Carbohydrate Polymers 79 (2010) 563–570

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Microencapsulation of oil by polymer mixture–ionic surfactant interaction induced coacervation

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ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form 2 September 2009
Accepted 9 September 2009
Available online 15 September 2009

Keywords:
Polymer–surfactant interaction
Polymer–polymer interaction
Thermodynamic incompatibility
Segregative phase separation
Coacervation
Microencapsulation
Spray drying

ABSTRACT

In a ternary mixture composed of 0.7% hydroxypropylmethyl cellulose (HPMC), 0.3% sodium carboxymethyl cellulose (NaCMC), and 0.00–2.00% sodium dodecylsulfate (SDS) various interactions between components take place. The interactions depend on SDS concentration and may result in HPMC–SDS complex formation which is thermodynamically incompatible with NaCMC. Such a ternary mixture phase separates into a coacervate rich in HPMC–SDS complex and equilibrium solution rich in NaCMC. In this paper, it was shown that viscoelastic properties of the coacervate are influenced by HPMC/NaCMC/SDS interaction. Emulsions of sunflower oil in ternary HPMC/NaCMC/SDS mixtures were prepared, and deposition of coacervate (of different viscoelastic properties) at the O/W interface was investigated in order to prepare oil-containing microcapsules with a coacervate shell of different properties. Deposition and stability of the coacervate shell depend on SDS concentration in emulsion. Powder of microcapsules was obtained by spray drying, and barrier properties of microcapsules' shell were investigated by oil extraction. Amount of extracted oil correlates with viscoelastic properties of corresponding coacervate.

1. Introduction

Microencapsulation of emulsified oil droplets can be achieved by deposition of coacervate phase at the oil–water interface. Basic concept behind microencapsulation by coacervation is phase separation of one or more macromolecules in their solution and subsequent deposition of newly formed coacervate phase around the emulsified core (i.e. drop) in the same reaction medium (Gouin, 2004). Employed mechanisms of coacervation involve simple coacervation, complex coacervation, or coacervation due to thermodynamic incompatibility (Baken & Anderson, 1976; de Kruiff, Weinbreck, & de Vries, 2004; Doublier, Garnier, Renard, & Sanchez, 2000; Goddard & Ananthapadmanabhan, 1993; Lindman, 2001; Piculell & Lindman, 1992; Turgeon, Schmitt, & Sanchez, 2007). Various macromolecular systems are used for this purpose. The system that is probably most widely investigated is gelatin/gum acacia (Chang, Leung, Lin, & Hsu, 2006; Lamprecht, Schafer, & Lehr, 2000; Luzzi & Gerraughty, 1964; Palmieri, Martell, Lauri, & Wehrle, 1996; Takenaka, Kawashima, & Lin, 1979). Other systems are also used: heparin/gelatin (Tsung & Burgess, 1997), gelatin/carboxymethyl cellulose (Sovilj & Dokić, 1997), polylactids and copolymers of lactic and glycolic acid (Nihant, Grandfils, Jerome, & Teyssie, 1995), polyvinyl alcohol (Bachtsi & Kiparissides, 1996), hydroxypropylmethyl cellulose phthalate (Weib, Knoch, Laicher, Stanislaus, & Daniels, 1995), plant proteins (Ducel, Richard, Saulnier, Popineau, & Boury, 2004), polyurethane (Saihi, Vroman, Giraud, & Bourbigot, 2005). Properties of coacervate layer, i.e. shell material (physico-chemical, thickness, microstructure, etc.) are key to determine behavior of microcapsules (stability, redispersibility, diffusion kinetics, microencapsulation efficiency, etc.).

In our previous work (Katona, Sovilj, & Petrović, 2008a, 2008b; Sovilj & Petrović, 2005, 2006, 2007) we investigated in details complex interactions between hydroxypropylmethyl cellulose (HPMC), a "slightly" hydrophobic nonionic derivative of cellulose, sodium carboxymethyl cellulose (NaCMC), an anionic derivative of cellulose, and sodium dodecylsulfate (SDS), an anionic surfactant. Water soluble polymers having hydrophobic moieties associate when their concentration in the solution is above the critical overlap concentration. The association is due to intermolecular hydrophobic interaction of the moieties, which results in cross-linking and a space spanning network formation in the system. Such a system shows viscoelastic properties which can be characterized by the elastic modulus (G') and the viscous modulus (G''). Viscoelastic properties of these systems are strongly influenced by addition of a surfactant (Egermayer, Norrman, & Piculell, 2003; Piculell, Egermayer, & Sjöström, 2003). On addition of SDS to HPMC solution, when concentration of SDS is higher than the critical association concentration (CAC), a HPMC–SDS complex is formed through the hydrophobic association (Sovilj & Petrović, 2005, 2006; Winnik &

