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ORIGINAL CONTRIBUTION

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Conductometric and potentiometric investigations of ionic surfactant–gelatin interaction

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Abstract The interaction between gelatin and ionic surfactant is relevant to many biological and industrial processes. Therefore, knowledge of the mechanism of ionic surfactant–gelatin interaction is an important factor influencing practical application of such systems.

In this paper, conductometric and potentiometric titrations were used to study the interaction of sodium dodecyl sulfate as an anionic and cetyltrimethylammonium bromide as a cationic surfactant with gelatin solutions of different concentrations. Titrations were carried out at 40 °C by adding surfactant to the gelatin solutions. The titration course was followed by measuring specific conductance and pH changes.

On the basis of the titration curves the prevailing mechanisms of surfactant–gelatin interaction, as well as the characteristic concentrations at which they are changed, were determined. From the linear relationship established between the characteristic surfactant concentrations and gelatin concentration, maximal amount of surfactant bonded per gram of gelatin was calculated.

Key words Surfactant–gelatin interaction – sodium dodecyl sulfate – cetyltrimethylammonium bromide – conductometric and potentiometric titration

Introduction

The interaction between gelatin and surfactants have been studied extensively over the past several decades. Because of its usefulness as an emulsifier, stabilizer, peptizer, binder, and film-forming agent gelatin is widely used in photography, food, biomedical, pharmaceutical and other industries. In such applications, gelatin is often used in conjunction with various surfactants.

The ionic surfactant modify the properties of gelatin through their interaction and formation of surfactant–gelatin complexes. There are two possible mechanisms of the ionic surfactant–gelatin molecular interaction: the ionic, and the hydrophobic one [1–5]. Depending on the mechanism of interaction involved, the complex formed can lead to drastic changes in conformation and dimension of gelatin molecule in solution [6–8], which is reflected on the consistency of gelatin solutions and gels [3, 6, 9–12], thickness, structure and swelling of gelatin films [13–15], adsorption at the interface [1–3, 16–19], structure and porosity of gelatin-walled microcapsules [19–21].

The interaction between charged polymers as gelatin and ionic surfactants has been extensively investigated by various methods. These methods included direct measurement of surfactant binding to gelatin molecule by equilibrium dialysis and using a surfactant-selective electrode [4, 5, 18, 22–24], whereas the commonly used experiments give indirect information about the changes of the system properties due to interaction between the two components. The type of molecular structure of the complexes or aggregates formed in the interaction of the ionic surfactant and gelatin molecules is still a matter of disagreement among different authors [10, 18, 24–26].

Electrochemical methods were widely used for investigation of interaction between ionic surfactant and water-soluble polymer, where polymer was mostly uncharged, involving only a hydrophobic mechanism of interaction [27–30]. The interaction between ionic components of which one is a protein is more complicated. There are not much data about such investigations by electrochemical methods [18, 22, 31, 32], that the results thus obtained are explained on the basis of the mechanisms of interaction derived by other methods.

In this paper, conductometric and potentiometric methods were used to investigate the interaction of gelatin molecules with anionic surfactant – sodium dodecylsulfate and cationic one – cetyltrimethylammonium bromide. On the basis of the titration curves obtained it was possible to determine the prevailing mechanism of surfactant–gelatin interaction, as well as the concentrations of surfactants at which solubilization of surfactant–gelatin complexes takes place.

Experimental

Materials

The experiments were carried out using alkali-processed gelatin, type B (225 Bloom), product of Sigma (USA). The isoelectric point (IEP) of gelatin, determined by viscosity measurements and mixed bed ion exchange, was found to be at pH = 5.2. Sodium dodecyl sulfate (NaDS) was a Merck (Germany) product with active substance >99%, and critical micelle concentration (CMC) of 8.8 mmol/l at 40 °C, determined by conductometric titration. Cetyltrimethylammonium bromide (CTMAB) used was a product of Sigma (Germany), with active substance >99%, and critical micelle concentration of 1.2 mmol/l at 40 °C, determined by conductometric titration. Both surfactants were used without further purification.

