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Viscosimetric and tensiometric investigations of interactions between gelatin and surface active molecules of various structures

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ABSTRACT

Gelatin is a protein widely used in food, pharmaceutical and cosmetic products. Polypeptide structure of gelatin molecule facilitates its interactions with different surface active ingredients that are often present in such products. These interactions can significantly change properties of gelatin solution in the bulk, as well as on the interface, and therefore influence the stability of the system. In this study interactions between gelatin and different surface active molecules: two small molecule surfactants (Tween 80, Triton X100) and two surface active polymers: starch derivative (octenyl succinic starch, OSA) and cellulose derivative (hydroxypropylmethyl cellulose, HPMC), were investigated using tensiometric and viscosimetric measurements.

The results show that possibility and mechanisms of interaction between gelatin and surface active molecules depend not only on the nature of molecules, but also on its chemical structure. Thus, non-ionic, branched small molecule surfactant Tween 80 shows hydrophobic mechanism of interaction with gelatin, while other used linear small molecule surfactant, Triton X100, does not interact. Polymeric surfactant OSA starch is a weak anionic polyelectrolyte, but due to hidden polar group, shows hydrophobic interaction with gelatin, dependant on pH of the solution. HPMC molecule, which is non-ionic with small hydrophobic substituents, does not interact at all.

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1. Introduction

Proteins are known specially for their surface activity, which allows them to play a major role in the formation and stabilisation of dispersed systems by a combination of electrostatic and steric mechanism. The long term stability can be further enhanced using surfactants or other macromolecular materials to improve surface properties and to control the rheology and network structure of the continuous phase of dispersed system, i.e. emulsions, hence retarding phase separation and gravity induced creaming (Benichou, Aserin, & Garti, 2002; Dickinson, 2008; Sovilj, Djakovic & Dokic, 1993).

Gelatin is a major compound in the formulations of a wide variety of products covering food, pharmacy, cosmetics, photography and many more. It is used as an emulsifier, peptizer, thickener, and binder, and great interest is taken in investigations of the interaction between gelatin and other ingredients, that are used cooperatively in formulated products. These interactions can significantly change properties and stability of the products (Dickinson, 1993). Therefore investigation of interactions between gelatin and other ingredients is of great practical interest.

The system gelatin/small molecule ionic surfactant is the most studied one and various techniques have been involved for that purpose such as: surface tension measurement (Buron, Filiatre, Membrey, Foissy, & Argillier, 2004; Onesippe & Lagerge, 2009), viscosimetry (Buron et al., 2004; Greener, Contestable, & Bale, 1987), surface shear rheometry (Ao et al., 2011; Kragel, Siegel, & Miller, 1994), conductometric and potentiometric measurement (Chauhan, Kumari, Pathania, Sharma, & Kumar, 2007; Sovilj, 1998; Whitesides & Miler, 1994), turbidity measurement (Onesippe & Lagerge, 2009) or fluorescence probe studies (Griffiths, Roe, Bales, Pitt, & Howe, 2000). These studies indicate in general that anionic surfactants interact strongly with protein molecule and form protein/surfactant complex (Buron et al., 2004; Onesippe & Lagerge, 2009; Sovilj, 1998). There are two possible mechanisms of interaction in such systems: the ionic and hydrophobic one and surface properties of complex, as well as their adsorption at the phase interface, depend on the mechanism of interaction. On contrary, cationic surfactants show a weak interaction with proteins (Ananthapadmanbhan, 1993; Sovilj, 1998). Interaction between proteins and non-ionic surfactants is less pronounced and

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poorly studied. Investigations of gelatin/non-ionic surfactant system have been focused on bulk properties of the system and showed that surfactant bind very weakly to protein (Ananthapadmanbhan, 1993; Chauhan, Jyoti, & Kumar, 2011). Such behaviour is attributed to the low critical micelle concentration of non-ionic surfactants and the absence of electrostatic interaction between protein and surfactant. There are little data about surface properties of these systems, according to their molecular structure.

In the recent years more attention is paid to the use of polymeric surfactants (PS), which structure could be very complicated, and their interactions with proteins, for stable dispersed system formation (Dickinson, 2009; Khristov & Czarnecki, 2010; Tadros, 2009; Tadros, Vandamme, Levecke, Booten, & Stevens, 2004). This is of special interest in the field of nano and multiple emulsions preparation, especially for improving their stability and achieving sustained and prolonged release of incorporated active materials. For that reason monomeric surfactants were progressively replaced by polymeric ones (Dickinson, 2011; Evison, Dickinson, Owusu Apenten, & Williams, 1995; Garti & Aserin, 1996; Garti & Bisperink, 1998; Lutz & Aserin, 2008). PS combine the desired properties of polymers, such as high viscosity, with the interfacial properties of conventional surfactants. Gelatin is a protein with known surface activity, plays a major role in formation and stabilisation of dispersed systems. But the long term stability can be further enhanced using PS molecules to control the rheology and network structure of the continuous phase, hence to improve stability of the dispersed system and prolong release of active material (Dickinson, 2008). Protein and PS molecules in such systems associate via physical interactions. These non-covalent interactions (electrostatic and hydrophobic interactions, steric exclusion, hydrogen bonding, etc.) between biopolymers have implications for interfacial properties of adsorbed films and for formation and stability of the dispersions. For charged molecules, on the other hand, the contribution of electrostatic interaction is predominant. Thus on adjusting the pH or ionic strength of the aqueous phase, the strength of interaction may vary substantially (de Kruif, Wienbreck & de Vries, 2004; McClements, 2006; Turgeon, Schmitt, & Sanchez, 2007).

