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The Role of Polymer-Surfactant Interactions in the Adsorption Process of Hair-conditioning Polymers

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Introduction

Hair-conditioning polymers are in most cases cationic. Their adsorption to the negatively charged hair surface is strongly affected by their interaction with the anionic surfactants, which are also present in modern "2-in-1" shampoos. Almost 20 years ago, Goddard proposed that the adsorption process takes place, when the shampoo is washed off the hair [1]. Upon dilution a phase boundary is crossed and the polymer-surfactant complex precipitates on the hair surface. Since then, no systematic investigations on the adsorption process of conditioning polymers have been published. We reinvestigated this model employing a variety of physicochemical methods: turbidity, surface tension and surface rheology, AFM were used to characterise the polymer/surfactant complex of two polymers (polyquaternium) and an anionic surfactant (Texapon® NSO).

1. Investigating Methods

1.1 Turbidity Determination

Turbidity Measurements were performed in a Metrohm 662 Photometer in the transmission mode using laser light at a wavelength of 635 nm. The polymer solutions were prepared in de-ionized water at pH 7 at concentrations of 5, 7.5, 12.5, 25 and 50 mg/l. There was no significant shift of the pH during the titration. Thus we did not use buffer solution. The polymer solutions was decarboxylated by a 5 min N_2 flux bubbling through the solutions before the titration. The titrating solution was a 10 g/l Texapon NSO solution at pH 7 added stepwise with 25 μl per dosage with a dosage rate of 1 ml/min. Between the dosages we waited 4 s for the system to equilibrate. The overall surfactant addition rate was thus 250 mg/min. The solution was weakly stirred during the titration.

To simulate the visual analysis reported by Goddard we normalized all titration curves to the interval [0,1]. We extracted from these plots the surfactant concentration at 66% of the maximum turbidity and plotted the polymer concentration vs. this surfactant concentration. The resulting phase diagram showed a great similarity with the ones published by Goddard. For the further study we used, however, the surfactant concentrations which belong to the beginning of turbity.

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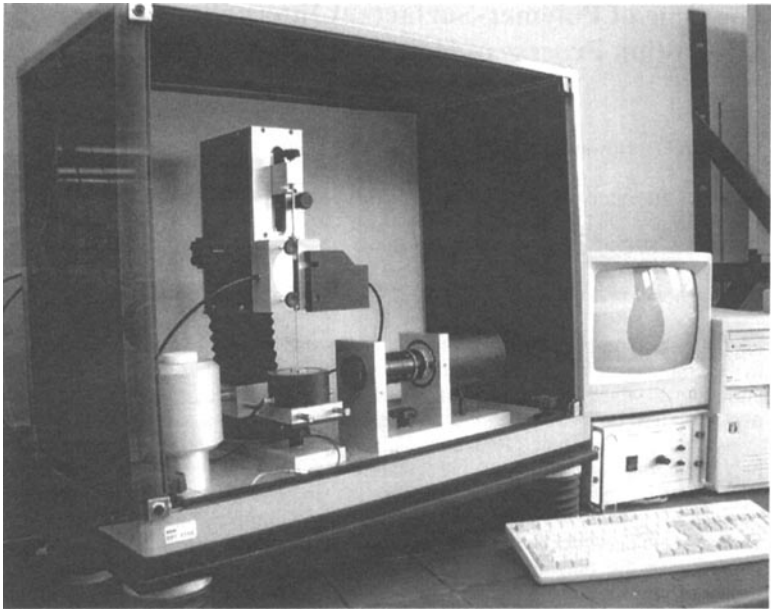

Figure 1. The Tracker® used in a pendant drop configuration for the surface tension and surface rheology measurements

1.2 Surface Tension : The Pendant Drop Method

If we consider a liquid droplet hanging from a capillary, its surface tension can be defined by the excess forces directed perpendicular to the inner phase. This fluid phase will form a structure corresponding to an energy minimum. At the same time gravitation pulls the droplet downward (buoyancy forces the droplet upwards, respectively) and deforms it (the droplet would remain round in the absence of gravity).

The droplet shape results from the influence of both forces and can be used to determine the surface tension. If we consider a liquid drop hanging from a capillary (or a syringe needle) the Laplace equation describes the equilibrium between gravitation and surface tension:

$$\Delta p = \gamma \, (1/R1 + 1/R2)$$

γ = surface tension (mN/m)
Δp = Laplace pressure difference
R1 and R2 are the principal radii of curvature.