Methods

Conductometric and potentiometric titrations were carried out at 40 °C in a jacketed beaker by adding the proper volume of 5% (g/100 ml) NaDS, i.e. 3% (g/100 ml) CTMAB solution by an automatic burette ABU-80, Radiometer (Denmark) to the 50 ml of unbuffered gelatin solution of various concentrations (0.1, 0.2, 0.5, 0.8 and 1.0% w/v). After adding each portion of the surfactant, the solution was stirred with a magnetic stirrer until a steady pH or conductance value was attained. Conductance of the solution was measured on a microprocessor conductivity meter Model MA 5964, Iskra (Slovenia), using a cell with the cell constant of 1.000. The pH changes of gelatin solutions during the titration were measured using a pH meter type MA 5721, Iskra (Slovenia), with glass–calomel electrode. The pH meter was calibrated using the titrival (Kemika, Croatia) buffer pH = 5.0 before each titration.

All solutions were prepared with bidistilled water which had a specific conductance between 2 and 3 μS/cm at 40 °C.

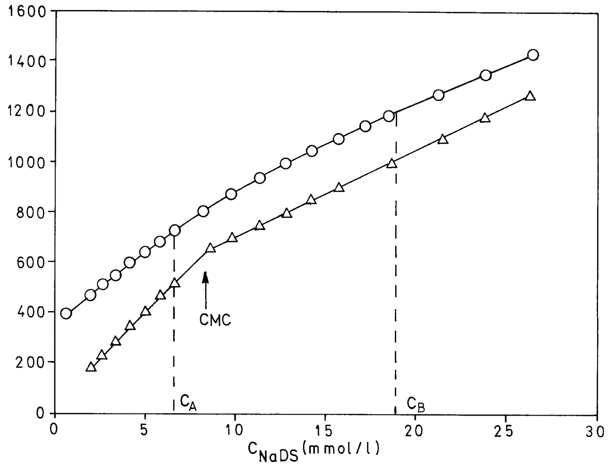
Results and discussion

The interaction of gelatin with sodium dodecyl sulfate

The addition of NaDS to water caused a linear increase of specific conductance χ(μS/cm) up to the surfactant concentration at which micelle formation began, i.e., up to the critical micelle concentration (CMC). After the CMC, the conductance increased further linearly, but with a smaller slope than before the CMC. The break on the conductance–concentration titration curve gives the CMC of the surfactant [29, 32, 33]. For NaDS, the CMC determined by conductometric titration was 8.8 mmol/l at 40 °C (Fig. 1).

In the titration of 0.5% gelatin solution with NaDS, the curve shows two linear regions, one below the concentration break C_A, and the other above the break C_B, which lie on either side of the CMC for pure NaDS. Between the concentration breaks C_A and C_B, there is no linearity of the specific conductance. This change in specific conductance is caused by the NaDS–gelatin interaction. The first addition of the surfactant resulted in a slight turbidity of the solution (which disappeared after further addition of surfactant) because the pH value was close to the IEP of gelatin.

Fig. 1 Conductometric titration curves of water (△) and 0.5% (w/v) gelatin solution (○) with NaDS



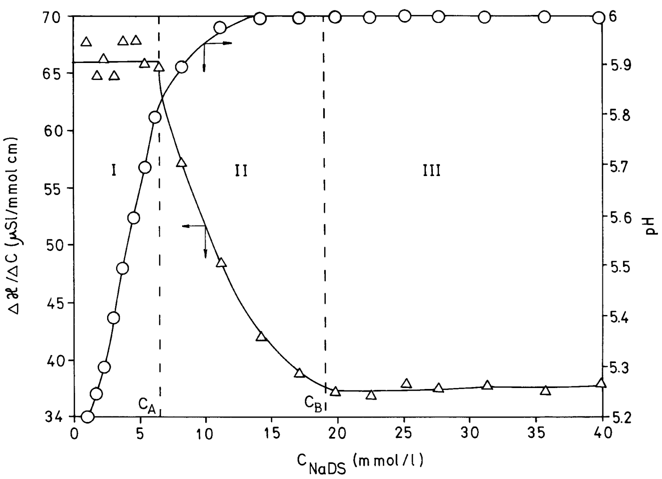


Fig. 2 Conductometric (△) and potentiometric (○) titration curves of 0.5% w/v gelatin solution with NaDS

