydrophobically-modified hydroxyethyl cellulose) with micelles**

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In general, hydrophilic polymers will phase-separate from concentrated liquid crystal phases by a mechanism of depletion that results from osmotic competition between the

components in such “crowded” situations. However, hydrophobically-modified hydrophilic polymers can be induced to interact with hexagonal liquid crystal phase and to penetrate the interlamellar layers of lamellar liquid crystal phase. The conditions for this occurring are that the reduction in free energy due to mixing of the hydrophobes more than compensates for the loss of conformational free energy of the chain when it changes shape from solution state to the stretched conformation within the galleries of lamellar phase<sup>9-11</sup> and the blob size within the gallery must be less than the width of the lamellar interlayer.<sup>12</sup>

### **Interaction of Polyelectrolytes with Ionic Surfactants of Opposite Charge**

Since the inception of conditioning shampoos in the 1970s, the concept of forming and depositing complex coacervates has held the attention of conditioning shampoo formulators. The interaction between a polyion and its counterions is described by a theory that was developed by Professor Gerald Manning at Rutgers University.<sup>13-16</sup> This theory is based upon the concept that counterions in the presence of polyions can exist in one of two states; that is, either free in solution or condensed to the counterion. Manning asserted that if the polyion possessed an ionic charge above a certain critical charge density, then sufficient counterions would condense on the polyion chain to maintain the charge density at its critical level.

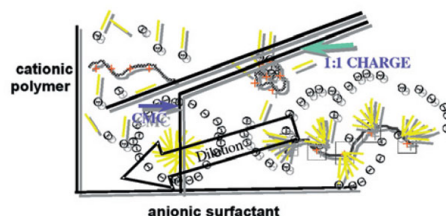
The significance of this is that the ultimate charge density of any polyion is limited to this critical value. Thus, Manning predicts that for sodium polyacrylate as the complete salt in pure water, about 65% of the sodium ions would condense on the chain and the maximum charge density that could be achieved for the polyacrylate ion would correspond to about 35% of the carboxylate groups. If the ionic charge of the counter ions is increased, then a higher proportion of the counterions would condense. Thus, Manning predicts that 82% of divalent counterions would condense on a polyacrylate chain and the highest change density that the polyion could reach would correspond to only 18% of the acrylate groups.

An increase in the ionic strength of the solution would also inevitably lead to a higher proportion of condensed ions. Decreased counterion solubility is also expected to lead to a greater proportion of condensed ions. Due to hydrophobic interaction, amphipathic surfactant ions are necessarily less soluble in water than simple salt ions, such as chloride or bromide. It would be expected, therefore, and it is observed in practice that surfactant ions condense readily upon polyions and that these amphipathic ions readily ion exchange for the more soluble chloride, bromide and sulfate counterions associated with cationic polyions.

Interaction of cationic polysaccharides with anionic surfactants forms the basis of the modern conditioning shampoo and the mechanism is well known. In the 1970s, Goddard, who continues to be the leader in field,<sup>17,18</sup> showed that polyquaternium-10 and common anionic surfactants formed coacervates that are one-phase systems at shampoo concentrations but they phase separate upon dilution during the shampooing process to deposit conditioning agents on the hair. Goddard’s explanation for the mechanism is presented in **Figure 7**, which is a depiction of a binary polymer- surfactant phase diagram.’

**Figure 7. The schematic illustration of the principle of conditioning shampoos, according to Goddard<sup>17, 18</sup>**

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At low surfactant concentration, below the CMC, the anionic surfactants condense on the polycation and the resulting ion-pair converts the cationic site into a hydrophobe-substituted site. Hydrophobic interaction within and between the modified polycation chains causes phase separation and this phase separation persists if the polycation: surfactant anion equivalent ratio is maintained at stoichiometric equivalence.

It is notable that the surfactant-treated polycation displays a rapid increase in viscosity around the surfactant CMC in similar fashion to hydrophobically-modified hydroxyethylcellulose and indeed for this system an elastic gel is formed.<sup>19, 20</sup> Above the CMC comicellization with surfactant micelles results in a one-phase system.