In order to measure the drop profile, the Laplace equation needs to be numerically solved. In the last few years many algorithms have been developed, and commercially available programs allow the fit of a theoretical profile with the measured one over the whole drop profile. It gives a very accurate value of the surface (or interfacial) tension. The device used was developped at the Company I.T Concept by Alain Cagna [2-3]. It consists of a light source to illuminate the drop (which hangs from a needle) and a CCD camera linked to an image processor (Fig. 1). The drop profile is transformed into a digitized image with the help of an edge detector at the sub-pixel level. Rising drops and pendant drops can be measured.

1.3 Surface Rheology with the Pendant Drop Apparatus

It is possible to use the same device to study the viscoelastic behaviour of the surface of the drop. The principle was developped by E. Lucassen-Reynders at Unilever [4] and transferred from the Langmuir-Blodgett technology to the pendant drop method [5].

A small deformation of the surface or the drop volume is given with a regular frequency (0,1 to 5 Hz) and the surface tension is measured simultaneously
(Figure 2). For small deformations one applies the Gibbs equation to define the viscoelastic modulus:

$$\varepsilon = \frac{d\gamma}{d\ln A}$$

If there is no phase transition between the surface tension and the volume, this means that the recovery of the surface tension is immediate and that we have to deal with a purely elastic deformation (this is the extreme case). It is then possible to write:

$$\varepsilon_0 = -\left(\frac{d\gamma}{d\ln\Gamma}\right)$$

where γ is the surface tension and Γ the adsorption at the surface.

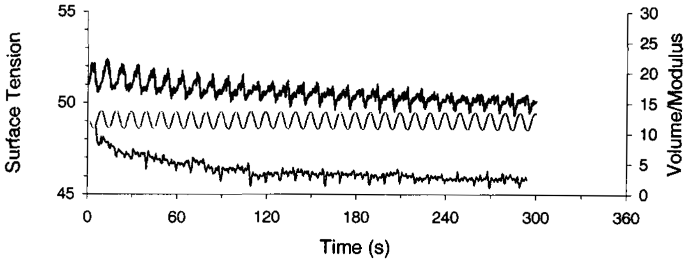

Figure 2: Example of the surface tension and surface deformation for a polymer solution at a frequency of 0,1 Hz

In reality relaxation processes take place near the surface and affect γ within the time of measurement. ε contains a storage contribution (ε') and an energy loss part (ε''):

$$\varepsilon = \varepsilon' + i\varepsilon'' = \varepsilon_d + i\omega\eta_d$$

ω: imposed angular frequency
η_d: viscosity

Experimentally the elastic and viscous contributions are given by

$$\varepsilon' = |\varepsilon|\cos\phi$$

$$\varepsilon'' = |\varepsilon|\sin\phi$$

where $|\varepsilon|$ is the absolute value of the elastic modulus and ϕ the phase angle.

In most cases where the modulus versus time remains constant (Figure 2) it is possible to calculate the slope of the modulus versus surface tension and characterise the adsorbed species at the interface.

1.4 AFM

AFM tapping mode images were recorded with a Nanoscope Dimension 3000 SPM (Digital Instruments) using Si cantilevers (35N/m, approx. 300 kHz, Nanoprobe). Single hairs were fixed in a special cell which allows in-situ washing treatments in the microscope. By this technique the same spot on the hair can be monitored before and upon adsorption of polymer of polymer-surfactant complexes [6].

2. Experimental Results

2.1 Phase Diagramm for PQ-16 and PQ-44 in presence of Texapon NSO

The turbidity measurements allowed us to identify the two-phase-regime of the polymer surfactant systems, which is believed to be crucial for the adsorption of conditioning polymers. The two phase diagrams for PQ16 and PQ44 are shown in Figure 3.

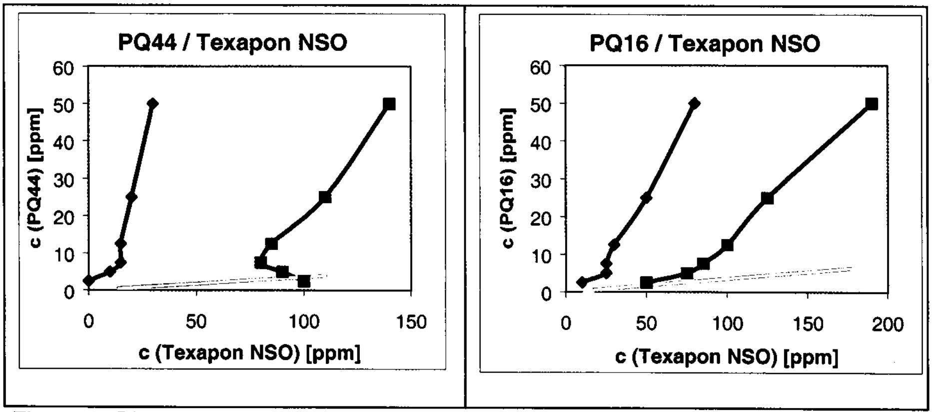

Figure 3: Phase diagrams of PQ16 and PG44 with Texapon NSO as determined by turbidimetric titration (in red the application line corresponding to the rinsing off of the shampoo).