More information about the NaDS–gelatin interaction can be obtained from the diagram which shows the changes of the slope $\Delta\chi/\Delta c$ and the pH of gelatin solution with increasing NaDS concentration (Fig. 2) [30]. In Fig. 2, we can distinguish three regions (I, II and III), between the two concentration breaks C_A and C_B. Each region is characterized by the different changes of conductance and pH values as a result of the ionic equilibrium in the aqueous medium during the NaDS–gelatin interaction.

Region I: This region lies below the concentration break C_A. The concentration break C_A is often called critical aggregation concentration (cac) and is lower than the CMC of pure surfactant [26, 34]. In this concentration range of the surfactant, investigations carried out by the method of equilibrium dialysis, viscosity, potentiometry and surface tension [4–6, 10, 12, 16, 18, 31], gave an indication about the stoichiometry of surfactant–gelatin interaction and formation of surface active gelatin–surfactant complex with reversible changes in the conformation of the gelatin molecule [7, 12]. By adding NaDS to the gelatin solution, due to electrostatic forces, the free NaDS molecules may bond ionically to the accessible–NH_3^+ groups on the surface of gelatin molecule, forming a surfactant–gelatin complex [3, 5, 10]. This ionic mechanism of NaDS–gelatin interaction causes the linear increase in specific conductance of the solution with increase in NaDS concentration to the first break C_A (Fig. 1). The specific conductance is proportional to the amount of free Na^+ ions released by the interaction of NaDS and gelatin molecules [32] and the slope $\Delta\chi/\Delta c$ is constant (Fig. 2). A smaller slope than that corresponding to the NaDS along (Fig. 1), indicates the presence of NaDS–gelatin interaction. Due to the ionic mechanism of NaDS–gelatin interaction, the exposed–NH_3^+ groups on the gelatin molecules are blocked by NaDS, and therefore, the pH value of the solution is this region is increased [15, 31] (Fig. 2).

The mechanism of NaDS–gelatin interaction in this region may be represented by the following equation

$$[G^{(s+i)^+}] + s[DS^-][Na^+] \rightarrow \underbrace{[G^{(s+i)^+}][DS^-]_s + s[Na^+]}_{K_I} \qquad (1)$$

where $[G^{(s+i)}]$ is the concentration of gelatin molecules with $(s+i)$–NH_3^+ groups of which s are on the surface and i inside the coiled gelatin molecule. The ionic complex K_I has screened i–NH_3^+ groups inside the folded gelatin molecule potentially capable for further ionic interaction.

Region II: The concentration break C_A has been attributed to induced micellization brought about by a condensation of the surfactant onto gelatin molecules [8, 12, 18]. This occurs in region II, between the concentration breaks C_A and C_B, involving both hydrophobic and ionic mechanisms of NaDS–gelatin interaction. First, each ionically bonded NaDS molecule favors the binding of an additional surfactant molecule in its vicinity by hydrophobic interaction between the paraffin chains of the surfactant [22], forming thus the NaDS–gelatin complex K'_{II}. The hydrophobically bonded NaDS molecules cause unfolding of the gelatin molecules [5, 7], followed by an increase in viscosity [6, 10], binding isotherm [5, 22], and in NaDS activity [18]. The exposed new i–NH_3^+ groups are available for further ionic interaction (complex K'_I). This stage of interaction could be expressed in a simplified way as

$$[G^{(s+i)^+}][DS^-]_s + s[Na^+] + (s+i)[DS^-][Na^+] \rightarrow \underbrace{[G^{s^+}][DS^-]_s[DS^-]_s[Na^+]_{s-x}}_{K'_{II}}\underbrace{[G^{i^+}][DS^-]_i}_{K'_I} + (s+x+i)[Na^+] \; . \qquad (2)$$

Studies with hydrophobic fluorescent probes indicated that the gelatin-bound surfactant is probably aggregated as micelles [10]. Therefore, the hydrophobic bonding decreases the mobility of Na^+ ions present on the gelatin molecules as gegenions (x). The specific conductance is not proportional to the NaDS concentration, and the slope $\Delta\chi/\Delta c$ decreases (Fig. 2). In this region, the pH value shows a further increase, but less pronounced, indicating that both hydrophobic and ionic mechanism of interaction are involved.

