

Radiochemical and Calorimetric investigations of Photogelatins in the Presence of Additives

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Introduction

The quality of the photogelatin is of importance for the sensitometrical parameters of photographic emulsions. In this case, the photogelatins were investigated by means of radiochemical, calorimetric, spectroscopical, cycloviscosimetrical measurements and photographical methods and the results were compared. Here, alkaline and acid processed bone and hide gelatins were used, which were obtained from the International Working Group for Photographic Gelatin (IAG). The velocity of the mass transfer and on the kinetics of the folding of gelatin could be investigated through the addition of different concentrations on foreign salts, surface active substances, polymeric substances, restrainers, spectral sensitisers, amino acids to the solution of gelatin.

Radiochemical

The kinetics of the mass transfer on the interface of the silver halide crystals could be investigated by means of radioactive isotopes in connection with modern measuring techniques for nuclear radiation. The effect of photographically active substances like photogelatins, restrainers, sensitizers and metal ions on the rate of the mass transfer processes during the Ostwald-ripening of AgBr- and AgI-crystals have been investigated in the earlier papers [1]-[7]. The influence of the gelatin on the interface processes on the silver halides in the presence of various concentrations of additives was measured using the systems AgBr-$^{82}Br^-$ and AgI-$^{131}I^-$. Because during the Ostwald-ripening a very low supersaturation exists very low concentration of gelatin reduces the rate of mass transfer processes.

It could be shown, that the activation parameters for the mass transfer processes are indicators of the interaction of photographically active substances or impurities with the gelatin molecules in the gelatin membrane covering the silver halide crystal surface.

The influence of Ca^{2+}-ions:

Figure 1 shows the influence of $CaCl_2$ on the activation energies of the $^{131}I^-$ mass transfer on AgI crystals in the presence of the limed processed bone gelatin Calbe 9552 (temperature range > 30 °C for the unfolded gelatin). It is shown, that with increasing the concentration of $CaCl_2$ the activation energies reach a maximum between 0,2 and 0,4 mmol $CaCl_2$ (related to 200 mg gelatin). In very low concentrations of $CaCl_2$ a stabilization of the structure of the gelatin takes place and it exists an optimal $CaCl_2$-concentration. At higher concentrations of $CaCl_2$ a destabilization of the gelatin (triple helical structure) takes place. This is in connection with a decrease of the activation energies for the $^{131}I^-$ mass transfer. WETZEL and co-workers have found additional, that Ca^{2+} ions retarded at higher concentrations the formation of the triple helix of the gelatin [8]. The refolding of the gelatin takes place in this case at lower temperatures.

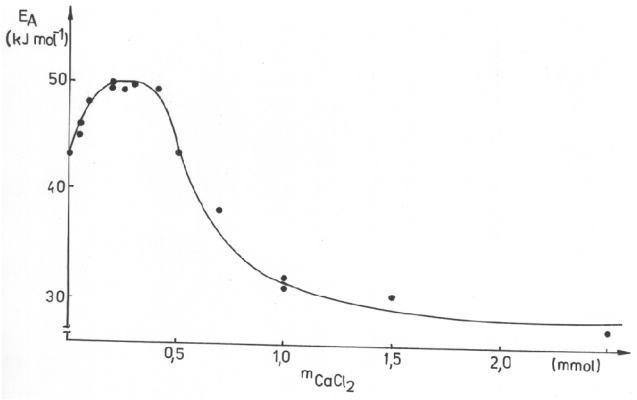

Figure 1: Influence of the $CaCl_2$ concentration on the $^{131}I^-$ mass transfer on AgI crystals in the presence of the inert lime processed bone gelatin Calbe 9552

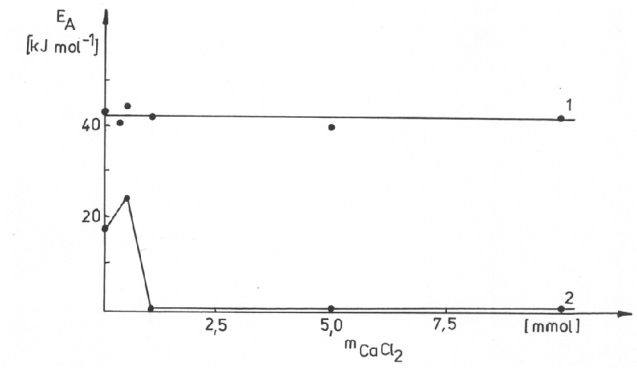

Figure 2: Influence of the $CaCl_2$ concentration on the activation energies of the $^{131}I^-$ mass transfer on AgI-crystals in the presence of the Ca^{2+} free lime processed bone gelatin PB 88210 in the temperature range of the unfolded (curve 1) and the folded condition (curve 2) of the gelatin