There are clear differences between the two systems. The PQ16 shows a two-phase regime that is enclosed by two phase boundaries which are continuous functions of the surfactant system. The phase separation takes place in a quite narrow surfactant concentration channel. The application line, shown as red line corresponding to a concentration ratio of 1:28 polymer to surfactant, intersects the outer phase boundary at a very small surfactant and polymer concentration, i.e. < 25 mg/l an <1mg/l, respectively. In the current understanding of the adsorption of conditioner polymers, only a very small amount of the active substance is deposited on hair.

In contrast, PQ44 shows an outer phase boundary, which does not continuously increase with the surfactant concentration. Instead, there is a tail at small polymer concentration and high surfactant concentration, which tentatively belongs to a second complex with a differing composition and most probably structure. Due to this tail the application line crosses the phase boundary at a rather high surfactant (ca. 100 mg/l) and polymer concentration (ca. 3 mg/l). Thus, there is much more active substance deposited on hair. We compared the phase diagrams with those of other well known conditioner polymers. We observed that in all cases there is a outer phase boundary that is intersected by the application line at high surfactant concentration. The shape of this boundary, however, varies from a continuous one (as with PQ16) to a tailing one (as with PQ44) to a surfactant concentration independent one. The performance of the conditioners cannot be correlated with the deposited amount of active complex.

This indicates that there is a specific influence of the underlying chemistry of the conditioner polymers. PQ44 is a polymer, which is deposited in relatively low amounts (compared to current conditioner polymers) and shows nevertheless a very good performance (comparable to and even better than the already existing ones).

2.2. Surface Tension of the Cationic Polymers in Water: Comparison between PQ-16 and PQ-44

2.2.1. Comparison between PQ-16 and PQ-44 in Water

First of all we compared the surface activity both polymers only in water and without salt and measured the surface tension for concentrations between 0,1 g/l to 10g/l (Figure 4). PQ-16 does not show any surface activity, independantly of the concentration, whereas PQ-44 shows a light decrease of the surface tension with increasing concentration. However we observed no such things as a critical micelle concentration or an aggregation concentration. The difference in surface activity can be explained by the molecular weight difference. PQ-16 has a weight of 0,1 MD whereas PQ-44 has 1 MD. It is possible that the hydrophobic character is higher in the case of a high molecular weight.

PQ-44 is also sensitive to salt content. As we could see the addition of 0,8% NaCl results in an increase of the surface tension from 50 mN/m to 53 mN/m (this is better seen on Figure 6).

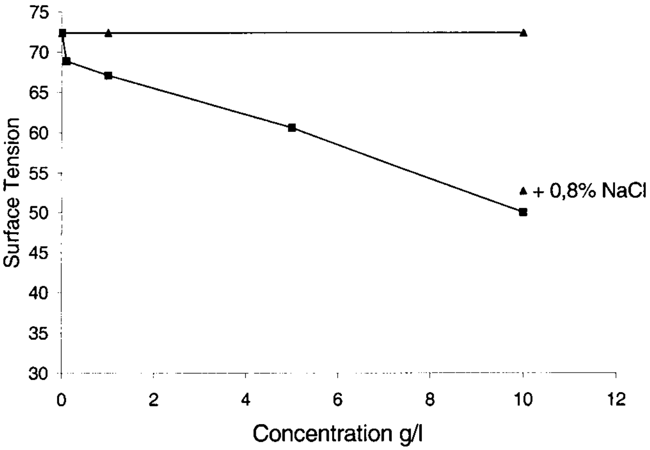

Figure 4: Surface Tension of PQ-16 and PQ-44 in water at different concentrations without salt

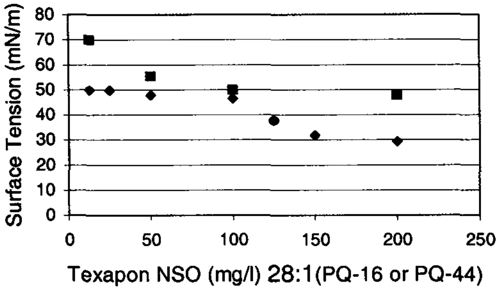

Figure 5 : Surface Tension of the Polymer/Surfactant System for different dilutions without salt

2.2.2. The polymer/surfactant complex

For this study we were particularly interested in explaining differences of efficiency between two polymers of quite similar chemical ground composition with a percentage of vinyle imidazole going from 20% for PQ-16 to 50% for PQ-44.