At a further increase in NaDS concentration up to the break C_B, the hydrophobic mechanism of NaDS–gelatin interaction is more pronounced, leading to saturation of all ionically bonded NaDS molecules (complex K'_I) with the excess NaDS and forming the complex K_{II} (Eq. (3)). Therefore, the slope $\Delta\chi/\Delta c$ slightly decreases, but the pH values remain constant because of the absence of ionic interaction at higher NaDS concentration:

$$[K'_{II}]_{s-x}[G^{i+}][DS^-]_i + (s+x+i)[Na^+] + i[Na^+][DS^-] \rightarrow \underbrace{[K'_{II}]_{s-x}[G^{i+}][DS^-]_i[DS^-]_i[Na^+]_{i-y}}_{K_{II}} + (s+x+y+i)[Na^+] \, . \quad (3)$$

As hydrophobic mechanism of interaction continues the multi-micellar complex is formed and the micelle can bind cooperatively two or more gelatin molecules to form a large complex [8, 12, 34], yielding an increase in the bulk viscosity [6, 10, 12, 35]. The conformation of gelatin molecules is significantly changed. Nevertheless, the interpretation of the structure of the gelatin–surfactant complex is difficult and rather controversial.

Region III: In this region, above the concentration break C_B, the slope $\Delta\chi/\Delta c$ and the pH value are constant with increase in NaDS concentration. The specific conductance changes as if the gelatin is not present, i.e., the slope reflects the sole effect of NaDS addition [25, 33], indicating the absence of interaction between NaDS and gelatin molecules. Namely, at the concentration break C_B, all the binding sites on the gelatin molecules are saturated with surfactant micelles, NaDS–gelatin complexes are solubilized, and free nonadsorbed micelles begin to form. This is consistent with the studies by other methods [1–12, 19], showing that gelatin saturation with NaDS molecules results in a significant change of the observed characteristics of the system, such as viscosity drop, disturbance of the gel structure, decrease of the surface tension, and adsorption of gelatin molecules at the interface.

The results of conductometric and potentiometric titration of gelatin solutions of various concentrations with NaDS are presented in Figs. 3 and 4. The positions of the characteristic concentration breaks C_A and C_B change with the gelatin concentration, as well as the concentration of NaDS at which a constant pH value is reached.

The conductometric curves (Fig. 3) consist of two linear regions with a constant $\Delta\chi/\Delta c$ slope, up to the concentration break C_A (region I) and after C_B (region III). In region I, the slope is dependent on the gelatin concentration, while in region III it is not (Fig. 5). The value of the slope in region III is practically the same as the observed for a solution containing solely NaDS micelle [2, 10]. This indicates the presence of the NaDS–gelatin interaction in region I and the absence of any interaction in region III.

The characteristic concentration breaks C_A and C_B of NaDS obtained for various concentrations of gelatin C_g shift linearly toward higher values with increasing gelatin concentration (Fig. 6). Parameters of the linear relationships

