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Influence of gelatin–sodium stearoyl lactylate interaction on the rheological properties of gelatin gels

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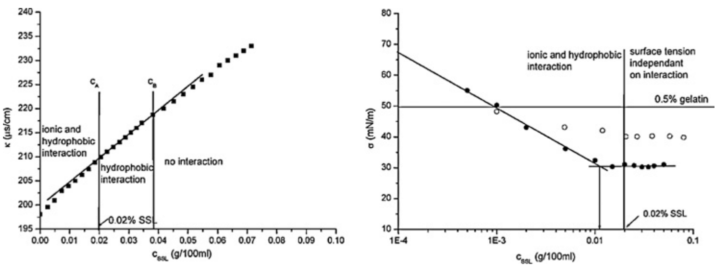
HIGHLIGHTS

- ► Conuctometric and tensiometric investigations of gelatin–SSL interactions.
- ► Influence of their interaction on rheological properties of gelatin gels.
- ► Viscoelasticity of gelatin gels in presence of SSL.

GRAPHICAL ABSTRACT



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ABSTRACT

Addition of surfactants to the polymer solutions induces changes in the bulk of solutions as well as at the interface due to their interactions, thus changing the properties of the systems. Therefore, investigations of these interactions have a great practical and theoretical interest. In the present study, interaction between gelatin and anionic surfactant sodium stearoyl lactylate (SSL) was investigated by different methods. Conductometry and tensiometry were applied to define a region of gelatin–SSL interaction. On the basis of these investigations: cac, defined as concentration at which SSL molecules start to form aggregates with gelatin molecules, and psp at which interaction finishes, were determined. Solutions of gelatin–SSL mixtures at characteristic mass ratios of components were prepared for detailed rheological investigations. Considering that gel formation and network stabilization is time dependent, rheological measurements were performed on gels after 2 and 6 days of storage. Rheological and viscoelastic investigations showed that the presence of SSL molecules influence gelatin ability for gel formation. Increase in SSL concentration decreases thixotropy of gelatin gels which show more viscose, fluid-like properties.

1. Introduction

Gelatin has wide range of applications in food and pharmaceutical industry, as an emulsifier, stabilizer, rheology modifier, peptizer, binder, and film-forming agent. In such products, gelatin is often used together with low molar mass surfactants. Polypeptide structure of gelatin molecule facilitates its interactions with different ionic and nonionic surfactants by hydrophobic or ionic mechanism forming various surfactant–gelatin complexes [1–3]. Depending on the mechanism of interaction involved, formed complex can change conformation of gelatin molecules in solution [2,4] and at interfaces [5,6], thus reflected on the rheological properties of gelatin gels and stability of dispersed systems [7–10]. As a major of food and pharmaceutical products are dispersed systems or gels, investigations of surfactant–gelatin interactions is of great practical interest.

Addition of surfactant to the gelatin solution, induces changes in the bulk of solutions and at the interfaces, so that there are variety of techniques that have been involved in investigations of their interaction like conductometry [3,11], tensiometry [12,13], viscometry [4,14], rheometry [7], equilibrium dialysis [15], NMR [16], fluorescence [17,18] and others.

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For the most investigated surfactants, that are water soluble, interactions between gelatin molecules is predictable, but if surfactant is partly water soluble, the interaction is dependent on the nature of surfactant, its solubility and possibility for liquid crystal formation. Such characteristics has sodium stearoyl lactylate (SSL) which is biocompatible and often used in food products as emulsifier, whipping agent, or rheology modifier [19,20]. The high emulsifying efficiency of SSL is based on amphiphilic nature of its molecule consisting of a hydrophilic charged head and long hydrophobic hydrocarbon tail. The hydrophilic polar chain (lactylate) allows SSL to interact with charged amino acid residues of gelatin through ionic bonds. But SSL chemical structure leads to the quite low solubility in aqueous phase [21–23]. In conjugation with gelatin in dispersed systems and gel products, their interaction can change consistency, i.e. rheological properties of gels or continuous phase, thus changing stability of the systems [24–26].

In the present study, interaction between gelatin and SSL was investigated by different methods. Conductometry and tensiometry were applied to define a region of gelatin–SSL interaction in dilute solutions. On the basis of these investigations, the rheological properties of SSL/gelatin gels formed in characteristic regions of interaction, were investigated. Considering that structuration and network formation in macromolecular systems is time dependant, rheological properties were determined on gels that are two and six days aged.

2. Materials and methods

2.1. Materials

The experiments were carried out using acid-processed gelatin, type A (300 Bloom), product of Serva (USA), with an isoelectric point (IEP) at pH 7.43. Sodium srearoyl lactylate (Grinsted SSL P 55 Veg), anionic surfactant with molar mass 451.6 g/mol, dispersible in hot water, dissolve in ethanol and hot oil and fat, was purchased from "Danisco" (Denmark).

