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Study of the complex formation between sodium dodecyl sulphate and gelatin

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ABSTRACT

In this paper, sodium dodecyl sulphate (SDS) and gelatin interactions in aqueous solution have been studied at room temperature (298 K) using a wide variety of physico-chemical methods. Binding isotherms (SSE) of surfactant onto protein have been correlated to surface tension measurements. Results of turbidity and conductometric measurements are presented in order to better understand bulk behaviour of such system. Finally, isothermal titration calorimetry (ITC) allows some interpretations about the thermodynamic steps of the interaction.

This study provides information about optimal ionic ratio of SDS/gelatin complexes in order to apply them for the formation of capsules using the coacervation process, for example.

1. Introduction

Gelatin is an available and biodegradable protein derived from collagen. Because of its great properties such as emulsifier, thickener, peptizer, it is involved in food, cosmetics, pharmaceutics or photography industries [1].

The purpose of this work is to use the complex formed between gelatin and surfactant as the wall material of microcapsules elaborated by coacervation process. A possibility to obtain the protein in its insoluble state is obtained via interactions with specific surfactants.

Complex formation between biopolymer gelatin and oppositely charged surfactant is well studied in the literature [2–4]. It usually sketches as polymer/surfactant interactions. The association, i.e. formation of aggregates starts at a defined concentration called critical aggregation concentration (CAC), which is well below the critical micelle concentration (CMC) of surfactant [5]. Several techniques were employed to investigate the nature of surfactant/protein interactions: turbidity measurements [2], conductometric and surface tension measurements, binding isotherms [2,6] for quantitative considerations but the determination of thermodynamics of the association is very poor in the literature [5].

In this paper, we present data on the interaction of gelatin with oppositely charged SDS, which indicates the formation of amphiphilic and neutral aggregates. In addition we propose qualitative understanding of thermodynamic processes involved in this binding. We choose SDS as a model anionic surfactant because it is well characterized in the literature, moreover, it is involved in many polymer/surfactant complexes [5–7].

2. Materials and methods

All measurements and preparation techniques were carried out at least three times.

2.1. Materials

Protein gelatin was obtained from Kamyshny.[1] It is a gelatin type A, 300 bloom, average molecular weight is equal to 80,000–120,000 from Sigma (USA). Gelatin has been used without further purification. Its isoelectric pH (determined in our laboratory by coupling pH-metric and conductometric measurements) is found to 7.6; this value is in good agreement with the literature [6].

Analytical grade surfactant, SDS, with a purity exceeding 99% and chlorhydric acid were purchased from Fluka (France). The water used was distilled and deionized with a Millipore "Super Q" system.

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Water was buffered to pH 4 using HCl solution and has been used as solvent. pH measurements were performed with a Tacussel 3000 pH-meter with a glass electrode.

2.2. Preparation of solutions

A stock protein solution was prepared by dissolving a given mass of gelatin in the pH 4 solvent under mild stirring at 311 K. After adjustment of pH to the appropriate value by addition of small aliquots of concentrated NaOH or HCl, solutions were stocked at 298 K and used before 72 h. The solutions of SDS were prepared at the same pH as the gelatin solutions before mixing. Solutions of SDS + gelatin were prepared by mixing the two separate solutions at the same pH at 311 K. pH was checked after mixture and if necessary, corrected to value 4. In these conditions (acidic pH), surfactant and protein are oppositely charged. It is well established that the SDS may be hydrolysed in an acidic solution during long storage to form dodecanol, which is known as a very surface-active substance [8]. Nevertheless, we think that this feature of SDS is avoided because acidic SDS solutions are prepared just before any use. Gelatin concentrations are expressed in weight % whereas surfactant concentrations are in mol/l.

2.3. Viscosity measurements

The kinetic viscosities (ν) of gelatin solutions have been determined using a capillary viscosimeter (Ubbelhode) at 298 K. Two types of capillaries of different diameters have been employed depending on protein solutions viscosities: Ubbelhode tubes (Viscosimetric MS, Fica) with diameters of 0.53 mm ($K = 0.00478\ \mathrm{mm^2/s^2}$) and 0.78 mm ($K = 0.03\ \mathrm{mm^2/s^2}$). The corresponding densities (ρ) were measured with a PAAR DMA 602 densimeter. The viscosities (η) were calculated with the following formula:

$$\nu = \frac{\eta}{\rho} \tag{1}$$

where viscosities η are expressed in mPa s, kinetic viscosities ν in $\mathrm{mm^2/s}$ and densities ρ in $\mathrm{g/cm^3}$.

