Tensiometric investigation of the interaction and phase separation in a polymer mixture–ionic surfactant ternary system

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Abstract: The interaction and phase separation in a ternary mixture composed of hydroxypropyl methyl cellulose (HPMC), sodium carboxymethyl cellulose (NaCMC), and sodium dodecylsulfate (SDS) were investigated by tensiometry. Surface tension measurements of binary mixtures (0.7 % HPMC and 0.00–2.00 % SDS) and of ternary mixtures (0.7 % HPMC, 0.3 % NaCMC, and 0.00–2.00 % SDS) were performed. The measurements indicated interaction between HPMC and SDS, which resulted in HPMC–SDS complex formation. The critical association concentration, *CAC*, and polymer saturation point, *PSP*, were determined. Phase separation of ternary HPMC/SDS/NaCMC mixtures occurs at SDS concentration > CAC, *i.e.*, when the HPMC–SDS complex is formed. The volume of the coacervate increases with increasing SDS concentration, and at SDS concentrations > 1.00 %, the coacervate vanishes. The surface tensions (σ) of ternary HPMC/SDS/NaCMC mixtures in the pre-coacervation region and at the onset of the coacervation region are similar to the σ of the corresponding binary HPMC–SDS mixtures, while in the coacervation and post coacervation region, they are close to the σ of the corresponding SDS solutions.

Keywords: polymer–surfactant interaction; complex formation; coacervation; phase separation; tensiometry; surface tension.

INTRODUCTION

Interaction between macromolecules may result in phase separation of a colloidal system into a coacervate (*i.e.*, liquid precipitate) and an equilibrium solution (supernatant). Depending on whether the interaction is of the associative or segregative type, either complex coacervation or coacervation due to thermodynamic incompatibility occurs, respectively.[1,2] During complex coacervation, a complex of two associative macromolecules (*e.g.*, polycation and polyanion) is formed which separates from the solution as a coacervate, while the equilibrium solution is more or less pure solvent. Thermodynamic incompatibility has been

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related to the classical Flory–Huggin's theory or to depletion interaction theories, depending on the characteristics of the two macromolecules, where both of the two phases formed are rich in just one of the two macromolecules.[3,4]

Coacervate formation is involved in a number of practical situations: it is of special interest to the food and cosmetic industries, where macromolecules are found in the coacervate state in a wide range of products, and thereby determine their properties, *e.g.*, texture, stability, taste *etc*.;[5] complex formation *via* polymer–polymer interaction occurs in cells and other biological systems, and is important for their functioning;[6] the coacervation method is a common microencapsulation technique,[7] *etc*.

In a ternary mixture composed of two water soluble cellulose ethers, non-ionic hydroxypropylmethyl cellulose (HPMC) and anionic sodium carboxymethyl cellulose (NaCMC), and an anionic surfactant (SDS), various interactions occur (*i.e.*, HPMC–NaCMC, HPMC–SDS, HPMC/SDS–NaCMC) which may result in the formation of a coacervate. The microstructural properties of the coacervate can be varied by controlling the HPMC–SDS–NaCMC interaction.[8] In a recent work, the interactions were successfully employed to obtain oil microcapsules stabilized with coacervate shells of different properties.[9]

The aim of the present work was to investigate how the interactions among the components of HPMC/SDS/NaCMC ternary mixtures of different composition influence the surface tension of the investigated mixtures, especially when phase separation is involved. This is of importance for the understanding of the complex behavior of phase-separated polymer mixture–surfactant systems and provides further insight into the mechanism of microcapsule formation by the previously published method.[9] For this purpose, the surface tensions of different binary HPMC/SDS and ternary HPMC/SDS/NaCMC mixtures were determined, in which the concentrations of the polymers were fixed while the concentration of the surfactant was varied. In addition, the influence of the SDS concentration on the relative volume of the coacervate in the ternary HPMC/SDS/NaCMC system was determined.