Also we have investigated the influence of $CaCl_2$ on the folding of the Ca^{2+} free gelatin PB 88210 (Figure 2). The activation energies (E_A) for the $^{131}I^-$ mass transfer on AgI-crystals in the presence of gelatin are different for the

temperature ranges of the folded and unfolded gelatin. The E_A for the unfolded gelatin is 40-43 kJ • mol^{-1} and for the folded gelatin is 18,5 kJ • mol^{-1}.

From these measurements the jelly-point is going down with increasing the concentration of $CaCl_2$ until ca. 0,75 mmol $CaCl_2$/200 mg gelatin PB 88210 (Figure 3). At concentrations greater than 0,75 mmol $CaCl_2$/200 mg gelatin PB 88210 the jelly-temperature is than constant at this concentration range (Figure 3). This shows, that the Ca^{2+} concentration has an influence on the folding process of the gelatin.

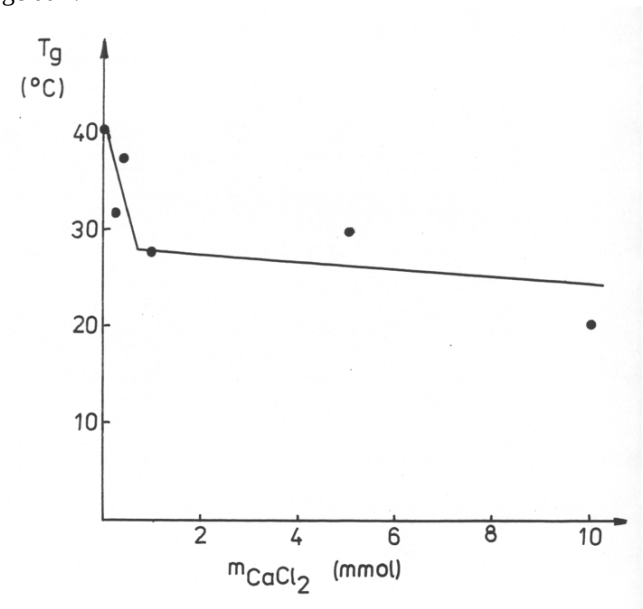

Figure 3: Influence of the $CaCl_2$ concentration on the jelly-point (T_g) of the Ca^{2+} free lime processed bone gelatin PB 88210 (calculated from the results of the radiochemical measurements)

Calorimetric

The transition enthalpies of the gelatin in the presence of increasing concentrations of additives were measured by means of calorimetric methods.

It is shown, that the calorimetric methods also suitable for measurements of the influence of additives and impurities on the folding of the triple helical structure in the photogelatins.

Preparation of the Gelatin Samples:

The photogelatin was pre-swelled at room temperature, then treated at 50 or 60 °C for 30 minutes. After this treatment an amount of additive or photographically active substances were added under stirring. The gelatin solution was then given in a sample cup. This gelatin filled sample cups were standing 3 days at room temperature to give them time for drying. After this the gelatin discs were removed from the sample cups. These in this way prepared and doped discs of photogelatin were measured with the help of the NETZSCH-THERMOANALYSIS-SYTEM in the case of the calorimetric measurements and with the NIR-Spektrometer BRUINS OMEGA 20 in the case of the spectroscopical measurements. During the spectroscopical measurements the content of the triple helical structure was investigated from the area under the band in the triple helical region (2110-2230 nm).

The heating rate was 0,1 K/min in the temperature range from 30 to 110 °C. In the temperature range of 65-85°C the transformation takes place. It could be shown, that with increasing the concentration of the additives the endothermic transition enthalpy decreased from 22,5 J/g to a very low value. This is a result of the inhibiting of the folding of the gelatin in the presence of these substances in the range of higher concentrations. From investigations by means of differential scanning calorimetry (DSC) results were obtained with respect to the photogelatins in the individual temperature range. The stability is influenced by the triple helix content, which is of importance to the quality of photogelatins.