2.4. Ionic conductivity measurements

These measurements were made at 298 K, using a Meterlab conductivity meter CDM 230 (Radiometer, France). The constant of the cell was determined before each measurement and was found equal to $1\ \mathrm{cm^{-1}}$.

2.5. Surface tension measurements

Two types of solutions were used: pure protein solutions and protein/SDS solutions. The mixed solutions were prepared by adding a volume of SDS solution to the same volume of gelatin solution – the SDS concentration varied systematically. The pH of mixed solutions was adjusted to 4 before any experiment.

Surface tension was measured at 298 K using the Wilhelmy plate method with K-12 tensiometer from Krüss (Germany) with the accuracy of $\pm 0.3\ \mathrm{mJ/m^2}$. γ is expressed in mN/m.

2.6. Turbidity measurements

Turbidity measurements were carried out using a spectroscopic technique (Metrohm 662 photometer at 600 nm) at 298 K. Aliquots (50 μl) of surfactant solution (0.04 mol/l) were injected, using an external syringe, into a beaker initially containing 20 ml of protein solution at the desired concentration. The turbidity change was followed by measuring the tension U of the spectrode after each injection. This tension U is normalized by the initial tension U_0. Typical solubilization curves could be constructed by plotting normalized tension according to SDS concentration, $U/U_0 = f(C)$.

2.7. Surfactant selective electrode (SSE) measurements

A SDS selective electrode adapted to our system was elaborated according to the procedure described in the literature [9]. A concentration cell was also constructed, the procedure of measurement is described in our previous studies [10].

Small aliquots (100 μl) of SDS micellar solution (0.04 mol/l) were injected stepwise, using an external syringe, into a beaker initially containing 25 ml of either HCl solution, pH 4.0 (blank experiment) or an homogeneous gelatin solution at various weight percent (binding experiment). After each injection, the system was kept under stirring during 4 min before measuring the emf relative to a commercial Calomel electrode connected through a NH_4Cl bridge. Measuring the emf after each injection follows changes in free SDS concentration.

2.8. Isothermal titration calorimetry (ITC) measurements

The microcalorimetric measurements were taken with a new "Calostar" batch microcalorimeter, which is an improved version of "Montcal 3" microcalorimeter. The principle is explained in our previous studies [10,11].

A 0.01 mol/l SDS stock solution was injected stepwise (series of 60 consecutive injections), into the calorimetric cell containing 8.0 g of solvent for the dilution experiment or 8.0 g of gelatin solution (different weights percent) for the complexation experiment.

The apparent differential molar enthalpies of dilution ($\Delta_{\mathrm{dil.}}\dot{h}$) and complexation ($\Delta_{\mathrm{com}}\dot{h}$) corresponding to a given dilution or complexation step were evaluated by means of the following equations:

$$\Delta_{\mathrm{dil.}}\dot{h} = \frac{\Delta_{\mathrm{exp.}}H}{\Delta n_2^i} \tag{2}$$

$$\Delta_{\mathrm{bind}}\dot{h} = \frac{\Delta_{\mathrm{exp.}}H - n_2^i \Delta_{\mathrm{dil.}}h}{\Delta n_2^a} \tag{3}$$

where $\Delta_{\mathrm{exp.}}H$ is the experimentally measured enthalpy change, $\Delta_{\mathrm{dil.}}\dot{h}$ is the differential molar enthalpy of dilution for the equilibrium concentration C of SDS in the calorimetric cell, n_2^i is the number of moles of SDS injected into the calorimetric cell, Δn_2^a is the change in the number of moles of SDS bound to the protein and is determined graphically with the aid of the binding isotherm, and $\Delta_{\mathrm{dil.}}h$ is the molar integral enthalpy of dilution for the equilibrium concentration of SDS in the calorimetric cell. All the adsorption experiments were conducted at $T = 298$ K.

3. Results and discussion

3.1. Characterization of gelatin type A

Gelatin is an amphoteric polymer. It is essential to know its isoelectric point, i.e. the pH where positive charges are equal to negative charges in the molecule because this value is determinant to choose the pH of the medium.

Positive charges in acidic medium are determined by protonation of NH_2-groups in side chains of arginine, asparagine and glutamine, while negative charges are the result of dissociation of COOH-groups in side chains of glutamic and aspartic acids in alkaline media. IEP value has been determined by a conductometric method described by Xing et al. [12]. Aliquots of 0.2 ml of NaOH 1% (m/m) solution have been injected in approximately 40 ml of a