The aim of this study was to investigate the interactions between gelatin and surface active molecules, of various structures, that are often used for stabilisation of food and pharmaceutical dispersions. As surface active molecules, the following compounds were used: two small molecule surfactants (Tween 80, Triton X100), and two surface active carbohydrates: starch derivative (octenyl succinic starch, OSA) and cellulose derivative (hydroxypropylmethyl cellulose, HPMC). Tween 80 is a non-ionic surfactant derived from polyethoxylated sorbitan (with three POE chains) and oleic acid, and very often present in food and pharmaceutical formulations (Hasenhuettl & Hartel, 2008, chap. 1). Triton X100 is also non-ionic linear surfactant which has one hydrophilic polyethylene oxide group and hydrocarbon lipophilic group. It is used in food industry and widely used in biological works (Chauhan et al., 2011; Mukherjee, Mitra, Battacharya, Panda, & Moulik, 2009). Proteins and carbohydrates are often found together in many food products and the examination of the interactions between them is very important, because it can significantly affect the quality and stability of the product, especially if carbohydrates behave as surface active molecules. For that reason two derivatives of natural carbohydrates, i.e. starch and cellulose derivative were chosen and possibility of their interaction with gelatin was investigated. OSA starch is a modified food starch, derived from waxy maize, especially suited for the encapsulation of flavours, vitamins and species at high oil loading. Modification of starch molecule with hydrophobic octenyl succinic group gives the molecule amphiphilic nature and thus surface active properties (Nilsson & Bergenstahl, 2007; Varona, Martin, & Cocero, 2009; Wang, Su, & Wang, 2010). Hydroxypropylmethyl cellulose (HPMC) is water soluble, nonionic cellulose derivative very widely used in foodstuff and pharmaceutical industry. The introduction of methyl and hydroxypropyl groups renders the cellulose molecule hydrophobic and thus it acquires surface active properties, so that HPMC can be regarded as a representative of polymeric surfactants (Kulicke, Arendt, & Berger, 1998; Zhang, 2001).

The interactions between gelatin and these surface active molecules were investigated by combination of tensiometric and viscosimetric techniques.

2. Materials and methods

2.1. Materials

Gelatin, type B, from bovin skin, 225 bloom, was obtained from "Sigma", USA. The isoelectric point (IEP) of gelatin, determined by viscosity measurements, was found to be at pH = 5.2. Tween 80 was obtained from "Serve", Germany, with HLB = 15, and molecular weight $M \approx 1300$ g/mol. Triton X100 was obtained from "Sigma", USA, HLB = 13.4 and $M = 625$ g/mol. OSA starch, modified food starch derived from waxy maize, was obtained from "National Starch & Chemical", USA. Hydroxypropylmethyl cellulose (HPMC) (trade name Methocel E3LV), pharmaceutical grade, methoxyl content 28.9%, hydroxypropyl content 8.9%, gel point at 70 °C, was obtained from "Colorcon Ltd.", England. Sodium chloride (NaCl), p.a., and sodium hydroxide (NaOH), p.a., were purchased from "Centrohem" Beograd. Hydrochloric acid (HCl), p.a., was purchased from "Zorka Pharma" Sabac. All materials were used without further purification. Distilled water was used as a solvent in all experiments.

2.2. Preparation of solutions

Stock solution of 2% (g/100 ml) gelatin was prepared by adding 1/5 of total amount of water to a given mass of protein and then left for 15 min to swell. Upon this, rest amount of water was added under mild stirring at 40 °C. For intrinsic viscosity of gelatin solution measurement, stock solution of gelatin was prepared in pH 5.2 buffer (0.1 M HCl/0.1 M NaOH). Stock solutions of 1% Tween 80, 10% Triton X100, and 8% OSA starch were prepared by dissolving in water by gently stirring and heating up to the temperature of 40 °C. Stock solution of 2% HPMC was prepared by dispersing HPMC in water at 80 °C (above gel point of HPMC). All stock solutions were used 24 h after preparation.

For investigations of interactions gelatin/surface active materials binary mixtures were prepared by mixing required volumes of stock solutions. Concentrations of surface active materials were varied (from 0.00001% to 0.5% for Tween 80; from 0.00001% to 2% for Triton X100; from 0.001% to 2% for OSA starch; from 0.0001% to 1% for HPMC) while concentration of gelatin was kept constant at 1%. Mixtures were left for 24 h at 40 °C, and after that viscosity and surface tension of these mixtures were measured.

For additive viscosity measurements of gelatin/polymeric surfactants (OSA starch, HPMC) mixtures, 1% solutions were prepared by mixing required volumes stock solutions of gelatin and PS to obtain 0.1/0.9; 0.2/0.8; 0.3/0.7; 0.4/0.6; 0.5/0.5; 0.6/0.4; 0.7/0.3; 0.8/0.2; 0.9/0.1 mass ratio of gelatin/PS. These solutions were also left for 24 h at 40 °C, after which viscosity of solutions were measured.

2.3. Methods

2.3.1. Surface tension measurements

For surface tension measurements digital tensiometer KSV – Sigma 703D (Finland) was used and the *Du Nouy* ring method was

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