

# Rheological Study of the Interaction Between Functionalized Latex Particles and Anionic Surfactants in Aqueous Gelatin Solutions

*Michael Dreja, Kurt Heine and Bernd Tieke*  
*Institut für Physikalische Chemie der Universität zu Köln/Germany*  
*Günter Junkers*  
*Agfa-Gevaert AG, Leverkusen/Germany*

## Abstract

As a model of the structure of gelatin-surfactant-complexes, a modified 'bead and necklace'-model is suggested. The gelation behaviour of gelatin is strongly affected by the addition of the surfactants. Gelation is hindered, but the effect is stronger at pH values below the IEP than above. Studying the flow properties of functionalized latex particles in aqueous solutions of gelatin and anionic surfactants, we found a strong dependence on charge and surface characteristics.

Hard and uncharged particles follow Einstein's theory on spheres. If anionic surfactants are added, the rheological behaviour is determined by the complex formation between gelatin and surfactants.

Soft and charged particles increase the viscosity of gelatin dispersions more than the hard-sphere model proposes. With additional surfactant the flow properties change from pseudoplastic to newtonian, possibly because adsorbed gelatin is displaced from the particle surface. The effective volume fraction of the disperse phase and interparticle interactions decreases. Latex stabilization is changed from steric to electrostatic. At high surfactant concentrations depletion flocculation is likely.

## Introduction

Upon the addition of surfactants, the viscosity of gelatin increases at pH values higher than the isoelectric point (IEP) of the gelatin. At the IEP and at pH values below, the addition of surfactants leads to flocculation because of electrostatic interactions. Surface tension measurements indicate the formation of gelatin-surfactant-complexes.

The rheological behaviour of gelatin containing colour coupler or latex dispersions is very important in the industrial production of photographic materials. Until now, only little systematic work has been published on that topic. The main reason is the complexity of the system, so that a detailed understanding of the interactions occurring in the

system and of the influence of the individual components on the resulting rheological behaviour of the dispersion is still lacking.

In the present work, the rheological behaviour of aqueous gelatin solutions will be investigated in the presence of two different surfactants and a dispersed particle phase. Studies will be carried out with a variety of core-shell particles of different surface structure, hardness, size and polydispersity using shear viscosity measurements. Special care will be taken on examining the flow behaviour of the dispersions as a function of the addition of surfactants in different concentration. The results allow to set up a model describing the gelatin-latex-surfactant interactions in the dispersion.

## Experimental Part

### Materials

An alkali processed, desalted photographic bone gelatin (average molecular weights  $\overline{M}_n = 196000$  and  $\overline{M}_w = 412000$  g/mol). was used. Gelatin concentration in water was 4.6% (w/w), i.e. 5.0 weight percent of gelatin as supplied were dissolved in water. Sodium dodecylbenzenesulfonate (DBS, MW=348.48) and Sodium di-sec-butyl-naphthalenesulfonate (BXG, MW = 342.43) were used without further purification as 10% (w/w) (DBS) and 20% (w/w) (BXG) aqueous solutions.

Due to the presence of carboxylate functions in the shell, PMMA and PU latex particles exhibit a negative surface charge. QUADI particles (low surface charge and a high polydispersity) consist of highly grinded quartz. Highly monodisperse ST-A (AS) and ST-H (HEMA) core-shell latex particles were prepared according to the method of soap-free emulsion copolymerization<sup>1</sup>.

### Methods

Rheological measurements were performed with a strain-controlled rheometer system SUCK V10 (SUCK, Siegen). Shear viscosity measurements were carried out in a

COUETTE-system with MOONEY-EWART geometry (ME 45,  $R_a = 22.5$  mm,  $R_a/R_i = 1.03$ ) at  $(313 \pm 0.1)$ K. At this temperature, gelatin can be considered as a random coil. Viscosity-strain curves were determined at shear rates  $D$  from 1 to  $1000$  s<sup>-1</sup>. Viscosities were always determined at a shear rate of  $100$  s<sup>-1</sup>. The gel strength and gelation kinetics were followed by using an oscillating parallel plate system (PP 20,  $R_a = 10$  mm,  $h = 0.1$  mm) at a frequency of  $0.2$  Hz and an amplitude of  $1^\circ$  after a fast temperature quench from  $313$  K to  $293$  K in  $<20$  s.

The surface charge of the particles was measured using a streaming potential detector PCD02 (MÜTEK/ PARTICLE METRIX INSTRUMENTS GmbH). Number and weight average particle diameters ( $D_n$ ,  $D_w$ ) were determined from REM and TEM pictures. For the determination of the average hydrodynamic particle radius ( $D_{hp}$ ,  $D_{gel}$ ), photon correlation spectroscopy (PCS, MALVERN AUTOSIZER II) was used.

## Results and Discussion

### Gelatin-surfactant-complexes

As a model of the structure of gelatin-surfactant-complexes, a modified 'bead and necklace'-model is suggested. This model proposes the nucleation of micelles at the hydrophobic gelatin regions. The gelation behaviour of gelatin is strongly affected by the addition of the surfactants. Gelation is hindered, but the effect is stronger at pH values below the IEP than above.

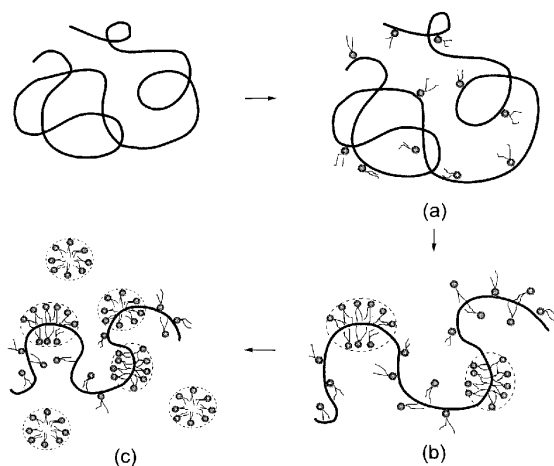


Figure 1: Possible structures of the gelatin-surfactant complexes formed in the various concentration regimes (a) A salt complex is formed by specific binding of surfactants to the gelatin; (b) micellar regions aggregated along the gelatin chain lead to an unfolding; (c) free micelles disturb the gelatin-micelle complexes by electrostatic repulsion.

### Gelatin-latex-surfactant interaction

On uncharged particles individual gelatin chains are adsorbed in multiple trains. Hard and uncharged particles follow Einstein's theory on spheres. On such particles, the surfactant molecules can hardly reach the surface, because the adsorbed gelatin is quite immobile. Hence the flow behav-

our remains Newtonian and micellar gelatin-surfactant complexes are formed.

On soft, charged particles, adsorption of gelatin molecules is preferentially driven by electrostatic interactions. Here the surfactant molecules are able to reversibly displace a gelatin chain from the particle surface because of a higher charge density (Figure 2 b, right side). If gelatin desorbs from the particle surface, the hydrodynamic particle diameter and thus the effective volume fraction decreases. As a consequence, the flow behaviour becomes more and more Newtonian. If at high surfactant concentrations the gelatin is completely desorbed, the system exhibits the minimum pseudoplasticity. Even higher surfactant concentrations favour a flocculation of the particles or the formation of free micelles in the dispersion, as can be concluded from the observed increase in viscosity.

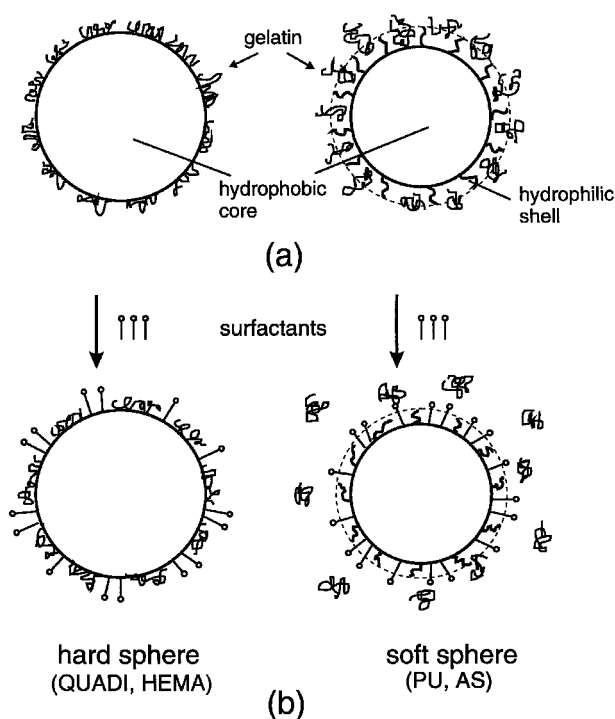


Figure 2: Schematic illustration of (a) gelatin adsorption on either hard spheres with nonionic shell or soft spheres with ionic hairy shell and (b) of effects resulting from surfactant addition. On hard particles, gelatin is flatly adsorbed with multiple train contacts on the particle surface (a, left side), so that no desorption takes place upon surfactant addition (b, left side). On soft particles, gelatin is adsorbed as a coil, penetrates into the shell (a, right side) and is desorbed upon surfactant addition (b, right side).

Presence of gelatin and surfactant in a distinct ratio can lead to a transition from a sterical stabilisation by the gelatin molecules to a stabilisation by the surfactant molecules or by micellar gelatin-surfactant-complexes, respectively. Thus, the rheological behaviour of the emulsions is predominantly determined by the kind of stabilisation and

the hardness of the dispersed phase. Our experiments also show that small, soft and highly charged particles are best suited to model the dispersed phase of photographic colour coupler dispersions.

## References

1. J.W. Goodwin, R.H. Ottewill, R. Pelton, G. Vianello, D.E. Yates, *Brit. Polym. J.* **10**, (1978) 173.