Figure 4 shows the enthalpies of the transition heat of the IAG-Photogelatin PB 88210 in dependence of the $CaCl_2$ content. The enthalpies of the transition ΔH (J/g) decreases with increasing the amount of $CaCl_2$/0,25 g of gelatin. Upon this concentration the heat flow is very low.

Table 1 shows the measured enthalpies of the transition enthalpy ΔH (J/g) in dependence of the $CaCl_2$ concentration for 0,25 g of gelatin.

Table 1: Transition enthalpies [J/g] of the gelatin PB 88210 in dependence of the concentration of $CaCl_2$ [mmol/0.25 g gelatin]

No.	concentration mmol	enthalpy J/g
1	$9 \cdot 10^{-4}$	23,8
2	0,0045	21,315
3	0,009	23,705
4	0,045	21,74
5	0,18	15,622
6	0,36	3,388
7	0,45	1,824
8	0,54	1,73
9	0,72	2,317
10	0,9	0

This experimental result shows the decrease of the content of the triple helix with increasing $CaCl_2$-concentration.

In the concentration range 0,5-0,75 mmol $CaCl_2$/ 0,25 g gelatin the calorimetric curves reach a lowest limit. This is characteristic for low concentration of the triple helical structure. The calorimetric results are also in agreement with radiochemical, NIR-spectroscopic and cycloviscosimetric

investigations. In agreement with these results it was found, that the content of triple helix in the photogelatin decreases with increasing the concentrations of $CaCl_2$ salt.

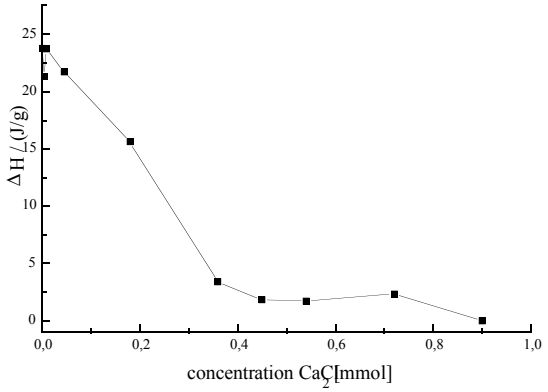

Figure 4: Transition enthalpies [J/g] of the gelatin PB 88210 in dependence of the concentration of $CaCl_2$ [mmol/0.25 g gelatin]

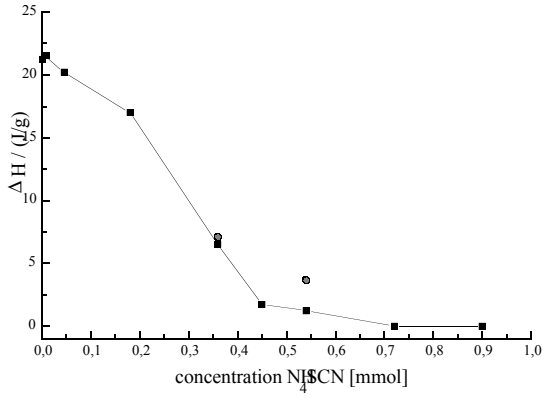

Figure 5: Transition enthalpies [J/g] of the gelatin Kodak EGDI-1 in dependence of the concentration of NH_4SCN [mmol/0.25 g gelatin]

The influence of NH_4SCN on the measured transition enthalpies is shown in Figure 5. It appears as a hydrogen bond breaker in the case of increasing the concentration of NH_4SCN. The formation of the triple-helix structure is inhibit under these experimental conditions.

It was found, that the anions have also an influence on the folding of the gelatin and on the content of the triple helical structures.

The influence of $La(NO_3)_3 \cdot 6\ H_2O$ on the transition enthalpies of the gelatin CRODA 1956 shows, that in the concentration region until 0,6 mg/250 mg gelatin the transition enthalpies are constant. At higher concentrations of this salt (until 1 mg/250 mg gelatin) the transition's enthalpies decrease. Also, it could be shown in a comparison of the radiochemical, spectroscopic and calorimetric investigations results, that the anions play an important role in the formation of the triple helical structures in photogelatins.