EXPERIMENTAL

Chemicals

Hydroxypropylmethyl cellulose, HPMC, (trade name Methocel K4M CR, methoxyl content: 22.7 %, hydroxypropyl content: 8.9 %) was obtained from Colorcon Ltd., England. The viscosity average molar mass of the HPMC was M_v = 91500 g/mol, while the critical overlap concentration was c^* = 0.1269 %, determined at 20 °C. Sodium carboxymethyl cellulose, NaCMC, degree of substitution DS = 0.77, purity >96 %, was obtained from "Milan Blagojević", Serbia. The viscosity average molar mass of the NaCMC was M_v = 121000 g/mol, determined at 25 °C and the critical overlap concentration c^* = 0.1927 %. Details of the viscosimetric characterization of the HPMC and NaCMC samples can be found elsewhere.[10] Sodium dodecylsulfate, SDS, purity > 99%, was obtained from Merck, Germany. Critical micelle

concentration was $CMC = 0.252$ % at 30 °C, as determined by conductometric titration.[11] All samples were used without any further purification. Bidistilled water was used as the solvent.

Preparation of the binary and ternary mixtures

Stock solutions of 2.00 % w/w HPMC and 1.00 % w/w NaCMC were prepared by dispersing the required mass of HPMC and NaCMC in water at 80 and 20 °C, respectively, with gentle stirring. The stock solutions were left for 24 h at room temperature prior to further use. A 5% w/v stock solution of SDS was prepared by dispersing the required mass of SDS in bidistilled water at room temperature. Binary mixtures of 0.7 % w/w HPMC and 0.00–2.00 % w/w SDS were prepared by mixing the required masses of HPMC stock solution with a suitably diluted SDS stock solution. The mixtures were left for 24 h at room temperature prior to further use. Ternary mixtures of HPMC/SDS/NaCMC were prepared by mixing water and stock solutions of HPMC, NaCMC and SDS. The ternary mixtures were composed of 0.7 % w/w HPMC, 0.3 % w/w NaCMC and 0.00–2.00 % w/w SDS, and were left for 48 h at room temperature prior to further use.

Tensiometry

The surface tension measurements of the solutions were performed using a KSV Sigma 703D at 25 °C. The *Du Noüy* ring method was employed. Prior to the measurements, the air––liquid surface was disturbed by vigorous mixing, the ring was then immersed in the liquid (below the surface) and the surface was left to equilibrate for 20 min for the binary and ternary mixtures and 3 min for the SDS 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.

Phase separation

The phase separation in the ternary mixtures consisting of 0.70 % HPMC, 0.30 % NaCMC and different SDS concentrations (0.00–2.00 %) was followed visually in 10 ml measuring cylinders. The relative volume of the coacervate, $v_{rel} = 100v/V$, in the ternary mixtures containing various concentrations of SDS was calculated, where v is the volume of the coacervate and V the volume of the whole ternary system in the measuring cylinder.

RESULTS AND DISCUSSION

Tensiometric investigation of the interaction between HPMC and SDS

Influence of the SDS concentration on surface tension of the SDS solution and the 0.70 % HPMC solution is shown in Fig. 1.

The surface tension of the SDS solution first decreased with increasing SDS concentration, passed through a minimum, then slightly increases and finally reached a constant value. The decrease in the surface tension is due to adsorption of surface active SDS molecules at the solution surface. The decrease occurs until the critical micelle concentration (*CMC*) is reached, when the surface becomes saturated with surfactant molecules and micelles begins to form in the solution. Above the *CMC*, there is no further adsorption of surfactant to the surface and thus no influence of the surfactant concentration on the surface tension of the solution. Such a dependence of the surface tension on the concentration of a surfactant can be used for the determination of the *CMC*. However, tensiometric de-

termination of the *CMC* is often difficult due to occurrence of a minimum in the surface tension *vs.* surfactant concentration curve around the *CMC*. The minimum in the surface tension curve, which can also be observed in Fig. 1, is typically ascribed to small amount of highly surface active impurities in solution.[12,13,14] In the case of an SDS solution, the occurrence of the minimum is often attributed to the presence of dodecanol in a SDS sample.[13,14] The impurities preferentially adsorb to the surface when compared to the surfactant and additionally lower the surface tension of the solution. Once micelles of SDS molecules are formed in a solution, solubilization of the impurities occurs and they desorb from the surface and are replaced by less surface active surfactant molecules. Consequently, a slight increase in the surface tension occurs. Therefore, the onset of the slight increase in the surface tension of a solution indicates *CMC*, which in the present case was found to occur at 0.23 % SDS. The *CMC* determined by tensiometric measurements (0.23 %) is somewhat lower than the *CMC* determined previously in the same laboratory[11] by conductometric titration (0.252 %). Finally, when all impurities are solubilized and the surface is saturated only with surfactant molecules, the surface tension of a solution becomes constant.
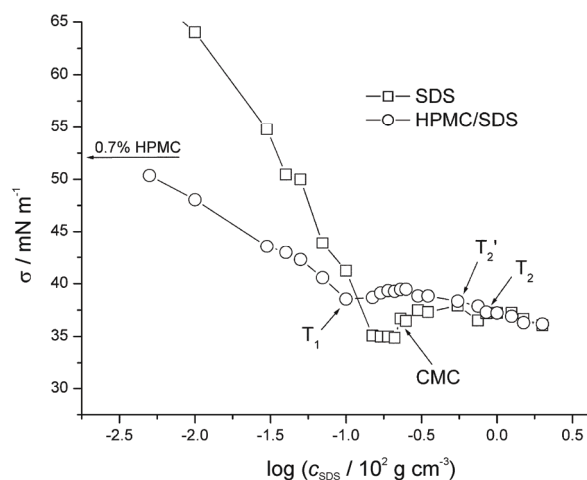