We studied the surface tension of the polymer/surfactant complex in the same range as in the conditionning shampoo. The concentrations are the following:

Polymer	0,5%
Texapon NSO	14%
NaCl	1%

This concentration ratio remains constant and solutions will be diluted as such by the addition of water, simulating thereby the rinsing off of the shampoo. For each measured point the given surfactant concentration corresponds to 28 times the concentration of the polymer. In the case where we have added salt there is always twice as much salt as polymer. We move then along a so called application line which crosses the phase diagramm twice for PQ-44 (at a concentration of 140 mg/l and 10 mg/l of Texapon NSO).

If we correlate those curves with the surface tension measurements, we see that despite the high surfactant concentration, the effect of the polymer is still noticeable. PQ-44 shows a lower surface tension than PQ-16 in the whole domain and especially after 100 mg/l Texapon NSO (Figure 5). For very high surfactant concentrations (above 150 mg/l) one has reached the CMC and the phase is always clear independantly of the amount of polymer (region A). The complex must however precipitate on the hair by rinsing off and this happens in region B where the surface tension undergoes a transition. These results tend to indicate that the polymer influences the kind of complex being built at the surface, which is in fact observed in praxis since PQ-16 does not give a good wet combability as opposed to PQ-44.

2.2.3 Influence of salt on the surface activity of PQ-44

We have studied the influence of salt on the surface activity of PQ-44, which is sensitive to salt (Figure 6). In that case we observe again an increase of the surface tension indicating a slightly lower surface activity. However the overall character of the curve remains the same as without salt. Only the light scattering data could tell us if and how the complex formation with the surfactant has been influenced.

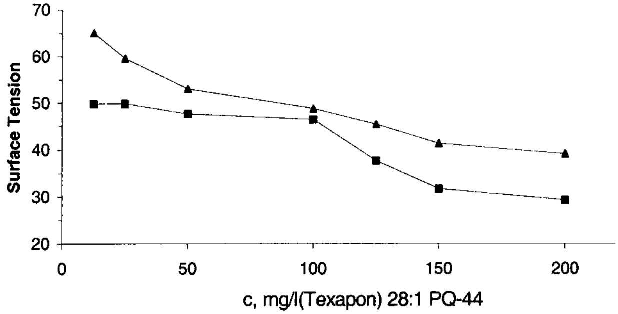

Figure 6. Influence of salt on the surface tension of the PQ-44/Texapon NSO Complex

2.3 Surface Rheology of the Polymer/Surfactant Complex

We performed compression-dilatation experiments in a frequency range of 0.1 Hz and compared PQ-16 to PQ-44 formulated with Texapon and without salt. The results can be seen on Figure 7 where the elastic modulus is plotted against the surface pressure of the polymer/surfactant complex for a concentration of 100 mg/l Texapon (for about 3 mg/l polymer). The difference between the polymers is very much emphazised and the slope of the two systems is quite different. The higher slope indicates a longer induction time for the polymer at the interface which is usually observed for more globular macromolecules [4]. PQ-44 shows a lower modulus which could explain a lesser flexibility at the interface and perhaps less association with the surfactant. We have also observed that it shows no induction time in compression-dilatation modulus (for solutions of 1g/l, 0.1 Hz, one hour of measurement).

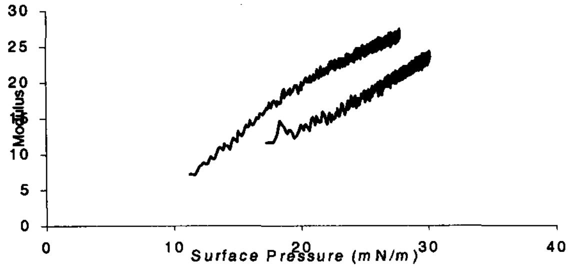

Figure 7: Elastic Modulus versus Surface Pressure for PQ-16 and PQ-44 in presence of 100 mg/l Texapon NSO and without salt. PQ-16 top left, PQ-44 below right (The surface pressure is defined as the difference between the surface tension of the solvent and the surface tension of the solvate)