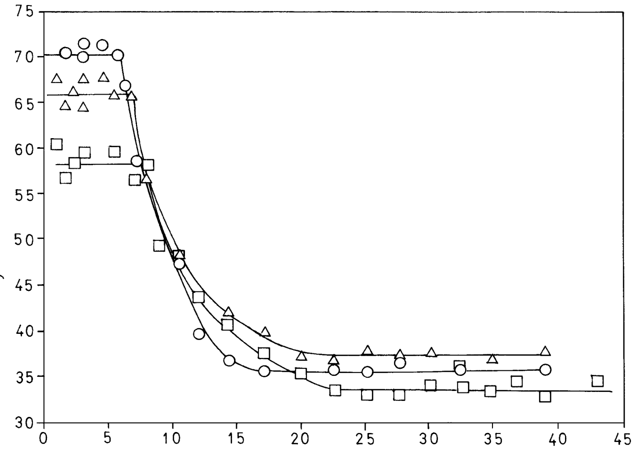
$$C_{NaDS} = aC_g + b \quad (4)$$

are presented in Table 1. Here, the concentration of NaDS is in mmol/l and gelatin in percents (g/100 ml). The parameter a is the slope of the linear relationship and represents the number of mmoles of NaDS bounded per 10 g of gelatin, and b is the intercept in mmol/l. In Table 1 is also presented the correlation coefficient r.

From the slope of the linear relationship of the break C_B, when the interaction is completed, it was calculated the maximal amount of NaDS bonded per gram of gelatin, amounting to 1.6 mmol NaDS/g of gelatin. This value is in good agreement with those obtained by other methods [3, 4, 31].

The characteristic concentration break C_A is slightly shifted to higher concentration with an increase in gelatin

Fig. 3 Conductometric titration curves of gelatin solutions of different concentrations: (○) 0.3% w/v; (△) 0.5% w/v and (□) 0.8% w/v, with NaDS



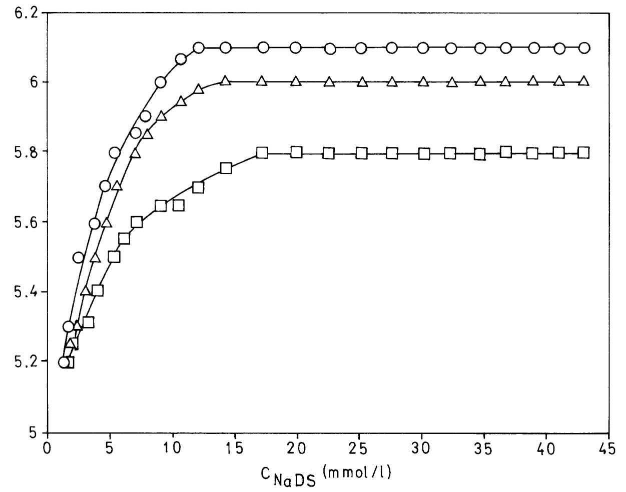


Fig. 4 Potentiometric titration curves of gelatin solution of different concentrations: (○) 0.3% w/v; (△) 0.5% w/v and (□) 0.8% w/v, with NaDS

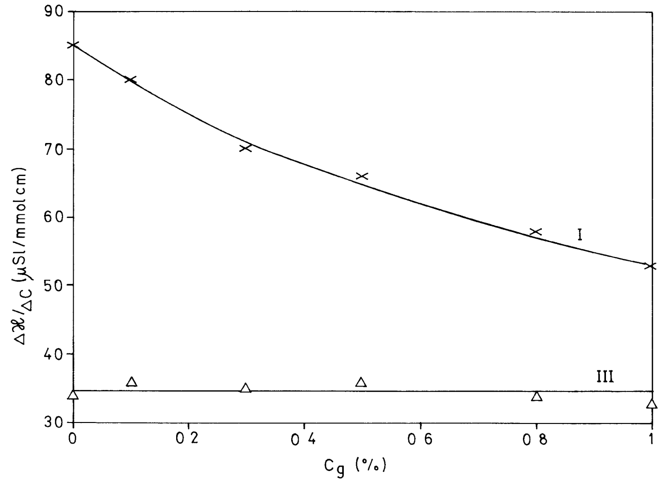


Fig. 5 Dependence of the slope of conductometric titration curves in region I and III on gelatin concentration

concentration (Fig. 6) because of a certain screening effect of the charged positive groups on gelatin molecules for ionic bonding at higher gelatin concentrations [5, 7]. In contrast, the characteristic concentration break C_B shows a significant increase with an increase in gelatin concentration. Namely, to reach the concentration break C_B, NaDS molecules should bind first hydrophobically to cause unfolding of gelatin molecules and exposing of new ionic groups for further ionic bonding. The binding continues by a combination of ionic and hydrophobic mechanisms of interaction until complete saturation of gelatin molecules with NaDS micelles is reached, and the formation of micelles of pure NaDS sets in. Therefore, the concentration break C_B depends significantly on gelatin concentration.