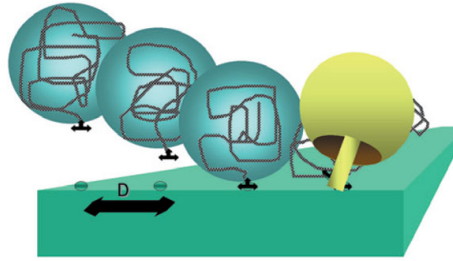
Fluorescence spectroscopy and <sup>13</sup>C NMR techniques have shown the presence of hemi-micelles along the polycation chain in the region of the phase separation and have delineated crucial differences in that hemi-micelle structure depending upon the detailed structure of the surfactant.<sup>21</sup> It was also shown in this work that the addition of sodium chloride moved the onset of the phase separation to higher surfactant concentrations, in accordance with Manning theory, and resulted in “resolubilization” at lower surfactant concentrations. This result is consistent with the salt-enhancing water structure, which in turn enhances the hydrophobic effect, and causes a lowering of the CMC.’

### **Polymer Adsorption at Interfaces**

When a dissolved polymer adsorbs at an interface, if the interaction free energy between the polymer and the interface is low, the polymer will adsorb close to its solution conformation. This type of interaction has been named “mushroom adsorption” because polymers with one anchor point appear to have a mushroom stem and a “button” made up of the cloud of polymer in its swollen conformation (**Figure 8**).

**Figure 8. Adsorption as mushrooms**

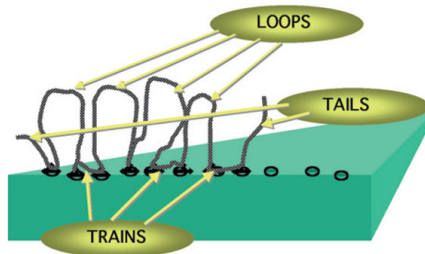
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It is generally accepted that most real polymers possess several anchor groups along the chain and these are adsorbed as trains where the interaction between polymer and surface is high, and as loops and tails where the interaction between the polymer and solvent is high (**Figure 9**).

**Figure 9. Loops, trains and tails**

It is generally accepted that most real polymers possess several anchor groups along the chain and these are adsorbed as trains where the interaction between polymer and surface is high, and as loops and tails where the interaction between the polymer and solvent is high.



For example, this should be the case for adsorption of slightly charged polyquaternium-11 to hair at pH values above the isoelectric point of the hair.

If the interaction between the surface and the polymer is strong, the polymer adsorbs in a conformation that is flat and aligned with the surface. For example, this would be the case with polyquaternium-6 and hair at high pH, where the polymer and the hair surface would carry opposite ionic charges.



### Recent Advances in Conditioning Shampoos

The interaction of polymer and surfactant bearing opposite ionic charges is utilized in conditioning shampoos and it results in the formation of a complex coacervate that separates upon dilution of the shampoo composition and during the rinsing stage of shampooing. Complex coacervate formation depends upon a number of parameters such as molecular weight, concentration, ionic strength of the solution, change density of the interacting components, pH and temperature.<sup>22-24</sup>

Confocal fluorescence scanning microscopy and scanning electron microscopy have been used to show that deposition of the coacervate occurs preferentially at the cuticle edges<sup>25</sup> but measurement of the wetting force of single hair fibers reveals that the coating on the hair has relatively uniform surface free energy along the hair fiber.<sup>26</sup>

Polyquaternium-10 is a water-soluble polymer that forms clear films and the improvement conferred upon hair appearance has been ascribed to such films.<sup>27</sup> It has been reported that polyquaternium-10 of high charge density forms solid-like gels over a limited concentration range, whereas the low charge-density species form a liquid-like gel over a much broader concentration range.<sup>26</sup> In this context, it is interesting that the inclusion of high molecular weight poly(ethylene oxide) reduces the particle size of the coacervate, produces higher foam volume and density, reduced combing forces, enhanced deposition and gives more uniform deposition on hair.<sup>28</sup> An investigation of the mechanism of poly(ethylene oxide) synergism is warranted.

