

Practical Modern Hair Science

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# Shampoo and Conditioner Science

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Shampoos and conditioners are the highest volume of products sold in personal care. In this chapter, we will consider the science that underpins the functioning of these product types. The principal function of shampoos is to cleanse the hair. However, since the introduction of two-in-one shampoos in the 1970s, it has not been sufficient for a shampoo to merely cleanse the hair. Modern shampoos should at least cleanse, condition, make the hair easier to style, and fragrance the hair with a pleasant, lingering smell. Modern conditioners should lower the friction between hair fibers to allow easier grooming and alignment of the hair fibers while leaving them glossy and avoiding lankness.

The science of shampoos and conditioners is still evolving and in addition to describing fundamentals, this chapter attempts to take the reader to the frontiers of research in shampoo and conditioner science.

## Introduction

Located within the hair follicle is a sebaceous gland that continuously excretes an oily material, known as sebum, onto the hair and scalp. This substance consists of compounds such as fatty acids, hydrocarbons, and triglycerides, and serves as nature's conditioning treatment—providing lubrication and surface

hydrophobicity, while potentially replenishing components of the cell membrane complex. However, after a day or so, buildup of this substance begins to result in a greasy look and feel. Moreover, particulate dust and dirt adhere readily to this sebum layer. In modern cultures such sebum-soiled hair is deemed to be undesirable, and therefore, it should be removed on a regular basis by a facile process. This process is, of course, shampooing. Sebum cannot be removed by water because oil and water do not mix. Aqueous shampoos can remove oily soil from the hair surface because shampoos contain surface-active agents, commonly abbreviated as *surfactants*. The molecules of these surface-active agents self-assemble into micelles, which are the agents that solubilize oily soils.

To understand how surfactants work, it is necessary to consider the exact process that leads to oil and water being incompatible. There are two different possibilities for substances to be insoluble in water. In one case, substances have stronger intermolecular cohesion than water. This is why substances like sand, clay, and glass are insoluble in water; the molecules of sand attract each other more strongly than the molecules of water and this attraction leads to the sand being insoluble. This reason for the insolubility is exactly opposite to the reasons for the insolubility of hydrophobic substances such as oils. The intermolecular forces between the oil molecules are weaker than the intermolecular bonds between water molecules and the oils are *expelled* from water. This expulsion arises largely from entropy and the effect has been coined *hydrophobic interaction*.<sup>1,2</sup> From the time of the Phoenicians, it has been known that oil spreads to calm troubled waters. This effect arises from the fact that the spread oil has a lower surface tension than the water. At this point it is appropriate to consider the effect known as surface tension. Molecules in the bulk of liquids are attracted on all sides by their neighboring molecules. However, molecules at the surface are subjected to imbalanced forces because they are attracted by the underlying liquid molecules, but there is essentially no interaction with the vapor/gas molecules on the other side of the liquid/vapor

boundary. This imbalance leads to a two-dimensional force at the surface, namely surface tension. The surface tension is numerically equal to the surface free energy.<sup>3</sup> The magnitude of surface tension directly correlates with the strength of the intermolecular forces. Water has hydrogen bonds, dipole-dipole interaction, and dispersion forces between its molecules, and as a consequence the surface tension of water is rather high—72 mN/meter at room temperature. On the other hand, only dispersion forces are present between the molecules of alkanes. As a consequence, the surface tension of alkanes is relatively low—ranging 20–30 mN/meter.

Surfactants comprise molecules that contain two parts: a hydrophobic segment that is expelled by water and a hydrophilic segment that interacts strongly with water. Such molecules are said to be amphipathic (*amphi* meaning “dual” and *pathic* from the same root as *pathos* which can be interpreted as “suffering”). Thus, a surfactant molecule “suffers” both oil and water. This dual nature confers interesting properties on surfactants in aqueous solution. At very low concentrations, the surfactant is expelled to the surface, a process called adsorption. This adsorption causes the surfactant concentration at the surface to be much higher than the surfactant concentration in the bulk of the solution. At extremely low concentrations, when the surfactant molecules on the surface are located too far apart to effectively interact with each other, Traube’s Rule applies. Traube’s Rule states that the ratio of the surface concentration to the bulk concentration increases threefold for each  $\text{CH}_2$  group of an alkyl chain.<sup>4</sup> This ratio is called the surface excess concentration.<sup>5</sup> According to this rule, soap with a dodecyl chain should have a surface excess concentration that is more than a half-million times its concentration in the bulk solution. At extremely low concentrations, the surfactant molecules on the surface act as a two-dimensional gas. As the concentration increases, the surfactant molecules begin to interact, but they are still mobile within the plane; they behave as two-dimensional liquids. At even higher concentrations, as the surfactant saturates the surface, the chains orient out of the surface plane and the chain-chain interactions

cause the surfactant to behave as a two-dimensional solid. Irving Langmuir was awarded the 1932 Nobel Prize in Chemistry for measuring this effect and explaining it on a molecular basis.<sup>6</sup>

When a surfactant adsorbs to saturate an aqueous surface, the surface is largely composed of the surfactant's hydrophobic groups; this means that the surface essentially has low surface energy. As a consequence of the low surface energy, the surface area is easier to expand to a film. This means that the system is easier to foam, since aqueous foams really consist of water films with entrapped gas. If the foam surface is structured by the adsorbed surfactant, then foam stability can be achieved.<sup>7</sup>

### Surfactant Micelles

Relatively large aggregates form within solution just beyond the concentration at which the surface becomes saturated with surfactant.<sup>8</sup> These aggregates are *surfactant micelles* in which the hydrophobes are segregated within the core of the aggregate and the hydrophilic groups are located on the surface where they interact strongly with water.<sup>9</sup> For a given system, micelles initially form at the precise concentration at which the driving force for surface adsorption becomes equal to the driving force for aggregate formation. This driving force is the chemical potential of the surfactant species. The lowest concentration at which micelles form is named the *critical micelle concentration* (CMC). The aggregates are large; for example, micelles of sodium dodecyl sulfate at the CMC contain about 100 molecules and the thickness of the head group layer is about 0.4 nm.<sup>10</sup>

Surfactant micelles have liquid centers. They effectively solubilize hydrophobic substances only when the temperature of the system is above the Krafft point. Krafft found this phenomenon in 1895, and 68 years later Shinoda explained that the Krafft point corresponds to the melting point of the hydrated solid surfactant.<sup>11</sup>

Micelles have different shapes. The simplest shape is the spherical micelle that was postulated by Hartley in 1936. The shape of a micelle can be explained on the basis of the principle

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