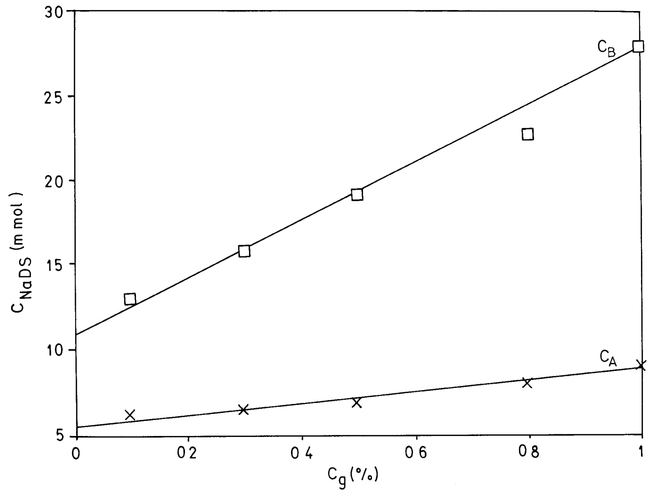


Fig. 6 Characteristic concentration breaks C_A and C_B of the conductometric titration curves for NaDS as a function of gelatin concentration

Table 1 Parameters of linear relationship of characteristic concentrations of NaDS at the breaks C_A and C_B

Break	Parameter		
	a [mmol/10 g]	*b* [mmol/l]	*r*
C_A	3.1	5.6	0.972
C_B	16.0	11.0	0.990

Note: *r* – correlation coefficient.

$$r = \frac{\left|\sum_{l}^{n}(X-\bar{X})(Y-\bar{Y})\right|}{[(n-1)\mathrm{SD}_x\mathrm{SD}_y]} .$$

SD_x – standard deviation of gelatin concentration, g/100 ml.

$$\mathrm{SD}_x = \left[\frac{1}{(n-1)}\sum_{l}^{n}(X-\bar{X})^2\right]^{1/2} .$$

SD_y – standard deviation of NaDS concentration, mmol/l.

$$\mathrm{SD}_y = \left[\frac{1}{(n-1)}\sum_{l}^{n}(Y-\bar{Y})^2\right]^{1/2} .$$

$X = C_g$ – gelatin concentration, g/100 ml.
$\bar{X}$ – mean value of X.
$Y = C_{\mathrm{NaDS}}$ – NaDS concentration, mmol/l.
$\bar{Y}$ – mean value of Y.

The interaction of gelatin with cetyltrimethylammonium bromide

The conductometric and potentiometric titration curves obtained for the titration of gelatin solution with the cationic surfactant cetyltrimethylammonium bromide are

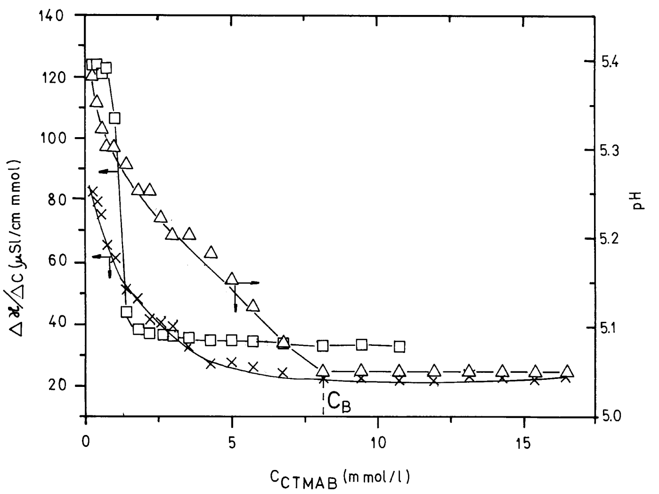


Fig. 7 Conductometric (x) and potentiometric (△) titration curves of 0.8% w/v gelatin solution with CTMAB, and conductometric titration curve of water with CTMAB (□)