2.4 AFM Results

AFM can give insight into the adsorption structure or layer structure of the polymer surfactant aggregates adsorbed on hair. Fig. 8 shows images – recorded with tapping mode AFM in air - of untreated hair (a) and hair with an adsorbed PQ44/Texapon NSO complex ((b): topography; (c) phase image). The adsorption treatment was done in-situ in the microscope by first flooding the cell with polymer/surfactant solution (0,5% PQ44, 14% Texapon NSO) and the rinsing with water. Upon drying the pictures (b) – representing topograph - and (c) – giving the phase-contrast image - were scanned. As reference the untreated surface is shown in (a). It should be noted that the same spot – as indicated by the arrow - on an individual hair has been monitored in (a) and (b) and (c). This experiment allows to attribute the net-like structures in (b) unambiguously to the polymer surfactant complex and to differentiate them from the structural irregularities also present on untreated hair (features on the terraces in (a)). This interpretation is further strengthened by the phase image in (c) which shows a clear "material contrast" between essentially uncovered areas (bright) and covered areas (dark) of the hair surface. By the outlined procedure, which is very close to the practical shampoo application, the adsorption capability of the polymer surfactant aggregates which form during the rinsing, can be monitored. On the other hand the degree of removal of these complexes by rinsing with surfactant solution can also be checked with this technique. Upon rinsing the hair – covered with polymer surfactant aggregates as shown in (b) and (c) – with a Texapon solution we find an essentially uncovered hair surface as seen from topographic as well as from phase images. This is well understood on the basis of the phase diagrams as discussed above.

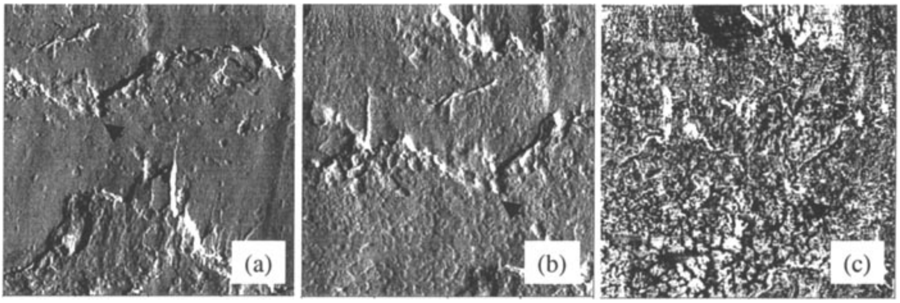

Figure 8: (a) Topographic image of an untreated hair surface. (b) Topographic image of a hair surface treated with PQ44/Texapon NSO, rinsed with pure water and dried. (c) Phase image acquired simultaneously to (b). The areas covered by polymer/surfactant aggregates appear dark in the image.
The scan area is 10µm x 10µm in all images.

3. Discussion

With the help of different methods we could characterise the behaviour of two BASF cationic polymers in water in presence of the anionic surfactant used in the typical shampoo formulation. First of all we established the phase diagrams for the polymers and observed a different behaviour for polymers which are chemically quite comparable (Vinyle Pyrrolidone-Vinyle Imidazole copolymers), but with very different molecular weight. PQ-16 has a much narrower 2 phase-domain than PQ-44. This precipitation domain starts also at a much lower surfactant concentration. In terms of efficiency it could mean that PQ-44 starts to precipitate sooner on the hair than PQ-16.

We determined for the first time the surface tension of the polymer/surfactant system along the application line (by adding water to the complex): again PQ-44 shows a higher surface activity as PQ16. This is observed for the polymer alone in water and is not changed by the addition of surfactant (1:28). This shows that the polymer indeed influences the structure of the complex in the solution and which precipitates later on the hair. These results were confirmed by the surface rheology study performed in compression-expansion mode with the pendant drop method. PQ-44 shows less associative tendency (to another molecule such as a surfactant, slope higher than one) than PQ-16 (slope 0,8): it is also less elastic or deformable at the interface. Somehow these factors seem to be relevant in regard to the efficiency of the polymer.

Conclusion

With the help of experiments performed in praxis conditions we could confirm the hypothesis of Goddard describing the behaviour of cationic polymers associated to anionic surfactant in solution. We were able to describe and understand the properties of the polymers in praxis conditions and determine the factors influencing the efficiency such as hydrophobicity and surface elasticity. PQ-44 is a better polymer for wet combability, has a high molecular weight and a good surface activity (although no CMC could be observed) for a rather hydrophilic substance and a poor elasticity compared to PQ-16 in the tested range. It also shows a rather wide 2 phase domain in presence of Texapon NSO.

We tried to determine the size of the polymer/surfactant micelles but this work is still in progress. The X-Ray scattering experiments were not sucessful even on the very concentrated range (10g/l) because of the too small size of the micelles probably. The determination of the size of the micelles will be approached with light scattering. More work is in progress in terms of surface rheology, thermodynamic characterisation and fit to the Lucassen-Reynders model.

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