Fig. 1. Influence of the SDS concentration on the surface tension 0.70 % HPMC solutions.

HPMC is a surface active macromolecule;[15] the surface tension of a 0.70 % HPMC solution was found to be 52.32 mN/m, as indicated by the arrow in Fig. 1. On addition of SDS to a 0.70 % HPMC solution, the surface tension of the solution decreased. Due to the adsorption of both HPMC and SDS molecules on the surface, the surface tension of the binary HPMC/SDS mixture was lower than that of the corresponding SDS solution. At $T_1 \approx 0.1$ % of SDS, the first transition point in the surface tension *vs.* SDS concentration curve occurred. The transition

point indicates the onset of HPMC–SDS complex formation as a result of hydrophobic interaction between SDS and HPMC, and is usually referred to as the critical association concentration, *CAC*.[16,17] The HPMC–SDS complex formation was previously detected using different experimental techniques.[8,11,18] On further addition of SDS, surface tension of the binary mixture slightly increased and after reaching a maximum, it decreased. Occurrence of the maximum in surface tension is not typical for a nonionic polymer–ionic surfactant systems,[16] but was also previously observed by *e.g*., Folmer and Kronberg in a mixture of SDS and poly-(vinyl pyrrolidone).[19] Such a behavior is certainly concerned with reorganization of the adsorption layer at the surface, however, details of the surface composition could not be provided solely by tensiometric measurements. At the transition point denoted as $T_2 \approx 0.85$ % SDS, the surface tension of the mixture became the same as the surface tension of the pure SDS solution, indicating the onset of free SDS micelle formation in the bulk. The idealized picture of a nonionic polymer––ionic surfactant interaction predicts the occurrence of one more transition point between T_1 and T_2.[16,17] It is usually denoted as T_2', and represents a surfactant concentration at which all the hydrophobic sites of a polymer are saturated with surfactant molecules (*i.e.*, polymer saturation point, *PSP*). This transition point is typically far less evident than is the case for T_1 and T_2. T_2' is defined as the first SDS concentration at which the surface tension of the binary mixture becomes lower than at T_1, which is ≈0.65 % SDS. The *CAC* and *PSP* values obtained by tensiometric measurements agree with the values obtained in previous investigations using other experimental techniques.[8,11,18]

Tensiometric investigation of the interactions and phase separation in ternary HPMC/SDS/NaCMC mixtures

The addition of NaCMC to a HPMC/SDS mixture brings about phase separation of the ternary HPMC/SDS/NaCMC mixture. The investigated ternary mixture (composed of 0.70 % HPMC, 0.30 % NaCMC and 0.00–2.00 % SDS) phase separated into a coacervate (bottom) and an equilibrium solution (top) when the SDS concentration was between 0.10–1.00 %, Fig. 2.