Clear depositing systems have been claimed for lower molecular weight guar hydroxypropyltrimonium chloride and it would be interesting to investigate if this finding correlates with a smaller polymer blob size.<sup>29</sup> The coacervate deposits on the hair and it can co-deposit other beneficial agents such as silicone fluids, gums and resins. Such conditioning shampoos should confer the wet hair attributes of softness and ease of wet-combing, and the dry-hair attributes of good cleansing efficacy, long-lasting smooth, moistened feel, manageability control, and no greasy feel. Particle sizes below 5 microns are reported to deposit efficiently on hair because they are trapped within the coacervate upon dilution.<sup>30</sup> It has been asserted that the polymer-surfactant coacervate alone delivers good wet conditioning but does not give good dry feel.

Recent patent applications have been directed towards insoluble particles other than silicones. For example, PPG-15 stearyl ether,<sup>31</sup> condensates of adipic acid and pentaerythritol, polybutene and mineral oil<sup>32</sup> have recently been revealed in the patent literature as attempts to provide manageability control for dry hair, reducing interfiber friction, providing a moisturized feel, while alleviating the “greasy feel” of conventional complex coacervate-based conditioning shampoos.

The opposite effect is targeted in coacervate-driven deposition of particles (titanium dioxide, clay, pearlescent mica, or silica) to confer interfiber friction in order to enhance styleability of the hair.<sup>33</sup> It is also seen in spherical particles (hollow silica, hollow polymer spheres) for slip and conditioning attributes.<sup>33</sup> In this case high molecular weight (100,000 to 3 million Daltons) cationic guar polymers are specified with a charge density of less than 4-5 meq/g.

Specific mixtures of cationic polymers have been claimed to deliver more uniform coverage and thinner deposited films than conventional coacervate-based conditioning shampoos.<sup>34</sup> This same source cites the use of mixtures of poly(acrylamide-*co*-

acrylamidopropyl trimonium chloride), hydroxypropyl guar trimonium chloride, and silicone quaternium-13.

The influence of cationic polymer on surfactant self-associated structures is shown in a recent patent application that reveals that synthetic polymers such as poly(methacrylamido propyltrimethylammonium chloride) (MAPTAC) cause phase-separated lyotropic liquid crystals to form in shampoo compositions and that these liquid-crystalline coacervates confer conditioning benefits on hair.<sup>35</sup> Another recent patent application<sup>36</sup> reveals that styling and gloss benefits can be conferred from rinse-off compositions containing an anionic surfactant, a cationic polymer and an amphiphilic, branched block copolymer. An investigation of the fundamental physical mechanisms that underpin this technology could lead cosmetic formulators to new and useful delivery systems.

### **Measuring and Characterizing Deposition from Shampoos**

The multiple attribute consumer assessment study is an important hurdle to qualify products for market. Common attributes that are tested by consumer study are cleansing, ease of wet and dry combing, hair softness, and lather amount and creaminess.<sup>34</sup>

Secondary ion mass spectrometry can be used to detect the distribution of silicone on the hair. This technique is especially useful to assess whether the distribution is even or localized on, for example, cuticle edges or regions of weathering or damage.<sup>34</sup>

The thickness of silicon layers on hair can be measured by X-ray photoelectron spectroscopy. This technique measures silicon:carbon:oxygen and because these ratios are different for the silicone and for the hair surface, the depth at which the ratio changes from silicon to hair can be measured. This technique can measure even one or two monomolecular layers of silicone.<sup>34</sup>

The Instron ring compression test is a useful technique to measure interfiber friction in a hair swatch. This has been claimed to correlate with ease of dry combing. In this test, the force required to thread a hair swatch through a ring of predetermined size is measured using the extension mode of an Instron tester.

### **Future Directions**

Shampoo depositing systems have largely concentrated on polyquaternium-10 and guar hydroxypropyltrimonium chloride as the “active” ingredients. As competition in this arena intensifies, as patents expire, and as our mechanistic understanding is enhanced by modern scientific methods, it is likely that new and improved cationic polymers will be identified to enhance conditioning attributes.

Also, we are now beginning to make headway in the experimentally and conceptually difficult area of polymer interaction in concentrated surfactant systems. Breakthroughs in understanding such concentrated systems should translate into better 2-in-one and 3-in-one cleansing products, emulsions, and conditioners.

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