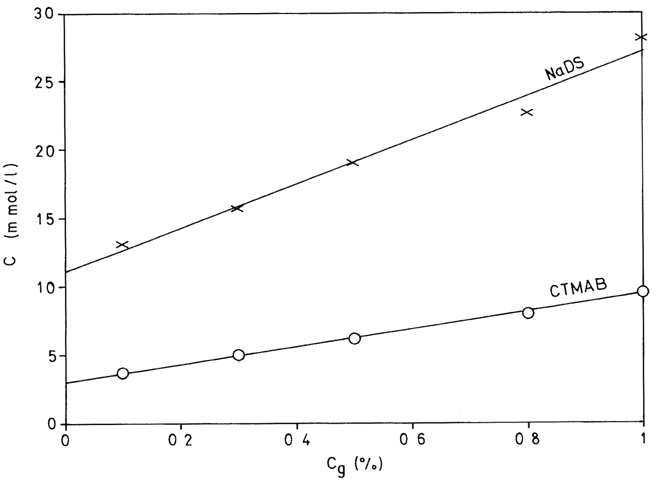


Fig. 8 Characteristic concentration breaks C_B for NaDS and CTMAB as a function of gelatin concentration

presented in Fig. 7. For comparison, in the same diagram is presented the conductometric titration curve of water with CTMAB, on which are evident two regions of constant slope $\Delta\chi/\Delta c$, one up to CMC of CTMAB (1.2 mmol/l), and the other after CMC. The conductometric titration curve in the presence of gelatin shows a constant decrease in the slope $\Delta\chi/\Delta c$ and the pH values with increasing CTMAB concentrations until the concentration break C_B is reached.

A further increase in the CTMAB concentration shows the constant slopes $\Delta\chi/\Delta c$ and pH, indicating the absence of CTMAB–gelatin interaction. The decrease in the slope and the pH value up to the concentration break C_B, indicates a simultaneous presence of the ionic and hydrophobic mechanisms of interaction in the whole concentration range. The absence of sole ionic mechanism of interaction at low CTMAB concentration could be explained by the low CMC of CTMAB and limited monomer activity due to micelle formation [22]. Furthermore, the more bulky head group affects the binding of CTMAB to gelatin [36, 37]. Therefore, the titration curves make possible only to determine the concentration of CTMAB needed for completing the interaction process, i.e., the characteristic concentration break C_B. This concentration increases linearly with increasing gelatin concentration (Fig. 8) according to the equation: $C_{CTMAB} = 6.3C_g + 3.1$ (coefficient of correlation $r = 0.999$).

Maximal amount of CTMAB bonded per gram of gelatin, calculated from the slope, is 0.63 mmol. It is obvious from Fig. 8, that the interaction between gelatin and CTMAB is much weaker compared to that of NaDS, which is in good agreement with the literature data [9, 22, 37]. Therefore, CTMAB produces weaker conformational changes on gelatin molecules [36, 38] and the properties of gelatin solution in the presence of CTMAB are not changed so much as in the presence of NaDS.

These investigations show that, the use of relatively simple electrometric techniques, can give useful information on the mechanisms of surfactant–gelatin interaction, as well as on the concentrations at which interaction is completed. From the linear relationships it is possible to calculate the concentrations of NaDS and CTMAB needed for a desired degree of interaction. The knowledge of the corresponding mechanisms of interaction is not only of fundamental interest but has also a practical importance. Namely, the surfactant–gelatin interaction is an important factor for the microencapsulation processes and microcapsules characteristics. The changes in adsorption layer structure due to the interaction [19] influence the porosity and permeability of the wall of the microcapsules, thus regulating release of the microcapsule content [20, 21].

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