Coacervate formation began at an SDS concentration which corresponds to the onset of HPMC–SDS complex formation, *i.e.*, at the *CAC*. This indicates that the formation of the HPMC–SDS complex is a prerequisite for phase separation of the ternary HPMC/SDS/NaCMC mixture. Previous rheological measurements indicated that the ternary HPMC/SDS/NaCMC mixture phase separates into an HPMC–SDS complex-rich coacervate phase and a NaCMC-rich equilibrium solution, due to the thermodynamic incompatibility between the HPMC–SDS complex and NaCMC.[8]

The relative volume of the coacervate in the ternary mixture increased with increasing SDS concentration, Fig. 3, and was determined by the governing interactions and a change in the microstructure of the HPMC–SDS complex.
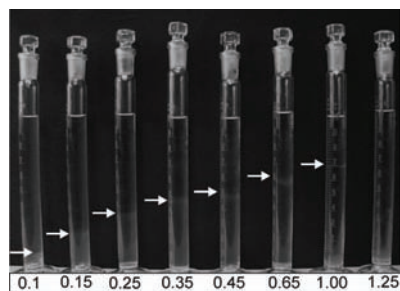
Fig. 2. Phase separation in ternary HPMC/SDS/NaCMC mixtures with varying SDS concentrations. The numbers indicate the SDS concentration (in %).
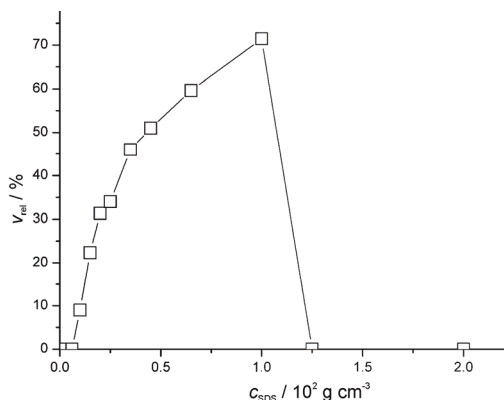

Fig. 3. Influence of SDS concentration on the relative volume of the coacervate in ternary HPMC/SDS/NaCMC mixtures.

The increase in the relative volume indicates an increase in the salvation of the coacervate. This was to be expected since the HPMC–SDS complex becomes increasingly more negatively charged as the SDS concentration is increased, due to the fact that more SDS is bound to the HPMC molecules.[8,9] The binding of SDS continues until the *PSP* is reached. As indicated by viscosimetry,[11] above the *PSP* there are additional conformational changes of the HPMC–SDS complex due to repulsion between the negatively charged complex and the free SDS micelles, which results in shrinkage of the complex. At sufficiently high SDS concentrations, the complex is able to be accommodated in the system, it becomes soluble even in the presence of NaCMC and thus the coacervate disappears when the concentration of SDS is >1.00 %.

The results of the surface tension measurements of the ternary HPMC/SDS/ /NaCMC mixtures are compared with the surface tensions of the corresponding binary HPMC/SDS mixtures and pure SDS solutions in Fig. 4.

In the pre-coacervation region, the surface tensions of the ternary mixtures were slightly lower than of the corresponding binary HPMC/SDS mixtures, indicating a similar composition of the surfaces, *i.e.*, adsorption of both HPMC and SDS molecules. This was expected since NaCMC shows only a small surface activity and contributes only slightly to surface tension of the ternary mixture. The surface tension of a 0.3 % NaCMC solution was found to be $\sigma_{NaCMC} = 70.7$ mN/m, which is very close to surface tension of bidistilled water ($\sigma_{water} = 72.1$ mN/m). At the onset of the coacervation region, the surface tensions of the binary and ternary mixtures were equal, indicating that phase separation only slightly influenced the balance between the components in the bulk and those adsorbed at the surface. This is somewhat surprising since the HPMC–SDS complex was separated as a coacervate at the bottom of the measuring vessel. It should be noted,