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doi:10.1016/j.carbpol.2009.09.007

Regismond, 1996). At the onset of HPMC–SDS interaction, due to attractive hydrophobic interactions, the binding of SDS to HPMC molecules supports physical cross-links between HPMC molecules, which results in an increase in G' of the binary mixture on increase in SDS concentration. On further increase in SDS concentration, G' reaches a maximum, then start to decrease, and finally vanishes (Katona et al., 2008a). Such a behavior is due to the fact that on additional increase in SDS concentration, more SDS is bound to HPMC chains which leads to gradual solubilization of hydroxypropyl and methyl groups, and an increase in negative charge of HPMC–SDS complex. Increase in the complex charge leads to electrostatic repulsion between different HPMC chains which gradually overpowers attractive hydrophobic interactions. Consequently, cross-links between HPMC molecules are being destroyed, number of elastically active chains decreases, which results in a decrease in G'. If concentration of SDS is higher than the polymer saturation point, PSP, individual HPMC molecules are fully solubilized with SDS, the network is completely broken, and the elastic modulus vanishes.

Binary mixture of HPMC and NaCMC shows viscosity synergism as a result of hydrogen bonds formation between HPMC and NaCMC macromolecules (Alvarez-Lorenco et al., 2001; Katona et al., 2008b; Zhang, 1999). There is no phase separation in the binary NaCMC–SDS mixture, while addition of SDS to NaCMC solution does not influence solution viscosity, and no interaction can be detected by conductometric measurements (unpublished results). However, addition of SDS to HPMC/NaCMC binary mixture induces phase separation when concentration of SDS in a ternary HPMC/NaCMC/SDS mixture is between CAC and PSP, i.e. when HPMC–SDS complex is formed (Katona et al., 2008a; Sovilj & Petrović, 2007). The complex behaves as an anionic polyelectrolyte which is incompatible with also anionic NaCMC, and thus segregative phase separation takes place in the ternary mixture. The ternary mixture separates in HPMC–SDS complex rich coacervate phase and NaCMC rich equilibrium solution (supernatant). If SDS concentration is >PSP, HPMC molecules are fully solubilized with SDS and the contribution of the small counterions, which for the electroneutrality reasons follow the bound surfactant molecules into the coacervate phase, to the osmotic pressure is sufficiently large so that HPMC–SDS complex becomes completely soluble even in the presence of NaCMC. Therefore, above PSP no coacervate phase is formed.

In this work, emulsions of sunflower oil in ternary HPMC/NaCMC/SDS mixture were prepared. Microencapsulation of emulsified sunflower oil droplets by deposition of coacervate of different viscoelastic properties at the O/W interface was investigated. Powder of microcapsules was obtained by spray drying and some properties of spray dried microcapsules (particle size, extraction of encapsulated oil) were investigated.

2. Experimental

2.1. Materials

HPMC, (trade name Methocel K4M CR, methoxyl content 22.7%, hydroxypropyl content 8.9%) was obtained from Colorcon Ltd., England. Viscosity average molar mass was $M_v = 91{,}500$ g/mol, determined at 20 °C. Critical overlap concentration of HPMC was $c^* = 0.1269\%$ w/w (Sovilj & Petrović, 2007). NaCMC, degree of substitution DS = 0.77, purity >96%, was obtained from "Milan Blagojević", Serbia. Viscosity average molar mass of NaCMC was $M_v = 121{,}000$ g/mol, determined at 25 °C, and critical overlap concentration $c^* = 0.1927\%$ w/w (Sovilj & Petrović, 2007). SDS, purity >99%, was obtained from Merck, Germany. Critical micelle concentration was cmc = 0.244% w/v at 20 °C, as determined by conductometric titration (Sovilj & Petrović, 2007). Sunflower oil was obtained from "Sunce", Serbia. Cyclohexane was obtained from "Kemika", Croatia. All samples were used without any further purification. Bidistilled water was used as a solvent.

2.2. