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ORIGINAL CONTRIBUTION

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Rheological study of the pH-dependence of interactions between gelatin and anionic surfactants: flow behaviour and gelation

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Abstract The interactions between gelatin and two anionic surfactants (sodium di-sec-butylnaphthalenesulfonate and sodium dodecylbenzenesulfonate, respectively) were investigated using rheological methods, charge and surface tension measurements. Upon the addition of surfactants, the viscosity of aqueous gelatin solutions increases at pH values higher than the isoelectric point (IEP) of the gelatin, provided that a distinct surfactant concentration is exceeded. The increase in viscosity depends on the structure of the hydrophobic moiety of the surfactant. Surface tension measurements suggest the formation of gelatin–surfactant-complexes. If the surfactant is added in high concentration, the viscosity does not further increase, and free micelles are formed in the solution. Directly at the IEP and at pH values below, the addition of surfactants leads to flocculation because of electrostatic interactions. At all surfactant concentrations, the flow behaviour was strictly Newtonian. As a model of the structure of the complex, a modified 'bead and necklace'-model is suggested. This model proposes the nucleation of micelles at the hydrophobic gelatin regions ('micellar surfactant–gelatin complexes'). The number of micelle moieties per gelatin chain could be estimated to be about three. The complex stability is dependent on the extent of hydrophobic interaction.

The gelation behaviour of gelatin is strongly affected by the addition of the surfactant. The ratio between the attainable linear storage and loss moduli, G' and G'', decreases strongly. Gelation is generally hindered, but the effect is stronger at pH values below the IEP than above.

Key words Rheology – gelatin – anionic surfactants – interactions – gelation – surface tension

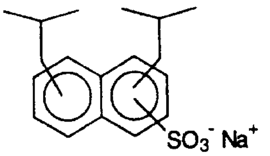
Introduction

Interactions between surfactants and synthetic or natural polymers have been studied extensively over the past several decades and they are thoroughly investigated at present. Gelatin is a well characterised, denatured protein (collagen), which shows the typical properties of an amphoteric polyelectrolyte, i.e., the existence of a pH-dependent net-charge and of an isoelectric point (IEP). Because of its utility as an emulsifier, peptizer, stabilizer and film-forming binder, gelatin is used in many important technical processes, as for example in pharmaceutical and food industry, and in the production of photographic materials. For the production of photographic films and papers, the wetting capability of gelatin-containing coating dispersions is as important as the bulk-properties of thermoreversible gelation and the flow behaviour. Coating processes should be controllable at high speed by the rheological properties of the dispersion. Therefore, surface active substances are added to the dispersions in order to stabilise the dispersed phase and to modify the wetting capabilities. Anionic surfactants increase the viscosity of aqueous gelatin solutions at pH values above the IEP, effecting remarkable changes in the flow and gelation behaviour of e.g. photographic colour coupler dispersions.

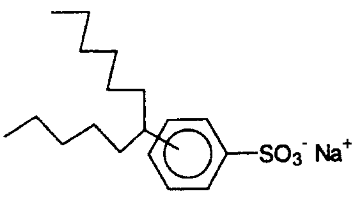
Although great efforts have been made to achieve more information about the structure of gelatin–surfactant-complexes, up to now a well defined picture is not available. In early work of Pankhurst [1] as well as Knox and Parshall [2] the complex formation was investigated by studying flocculation phenomena and changes in surface tension. More recent studies of the interactions between gelatin and surfactant were reported from Tavernier [3] and Greener, Contestable and Bale [4]. While Tavernier postulates a network formation between the gelatin and the surfactants via the hydrophobic interactions of the surfactant tails, Greener et al. assume that surfactant micelles are formed, which act as nodes between individual gelatin chains, because the gelatin chains become attached to the surface of the micelles. It has been shown that the extent of viscosity increase is directly related to the hydrophobic chain length of the surfactant [4]. In additional oscillation and relaxation measurements, Howe, Wilkins and Goodwin [5] were able to prove that the loss modulus dominates for all surfactant concentrations investigated. This, however, does not coincide with the assumption of a network formation. As the structure of the resulting gelatin-surfactant-complex, they favoured the ‘bead and necklace’-model originally introduced by Cabane and Duplessix [6] in order to explain the interactions between non-ionic surfactants and polymers. In that model, the micelles are lined up on the gelatin chain like beads on a necklace.

During the gelation of gelatin, a partial renaturation of the original, highly ordered collagen structure takes place. Triple helical domains are formed, which are held together by hydrogen bonds. Interconnection of all the chains through these triple helices leads to gelation. The gelation is influenced by the pH value and the addition of ionic substances. While the gel formation has been thoroughly studied in aqueous gelatin solution [7–10], the gelation behaviour of surfactant-containing gelatin solutions has been investigated less accurately. Lips et al. [11] showed that an addition of sodium dodecylsulfate (SDS) at pH > IEP leads to a maximum in the storage modulus G'. The capability of gel formation decreases at higher surfactant concentrations. Recently Heenan et al. studied the interactions between SDS and gelatin by small-angle neutron scattering (SANS) [12]. From the results they concluded a model which was quite similar to the ‘bead and necklace’-model. They also concluded the number of micelles per gelatin chain to be about two. The interactions between the micellar regions were considered to be dominant for the network structure.

Nevertheless, only little is known on the pH-dependence of viscosity changes caused by surfactants, although such information is of great importance for the production and manufacture of photographic colour coupler dispersions. We therefore studied the influence of the pH on the rheological behaviour of aqueous gelatin solutions containing surfactants more in detail. The pH-dependence was studied by measuring the viscosity and surface tension. Two anionic surfactants with different structure of the hydrophobic part, the sodium salts of i-dodecylbenzene sulfonate (DBS) and di-sec-butyl-naphthalene sulfonate (BXG), were used.



BXG



DBS

The interactions between surfactant and gelatin will be investigated by measuring the sol viscosity and surface tension, and studying the gelation kinetics. Based on the results, a model of the structure of the gelatin-surfactant-complex will be presented and discussed.

Experimental part

Materials

An alkali processed, photographic bone gelatin (Agfa) with a moisture content of 9.6% (w/w) was used. The molecular weight distribution was checked by SEC-measurements in aqueous solution. The average molecular weights were $\bar{M}_n = 196000$ and $\bar{M}_w = 412000$ g/mol. In all experiments the gelatin concentration in water was 4.6% (w/w), i.e., 5.0 weight percent of gelatin as supplied were dissolved in water. DBS (MW = 348.48) and BXG (MW = 342.43) were commercially available (Agfa) and used without further purification as 10% (w/w) (DBS) and 20% (w/w) (BXG) aqueous solutions.

Gelatin solutions were prepared by soaking raw gelatin flakes in distilled water for 30 min (293 K), followed by heating to 313 K with gentle stirring. Yellowish, transparent stock solutions were obtained which were subsequently mixed with the desired amount of surfactant. Then the pH value was adjusted at 313 K and the solutions were stored in a closed vessel at 278 K for 24 h. Directly before use, they were transformed to the sol state and the pH was checked.

Measurements of the sample pH values were carried out using a Knick pH analyser Calimatic 765. The apparatus was equilibrated with standard puffer solutions (Merck). The sample pH values were adjusted using NaOH (1 mol/l) and H_2SO_4 (1 mol/l) standard solutions (Merck). No attempts were made to buffer the solutions or to keep the ionic strength constant, because salt addition would have affected the charge conditions of the gelatin [11].

Methods

All rheological measurements were performed with a strain-controlled rheometer system Suck V10 (Suck, Siegen). The 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 ± 0.1) K. At this temperature, gelatin can be considered as a random coil. Viscosity-strain curves were determined at shear rates D between 1 and $1000\,\mathrm{s}^{-1}$. In case of Newtonian flow behaviour, viscosities were always determined at a shear rate of $D = 100\,\mathrm{s}^{-1}$. Additionally, flow curves were recorded and a regression was carried out. A good agreement between both methods was found. 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°. The very fast temperature quench (from 313 K to 293 K in < 20 s) was achieved by using a combined system consisting of a Peltier element and a thermostated static lower plate. The time of gelation, t_g, is defined as the time necessary for attaining a minimum modulus of $G' = 10$ mPa. In all rheological measurements, solvent traps were used to minimise error caused by evaporation.

Surface tension measurements were performed using a drop volume tensiometer constructed by Bayer AG, Leverkusen. The apparatus operated quasidynamically according to the stalagmometer principle, the sample solution flowing out of a capillary. Surface tension measurements were carried out while the surfactant solution was continuously added to the gelatin solution at 313 K.

The surface charge of the gelatin was measured using a streaming potential detector PCD 02 (Mütek/Particle Metrix Instruments GmbH). Depending on the pH-region, titrations were carried out with aqueous 10^{-3} molar solutions of either poly(diallyldimethyl ammonium chloride) (PDADMAC) or poly(ethylene sulfonic acid) (PES).

Results and discussion

Flow behaviour of aqueous gelatin solutions

In Fig. 1, the shear viscosity of a pure 4.6% (w/w) aqueous gelatin solution is shown as a function of the pH value of the solution. In the same figure, the pH-dependence of the specific charge of the gelatin is also shown. At pH 4.9, a distinct viscosity minimum can be seen, while the viscosity increases at higher and lower pH values. At pH 3.0, a relative maximum of the viscosity is reached, and an absolute maximum at pH 7.5. If the pH of the solution is further increased or lowered, the viscosity decreases again. A Newtonian flow behaviour was observed over the whole pH range.

In principle, such a pH dependence of aqueous gelatin solutions is known [13], but the extent of the viscosity change depends on the kind of gelatin used, its processing and molecular weight. For example, a protonation of the gelatin produces a certain concentration of net charges which strongly depends on the portion of ionizable amino acids in the gelatin such as asparaginic acid, glutaminic acid, histidine, lysine, or arginine. At pH values above the IEP, net charges are mainly formed by deprotonation of carboxylic groups, whereas below the IEP net charges are due to quaternation of amino functions. The pH value at zero specific charge is equivalent with the IEP of the gelatin used, which is pH 4.9 in our case. At the IEP, the net charges of the gelatin are fully compensated, which has the consequence that the molecule is strongly contracted, and thus also a minimum in the hydrodynamic volume is reached. On the other hand, at a net positive or negative charge, the gelatin molecule becomes uncoiled because equal charges along the polymer backbone cause repulsive forces, which compel the molecule to attain a more extended conformation. More energy can be dissipated and so the viscosity is increased.

Introducing surplus charges in the solution, however, favours a salt formation, lowers the substituent interactions and thus the coil dimensions and the viscosity are reduced. The maximum in viscosity is less pronounced at pH < IEP than at high pH values, because the specific charge of the gelatin is more steeply increased at low pH values. At pH values above 8.0 the charge on the gelatin molecules is increased to a level comparable with low pH values, and an analogous decrease of the viscosity sets in.

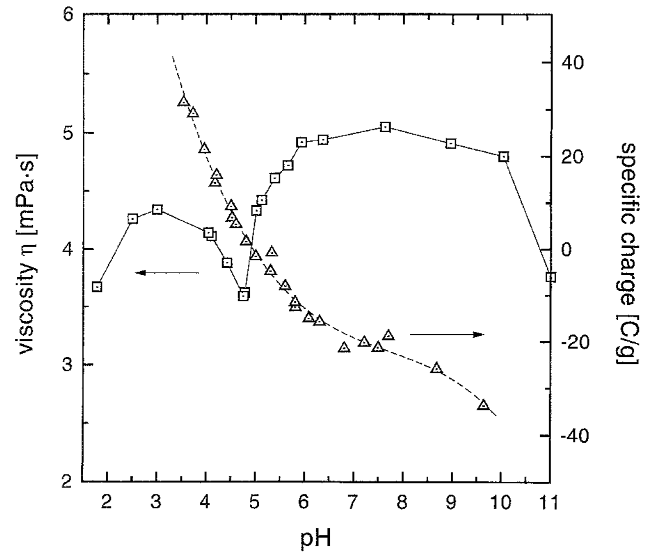


Fig. 1 pH-dependence of the shear viscosity η and of the specific charge of the gelatin for 4.6% (w/w) aqueous gelatin solutions ($D = 100\ \mathrm{s}^{-1}$)

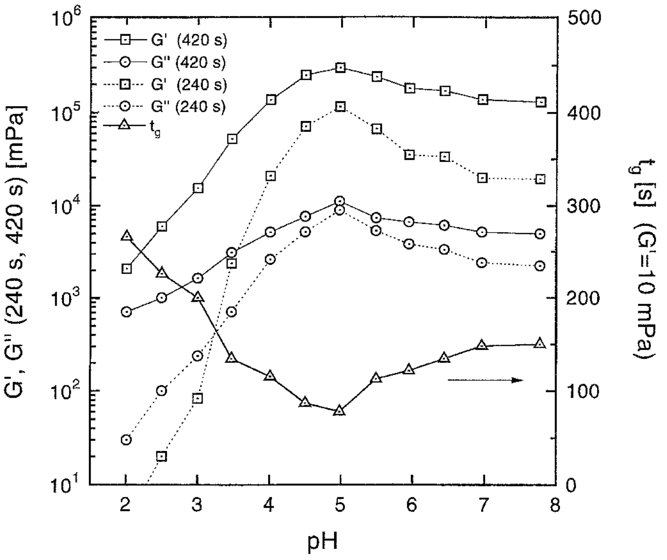


Fig. 2 pH-dependence of moduli G', G'' and gel time t_g for the gelation of 4.6% (w/w) aqueous gelatin solutions, monitored after 240 s and 420 s

Gelation of aqueous gelatin solutions

The reversible protonation of the amino acid functions of the gelatin also leads to a significant change in the gelation behaviour. The gelation of 4.6% (w/w) aqueous gelatin solutions was studied by measuring the moduli G' and G'' at different pH values. Figure 2 shows the dependence of G' and G'' on the pH value measured after two waiting times, 240 s and 420 s. From these values, the gelation kinetics can be derived. In addition, the time of gelation t_g is plotted in Fig. 2 for different pH values. As a result of the very fast drop of the temperature, a quasi stationary state of the moduli is reached after 420 s. However, a constant final value could not be reached even after very long observation times, in agreement with observations by others [14]. Our measurements indicate a correlation between the moduli G', G'' and the time of gelation. Around the IEP, G' as well as G'' exhibit a maximum after the two waiting times. The time of gelation becomes minimum at the IEP. For higher pH values, a decrease in G' and G'' is found. At pH < IEP, the changes in the moduli are even more pronounced. G' decreases nearly twice as much as G'', when the pH is lowered.

From the results it can be concluded that the sol–gel transition strongly depends on the ratio of cationic and anionic functional groups in the gelatin molecules. Furthermore, the coil diameter of the gelatin chains has to be considered, which affects the chain mobility and hence the gel formation. It is known that the gelation of gelatin takes place in several steps consisting of the formation of helical units along single gelatin chains, aggregation of individual chains under formation of intra- and intermolecular triple helices, and rearrangement of the triple helical regions into ordered domains. The helix formation results from the formation of interchain hydrogen bonds and will thus depend on the pH of the aqueous solution. Blocking of ionic functions by protonation/deprotonation will immediately lead to a less complete and less homogeneous formation of hydrogen bonds, which influences the overall strength of the gel. Consequently, the renaturated collagen structure will only contain shorter triple helical regions and thus its stiffness will be decreased.

Flow behaviour of aqueous gelatin solutions containing anionic surfactants

In order to describe the influence of anionic surfactants on the flow and gelation behaviour of aqueous gelatin solutions, different concentrations of BXG and DBS were added to the gelatin solutions and the viscosity was studied as a function of the pH value. In Fig. 3a and b, the relative viscosities $\eta_{\mathrm{rel}} = \eta/\eta_0$ are shown. η is the measured shear viscosity and η_0 is the shear viscosity of the pure gelatin solution at the same pH. As already observed for surfactant-free gelatin solutions, two regions can be distinguished. At pH values above the IEP, the addition of surfactant leads to a distinct increase in the viscosity. Moreover, the maximum of the relative viscosity is shifted from pH 5 to 6. The increase in viscosity is more obvious

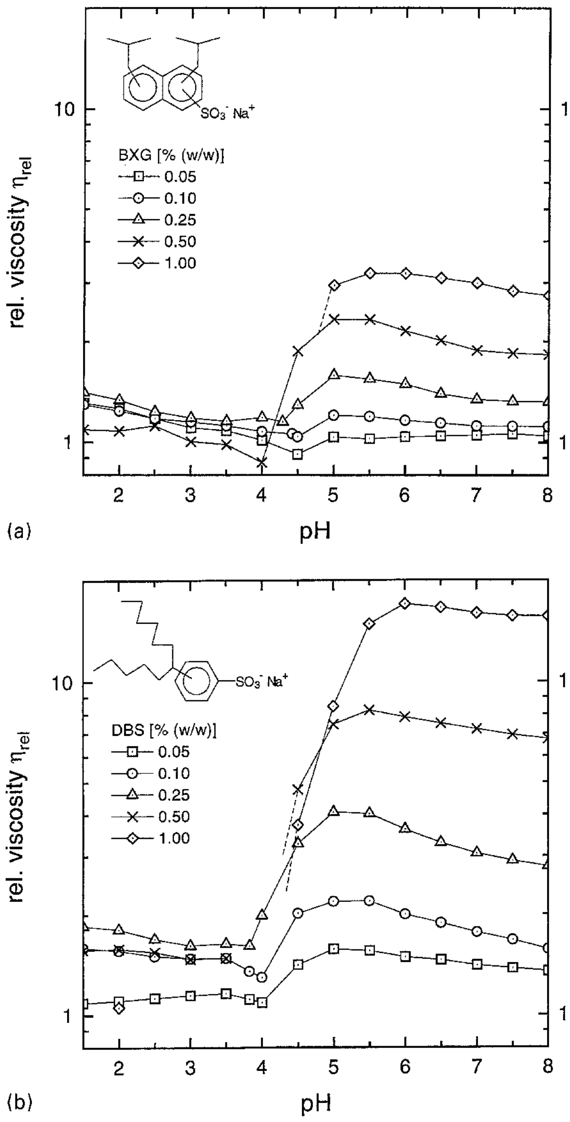


Fig. 3 pH-dependence of the relative viscosity η_{rel} for 4.6% (w/w) aqueous gelatin solutions containing various (a) BXG and (b) DBS concentrations

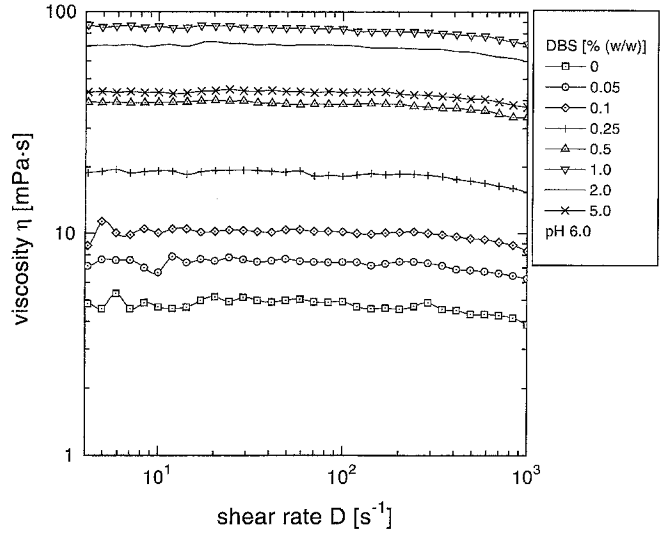


Fig. 4 Viscosity-shear rate profiles of 4.6% (w/w) aqueous gelatin solutions containing various DBS concentrations in the solution

for the addition of DBS (Fig. 3b) than for BXG (Fig. 3a). At pH values lower than the IEP, only a slight increase in viscosity is observed, when a surfactant is added. At higher surfactant concentrations, a flocculation sets in. The flocculate can be resolubilized at very low pH. It is remarkable that the increase in viscosity is strongly dependent on the structure of the added surfactant. It indicates that the structure of the hydrophobic part of the surfactant is decisive for the stability of the resulting gelatin–surfactant-complex.

In Fig. 4, the viscosity is plotted vs. the shear rate for aqueous gelatin solutions of constant pH value. As can be seen, the flow behaviour is Newtonian up to shear rates of 200 s^{-1}. It may be added that oscillation measurements confirm the Newtonian viscosity-shear rate curves. The shear rate independence, which we observe, is really unexpected for a 5% (w/w) polymer solution of that molecular weight. It is not in agreement with the assumption of long-range interactions leading to a network structure between gelatin and surfactant that is destroyed upon a shearing. In such a case, shear-thinning would have been observed.

The existence of polymer–surfactant interactions is also indicated by the dependence of the shear viscosity on the surfactant concentration (Fig. 4). If 1% (w/w) DBS is added, a maximum of the viscosity level occurs, but at higher surfactant concentrations the viscosity decreases again. The results are in good agreement with observations of other groups [4, 5]. For a conclusive explanation of these phenomena, an exact knowledge is required about the dynamic processes taking place in the solution. Also, more information is needed on the association behaviour of the polymer and gelatin. Transmission electron micrographs of freeze fractures of surfactant containing aqueous gelatin solutions did not show any significant differences to corresponding micrographs of surfactant-free solutions [15].

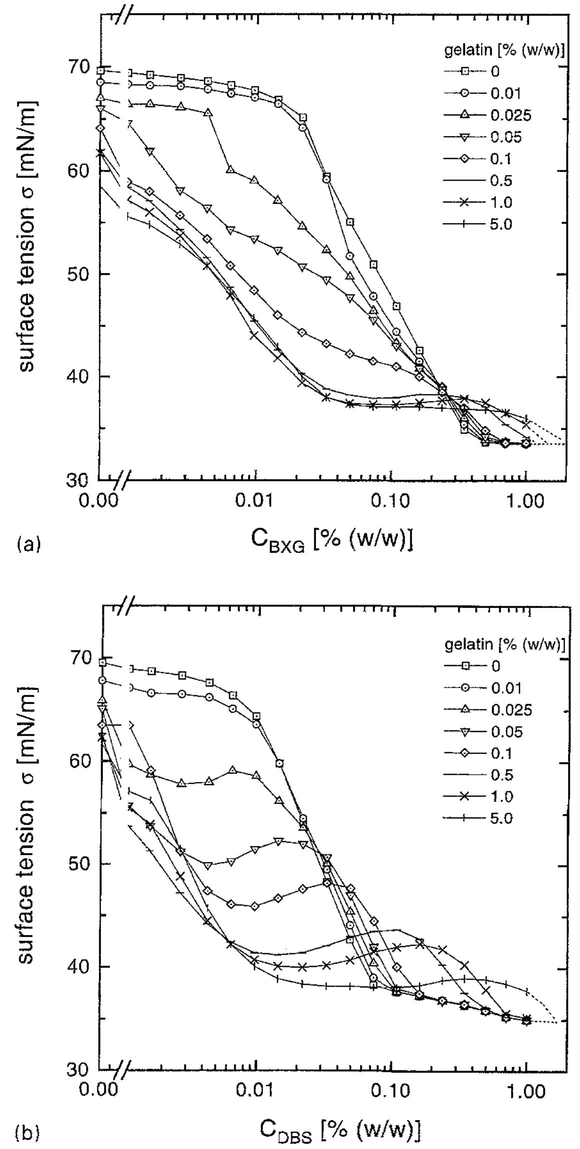
Surface tension measurements

It is known [16] that the viscosity of aqueous surfactant solutions only increases remarkably, if the CMC of the surfactant is exceeded and spherical micelles are formed.

The same is true for BXG and DBS. Thus it is obvious to investigate the influence of the gelatin in the solution on the micelle formation of the surfactant molecules. This can be done by measuring the surface tension σ of aqueous gelatin solutions for different surfactant concentrations c. For this purpose the drop volume tensiometry is a useful method, since it allows to obtain stable values for the air–water interface within a few minutes.

In Figs. 5a and b, σ-values are plotted as a function of the gelatin concentration c for the two surfactants. With growing gelatin content, an increasing deviation from the original curve shape is observed. The decrease of σ has its origin in the amphiphilic properties of the polypeptide.

Fig. 5 Surface tension vs. concentration plot of (a) BXG and (b) DBS for various concentrations of gelatin in the aqueous solution



However, if the gelatin concentration is higher than 0.025% (w/w), two additional regions are apparent in the curve. After the steep decrease of σ, a plateau is reached, which is followed by a second decrease. Then, the curve merges in the curve for pure surfactant for all concentrations investigated. The effects are more pronounced for DBS than for BXG. Schematic σ-c-plots for solutions with and without gelatin are shown in Fig. 6. In these plots, T_1 is the critical association concentration, T'_2 the critical saturation concentration and T_2 the critical micelle concentration in a solution containing more than 0.01% (w/w) gelatin. A comparable scheme has already been introduced by Jones [17] and was discussed by Goddard in order to describe the interaction of non-ionic polymers with ionic surfactants [18].

In Table 1, the measured values are compiled. The T_1-values are lower than the CMC of the pure surfactant and are increased as soon as the gelatin concentration becomes higher. Simultaneously, σ strongly decreases, which means that the resulting gelatin–surfactant-complex has a higher surface activity than each of the individual components alone. Hence, the surfactant addition must have rendered the gelatin more hydrophobic, e.g. by a salt formation between the anionic surfactant and the positive charges on the amino acid functions along the gelatin chains (Fig. 7a). However, the salt formation alone cannot explain the observed increase in viscosity, because the number of surfactant molecules added is much higher than the number of cationic functions per gelatin molecule. It is likely that additional hydrophobic interactions occur, which cause an aggregation of the excess surfactant molecules.

Fig. 6 Schematic plot of surface tension vs. concentration of a surfactant in aqueous solution with and without a complex forming polymer. T_1 is the critical binding concentration, T'_2 the saturation concentration and T_2 the critical micelle concentration in solution

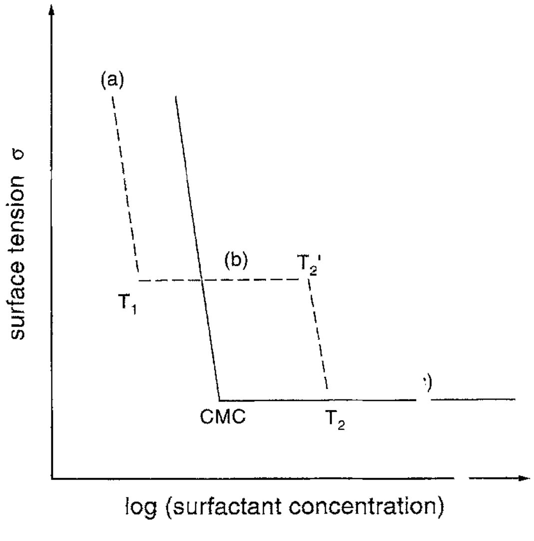


Table 1 Critical association concentrations T_1, critical micelle concentrations T_2 with and without gelatin added and critical saturation concentrations T'_2 of the surfactants

surfactant + gelatin [% (w/w)]	T_1		T_2		T_2'	
	σ [mN/m]	c [% (w/w)]	σ [mN/m]	c [% (w/w)]	c [% (w/w)]	$n(s)/n(g)$[a]
BXG 0	–	–	33.5	0.374	–	–
BXG 0.01	–	–	33.5	0.422	–	–
BXG 0.025	–	–	34	0.522	–	–
BXG 0.05	–	–	33.5	0.586	0.05	573
BXG 0.1	41	0.020	33	0.829	0.10	573
BXG 0.5	38	0.028	33	0.987	0.30	344
BXG 1	37.5	0.029	33	1.3	0.50	286
BXG 5	37	0.034	33	2.0	1.00	115
DBS 0	–	–	38.5	0.067	–	–
DBS 0.01	66	0.0016	37.5	0.078	–	–
DBS 0.025	57.5	0.0021	37	0.092	0.008	450
DBS 0.05	49	0.0036	36.5	0.115	0.018	202
DBS 0.1	45	0.0040	36	0.18	0.035	199
DBS 0.5	41	0.0065	35.5	0.4	0.150	169
DBS 1	40	0.0070	35	0.7	0.300	169
DBS 5	37.5	0.0085	34.5	1.5	0.800	90

[a] number of molecules (surfactant)/number of molecules (gelatin).

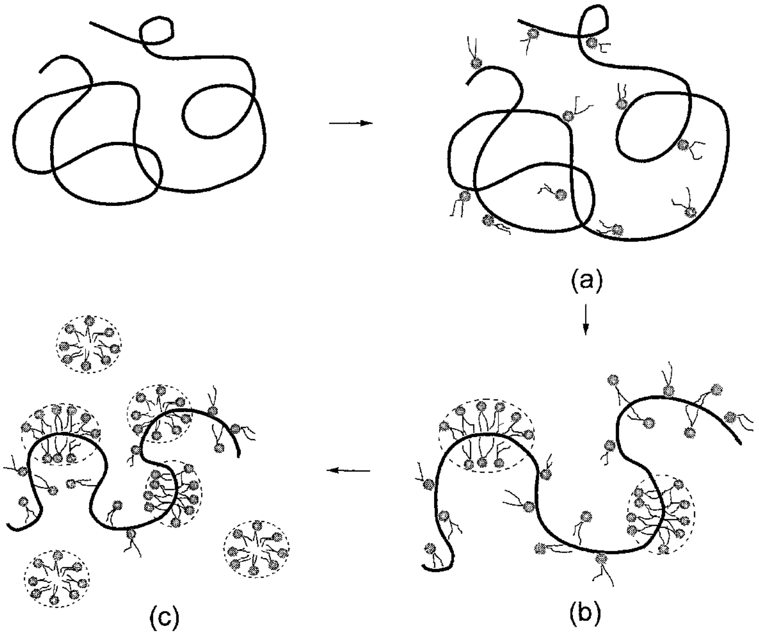


Fig. 7 Possible structures of the gelatin–surfactant complexes formed in the various concentration regimes marked in Fig. 6. a) A salt complex is formed by specific binding of surfactants to the gelatin; b) micellar regions aggregated along the gelatin chain lead to an unfolding; c) free micelles disturb the gelatin–micelle complexes by electrostatic repulsion

Nevertheless, the interpretation of the structure of the gelatin–surfactant-complex is difficult and controversial [4–6, 12].

Micellar gelatin–surfactant complex model

However, the observed phenomena can be explained more easily, if the relative viscosities plotted in Figs. 3a and b are compared with the extrapolated T_1- and T_2-values. In Fig. 8, η_{rel} is plotted vs. the surfactant concentration in a gelatin solution of constant pH value at 6.0. It is obvious that for both surfactants an increase in viscosity only takes place after the T_1-value has been exceeded. Simultaneously, the maximum of the relative viscosity can be well correlated with the T_2-value. This means that once free micelles are formed in solution, a decrease in viscosity takes place. Conclusively, at low surfactant concentration

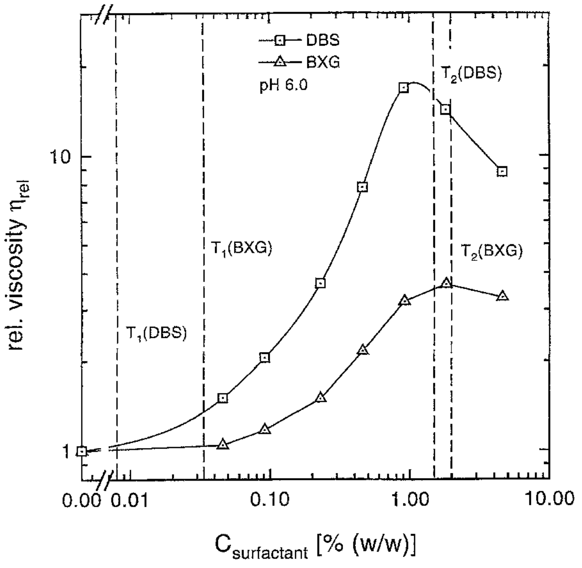


Fig. 8 Relative viscosity η_{rel} of 4.6% (w/w) aqueous gelatin solutions as a function of the surfactant concentration at pH 6.0. The dashed lines show the critical concentrations T_1 and T_2 of the surfactants

a kind of aggregates being different from free micelles must have been present in the solution. Upon an increase of the surfactant concentration to values higher than T_2, these aggregates are disturbed by the free micelles. Let us discuss the possible structures of these aggregates more in detail. At a pH of 6, gelatin molecules already exhibit net-negative charges. So they should only be loosely coiled and should be quite flexible. Due to the high concentration of hydrophobic chain regions along the gelatin chain, one can assume the nucleation of micellar structures along these hydrophobic regions as schematically outlined in Fig. 7b. We call these structures 'micellar gelatin–surfactant complexes'. The micellar gelatin–surfactant complexes render the gelatin molecules more hydrophilic. As a consequence, the gelatin chains uncoil, become more soluble and are increasingly displaced from the air–water-interface by free surfactant molecules. This is confirmed by the surface tension measurements (Figs. 5a and b), which indicate identical σ-values at high surfactant concentrations. Hence the increase in viscosity (Figs. 3a and b) is simultaneously explained by the partial uncoiling of the gelatin chains and by the formal increase of the molecular weight of each gelatin chain due to the association of surfactant molecules. In a recently published work, Turro et al. came to a similar conclusion when they studied the interactions between the hydrophobic protein BSA with sodium dodecylsulfate (SDS) and discussed the association behaviour [19]. However, their NMR-measurements give evidence for the classical 'bead and necklace'-model.

It does not seem reasonable to us to postulate a network structure which cannot take into account the dynamic aspects of the micelles. Micelles are known to be dynamic, movable spheres, which are in steady exchange with the surrounding medium. The mean lifetime of a micelle is much higher than the mean dwelling time of a surfactant molecule in a specific micelle. If free micelles are present in the aqueous gelatin solution, a mutual electrostatic repulsion will take place between these micelles and the micellar gelatin–surfactant complexes. Again, the coiling will increase and the viscosity will decrease, as it is in fact observed (Fig. 7c). Moreover, for even higher surfactant concentrations a further rise in viscosity is reported [4]. In that concentration regime, which was not studied by us, a rearrangement of the complex structures might take place. Supposing that the gelatin chains become even more unfolded, the surfactant molecules could form double layered structures along the chains such as rods or lamellae.

From the ratio of the critical association concentration T'_2 and the respective gelatin concentration, an average number of complex forming surfactant molecules can be calculated (Table 1). Average numbers of approximately 380 BXG- and 213 DBS-molecules are obtained per gelatin chain. If one assumes 125 BXG- and 75 DBS-molecules per micelle [20], a number of three micellar regions per gelatin chain can be estimated for both surfactants. This is in good agreement with values from SANS-measurements [12].

Gelation of aqueous gelatin solutions containing anionic surfactants

Besides the flow behaviour, the influence of the two surfactants on the gelation was also investigated. The gelation was studied by measuring the moduli G' and G'' for 4.6% (w/w) aqueous gelatin solutions to which 0.5 and 1% (w/w) BXG were added. In Figs. 9a and b, the two moduli G' and G'' and the time of gelation t_g are plotted as a function of the pH value. Again, the values were registered after two waiting times, 240 s and 420 s. A comparison with Fig. 2 clearly shows that the gelation is strongly affected by the addition of the surfactant.

For the solution containing 0.5% (w/w) BXG, the moduli are decreased in the pH region between pH 3.6 and 4.8, while the gelation time increases. These phenomena can be explained by the salt formation between the positively charged amino acid functions on the gelatin and the anionic surfactant, as schematically indicated in Fig. 7a. Just around the IEP, a saturation can be rapidly reached, and the gelation is reduced by a blocking of the hydrogen bondings. At 1% (w/w) BXG, so many functional groups are blocked that the gelation at pH < IEP is now fully prevented. The system

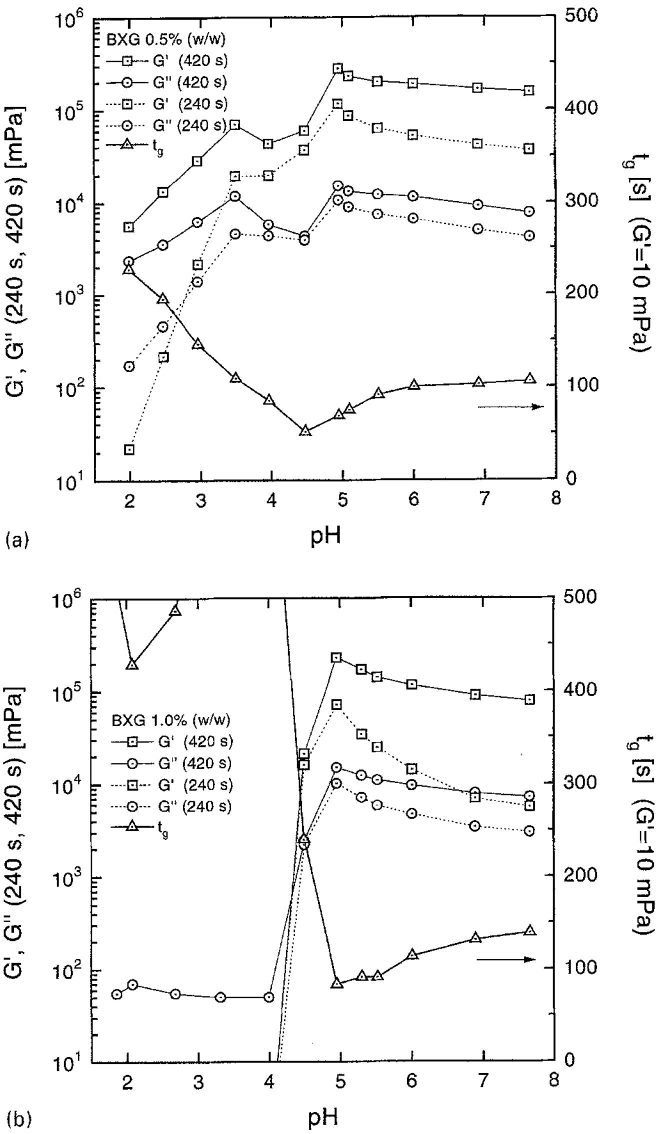


Fig. 9 pH-dependence of moduli G', G'' and gel time t_g for the gelation of 4.6% (w/w) aqueous gelatin solutions containing (a) 0.5% (w/w) BXG and (b) 1.0% (w/w), monitored after 240 s and 420 s

responds to the decreased solubility by flocculation. At pH > IEP, the G' and G'' moduli are very high and approach. This means that the resulting gel becomes more deformable or 'greasy'. The reason might be that the micellar gelatin–surfactant complexes block the hydrophobic gelatin regions, which are responsible for the domain formation of triple helical regions, but they do not block residual ionic groups that are essential for the helix formation between individual gelatin chains. Hence, the resulting gel has a similar cross-linking density as the pure gelatin, but the order within the cross-linked domains is reduced.

Studying the influence of SDS on the gelation of gelatin sols, Lips et al. [11] assume a bridging of the gelatin chains by micelles acting as nodes which leads to a reinforcement of the gel strength. This model is based on the suggestions made by Greener et al. [4]. In contrast, we suggest that the higher viscosity obtained upon addition of a small quantity of surfactant reduces the mobility of the gelatin chains, so that helical regions have more time to organize. Therefore, at low surfactant concentration a higher cross-linking density and tighter network structure will be formed than without surfactant. Nevertheless, we must admit that presently we do not have a direct proof of our considerations.

However, at very high surfactant concentrations of 2 or 5% (w/w) the viscosity of the solutions decreases again and no gelation can be observed anymore. Then, at pH > IEP potential positions for a cross-linking along the chain might have disappeared due to a structural change into lamellar structures as described above.

Conclusion and outlook

In the present work, the formation of micellar gelatin–surfactant complexes is indicated by rheological experiments and surface tension measurements. The complexes are obtained upon the addition of anionic surfactants to aqueous gelatin solutions. At pH values higher than the IEP of the gelatin, the complex formation is accompanied by an increase of the sol viscosity. Since the viscosity increase starts at a critical association concentration and since the decrease at high surfactant concentrations indicates that free micelles are formed in gelatin solutions, the 'bead and necklace'-model had to be modified with respect to the proposed structure of the resulting complex. According to the new model, surfactant molecules form aggregates on the gelatin chains with their hydrophobic tails attached to the chains ('micellar gelatin–surfactant complexes'). Furthermore these micellar complexes strongly affect the gelation behaviour of the gelatin. At pH < IEP, the simple salt formation between gelatin and surfactant leads to a blocking of cationic charges and thus prevents the triple helix formation, while at pH > IEP the formation of micellar gelatin–surfactant complexes leads to a blocking of the hydrophobic parts of the gelatin chains so that they are no longer able to organize in domains.

Additional work should be done to extend the new perceptions on the interactions between gelatin and surfactants in aqueous phase towards the rheological behaviour of photographic colour coupler dispersions. Especially the amphiphilicity of the surfactants is of great importance. Until now the question of whether a dispersed phase is stabilised by surfactant molecules or by the amphiphilic gelatin is still unanswered. Our future research will be concerned with a study of the role of a dispersed phase in gelatin solutions. The dispersed phase can be simulated, for example, by spherical, monodisperse latex particles with controlled surface properties [21]. Such a model system may be useful in predicting the rheological properties and gel formation in the very complex, technically used dispersions.

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