however, that previous rheological measurements[8] indicated the presence of HPMC in the equilibrium solution at the onset of the coacervation region, which also suggests that some of the HPMC molecules could be adsorbed at the surface at the beginning of the coacervate region. On further increase in the SDS concentration, the surface tension of the ternary mixture dropped; it became lower than in the binary mixtures and equaled the surface tension of the corresponding SDS solutions. In this part of the coacervate region, the dependence of the surface tension on the SDS concentration was very similar to the dependence in the pure SDS solution and bore no resemblance to the dependence observed in the binary HPMC/SDS mixtures. This indicates that the HPMC molecules gradually desorbed from the surface and were replaced by SDS molecules, and that the surface of the supernatants of the ternary mixture became free of HPMC molecules and free of the HPMC–SDS complex. The surface became saturated with only SDS molecules, the concentration of free SDS in the bulk was in the vicinity of the *CMC*, while the excess SDS was bound to HPMC and formed HPMC–SDS complexes. This phase separated from the solution. After reaching the *PSP*, in the post-coacervation region, the surface tension of all three systems (SDS solution, the binary and the ternary mixtures) became equal and free micelles of SDS appeared in the solution.[20,21]
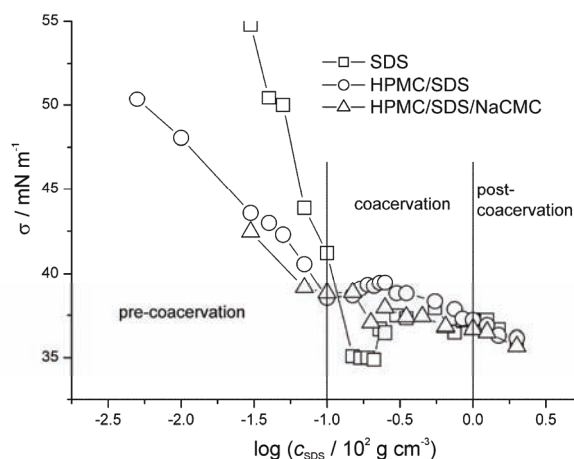

Fig. 4. Influence of the SDS concentration on the surface tension of
ternary HPMC/SDS/NaCMC mixtures.

CONCLUSIONS

Tensiometric measurements of the binary HPMC/SDS and ternary HPMC//SDS/NaCMC mixtures with constant polymer(s) and different SDS concentrations were carried out in order to investigate interaction and phase separation in the ternary mixture. It was shown that the formation of the HPMC–SDS complex

influenced the surface tension of the binary mixture, and resulted in a characteristic dependence of the surface tension on the SDS concentration. Characteristic transition points of the dependence were used to determine the interaction regions of HPMC–SDS, *i.e.*, *CAC* and *PSP*, which were found to be in agreement with the values obtained previously using other experimental techniques. The ternary HPMC/SDS/NaCMC mixture phase separated when the SDS concentration was above the *CAC*, *i.e.*, when the HPMC–SDS complex was formed. The volume of the coacervate increased with increasing SDS concentration, and at an SDS concentration >1.00 % (*i.e.*, in the post-coacervation region), the coacervate vanished. The surface tension (σ) of the ternary HPMC/SDS/NaCMC mixtures in the pre-coacervation region and at the onset of the coacervation region were similar to the σ values for the corresponding binary HPMC–SDS mixtures, while in the coacervation and post coacervation region, it was close to the σ of the corresponding SDS solutions, indicating that the supernatants became free of HPMC and HPMC–SDS complex.

ИЗВОД

ТЕНЗИОМЕТРИЈСКО ИСПИТИВАЊЕ ИНТЕРАКЦИЈЕ И СЕПАРАЦИЈЕ ФАЗА У ТЕРНЕРНОМ СИСТЕМУ САСТАВЉЕНОМ ОД СМЕШЕ ПОЛИМЕРА И ЈОНСКЕ ПОВРШИНСКИ АКТИВНЕ МАТЕРИЈЕ

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Испитивана је интеракција и сепарација фаза у тернерном систему састављеном од хидроксипропилметил целулозе (HPMC), натријум-карбоксиметил целулозе (NaCMC), и натријум-додецилсулфата (SDS) употребом тензиометрије. Измерени су површински напони HPMC/ /SDS бинарних смеша (0,7 % HPMC и 0,00–2,00 % SDS) и тернерних смеша HPMC/SDS/ /NaCMC (0,7 % HPMC и 0,00–2,00 % SDS). Мерења указују да долази до интеракције између HPMC и SDS, и до формирања HPMC–SDS комплекса. Одређена је критична концентрација асоцијације (*CAC*) и критична концентрација засићења полимера (*PCP*). До сепарације фаза и формирања коацервата у тернерној HPMC/SDS/NaCMC смеши долази при концентрацијама SDS већим од *CAC*, односно када је у смеши формиран комплекс HPMC–SDS. Запремина коацервата се повећава са повећањем концентрације SDS, док при концентрацијама >1,00 % коацерват нестаје. Вредности површинског напона HPMC/SDS/NaCMC тернерне смеше у области пре коацервације као и у области почетка коацервације су блиске вредностима површинског напона одговарајуће HPMC/SDS бинарне смеше. У области коацервације и у области након коацервације вредности површинског напона тернерне смеше се поклапају са вредностима површинског напона чистих раствора SDS.

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