2.2. Conductometry

Conductometric titration of gelatin with SSL was carried out at 35 °C in a jacketed beaker by adding the proper volume of 0.25% (w/v) SSL solution to the 50 ml of 0.5% (w/v) gelatin solution. After adding each portion of the surfactant, the solution was stirred with magnetic stirrer until a steady conductance value was attained [3,27]. Specific conductance of the solution was measured on a microprocessor conductivity meter model INOLAB (WTW, Germany). Specific conductance of bidistilled water used for preparation of solutions was between 2 and 3 μS/cm at 35 ° C.

2.3. Tensiometry

Surface tension measurements of SSL solutions and mixtures of gelatin /SSL were performed at 35 °C, using tensiometer Sigma 703D, (KSV Instruments, Finland). The Du Noüy ring method was employed. Prior to the measurements of surface tension, the ring was immersed in the liquid (below the surface) and the surface was left to equilibrate for 20 min for the mixtures of SSL/gelatin and 3 min for the SSL solution. The reported values of the surface tension are average values of at least three measurements. The surface tension of the bidistilled water used for the preparation of the solutions was $\sigma = 72.1$ mN/m.

2.4. Rheometry

For rheological investigations 1.5% (w/v) gelatin solution and mixture of 1.5% gelatin and various concentrations of SSL were prepared at 40 °C. After preparing, gels were obtained by cooling solutions to the room temperatures and stored in a refrigerator at 7 °C. Measurements were performed with gels after 2 and 6 days of storage.

Rheological measurements were carried out by means of rheometer RS600 (Thermo Haake (Karlsruhe), GmbH, Germany), at 25 ° C. The cone-and-plate geometry was used ($d = 60$ mm, $\alpha = 1°$). It was found that flow curves of gelatin and mixtures SSL/gelatin show thixotropic behaviour and the continuous hysteresis loop method was employed [28] to obtain flow curves. Thixotropic loop were obtained by continually changed shearing rates D (s^{-1}), from zero ($D = 0$) to maximal one ($D_{\max} = 500\,s^{-1}$), and reversely (after 5 min shearing at $D_{\max}$). Obtained thixotropic loops areas was characterized by coefficient of thixotropy K defined as [29,30]:

$$K_t = (\frac{1}{n})\Sigma\Delta\tau_i$$

n- is number of differences $\Delta\tau_i = \tau'_i - \tau''_i$ in (Pa) of "up" (τ'_i) and "down" (τ''_i) flow curves for a given D_i values.

The oscillatory measurements were carried out to investigate viscoelastic properties of SSL/gelatin gels. The amplitude sweep method was used [31]. The oscillating frequency was 1 Hz. Plateau values of elastic, G', and viscous modulus, G'', were determined from the linear visco-elastic region. Relative contribution of viscous to elastic component of the investigated systems was evaluated by means of the tanδ value:

$$\tan\delta = \frac{G''}{G'}$$

tanδ is useful quantifier of the presence and extent of elasticity in a fluid, tan$\delta > 1$ marks a sample with predominantly viscous characteristics and tan$\delta < 1$ marks a sample with predominantly solid characteristics.

3. Results and discussion

3.1. Tensiometric and conductometric investigation of gelatin–SSL interaction

Tensiometry is often used method for investigation of interaction between polymers and surfactants [13,32,33], because it could be applied on both, ionic and nonionic molecules in the dilute systems, while conductivity is convenient only for the ionic ones.

Gelatin is a good stabilizer for various systems and it is known that gelatin show surface activity, i.e. tendency to adsorb at the phase interface, thus decreasing surface tension. In the presence of ionic low molecule surfactants, due to their interactions, conformation of gelatin molecules changes which affect the structure of adsorption layers and can even induce desorption of gelatin molecules from the surface. Changes at the phase interface caused by interaction could be detected by surface tension measurements.

Tensiometric and conductometric measurements were performd at gelatin concentration of 0.5% and temperature of 35 °C to avoid gel formation and enable interactions at molecular levels.

Influence of the SSL concentration on the surface tension of pure water and 0.5 % gelatin solution is shown in Fig. 1. Surface tension of the SSL solution in water decreases with increasing SSL concentration until reach value of 0.0121% SSL. After that, surface tension is constant independent on SSL concentration. Decrease in the surface tension is due to adsorption of surface active SSL molecules at the surface. When the surface becomes saturated with surfactant molecules, micelles begin to form in the solution, and surface tension reaches constant value at characteristic concentration defined as the critical micelle concentration (*cmc*) [27,33]. Above the *cmc*, there is no further adsorption of surfactant to the surface, because micelles are not surface active, and have no influence on the