Spectroscopic

Near-Infrared Spectroscopy (NIR) was used in the analysis of photogelatins in the presence of additive and photographically active substances. Applications of NIR are in the field of food analysis, polymer sciences and agricultural products.

For the use of photogelatins the influence of impurities, constituents or photographically active substances are of importance on the folding of gelatin. The influence of the following substances could be investigated by means of NIR-spectroscopy:

- inorganic salts
- anions
- stabilizer, restrainers
- sensitizers
- surface active substances

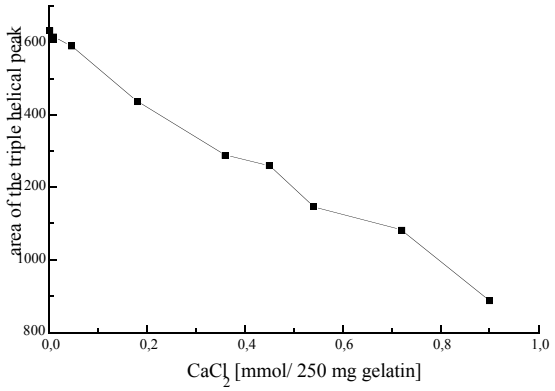

Figure 6: Area of the triple helix band in dependence of the content of $CaCl_2$ [mmol/250 mg gelatin PB 88210]

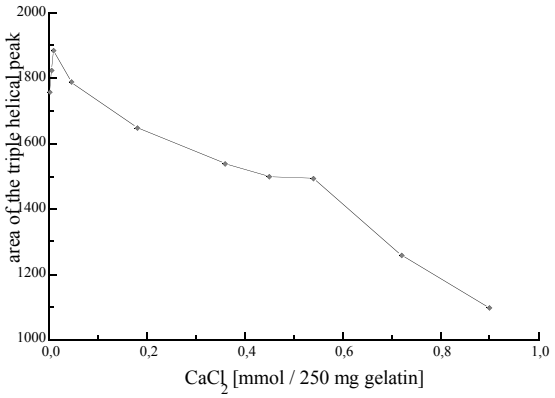

Figure 7: Area of the triple helix band in dependence of the content of CaCl2 [mmol/250 mg gelatin Croda 18692]

Figure 6 shows the influence of different concentrations of $CaCl_2$ on the area of the triple helix band for the Ca^{2+} free lime processed bone gelatin PB 88210. With increasing the concentration of $CaCl_2$ the area of the triple helix band decreases. This shows, that with increasing the

concentration of $CaCl_2$ the content of the triple helix in the gelatin decreases. Figure 7 shows the influence of $CaCl_2$ on the folding of gelatin Croda 18692. The addition of very low concentrations of $CaCl_2$ shows an increase of the triple helix band. This is due to the stabilization of the triple helix structure.

Cycloviscosimetric

Using cycloviscosimetry the kinetics of the folding of gelatin was investigated. The half live time, which was found in the individual time intervals could be assigned to folding like nucleation, cis-trans isomerization and growth of the triple helix helical structure of gelatin [9].

The folding of the gelatin was investigated by measuring the torque wit a Barbender Cyloviscosigraph using convex-concave discs with a slit width of 0,2 mm and a frequency of 0,1 Hz. The shear angle was 1.1°. The measurements were started at 22 ± 1,5 °C. Simultaneously the temperature was measured during the gelatin folding. The torque is a viscosity proportional size.

Sample Preparation:

1 g of the gelatin PB 88210 that is calcium free was dissolved in 5 ml of water and a foreign salt containing solution of definite concentration, respectively. The gelatin was swelled in the solvent as mentioned above at room temperature for 30 min, and then tempered on a water bath at a temperature of 50 °C. A small amount of the unfolded gelatin was used for the torque measurements. The folding process of the gelatin was measured during a time range of 30 min in each case. The influence of different Ca^{2+} and Mg^{2+} salts was investigated on the gelatin folding process.

The mathematical analysis of the torque depending on the folding time shows the three different processes of the gelatin folding:

- nucleation
- cis-trans-isomerization
- growth of the triple helix

From experimental data it was possible to characterize the triple helical content of the photogelatin after the folding in the presence of additives, impurities and photographically active substances. The results indicate the utility of the aplied method for process and quality control.

References

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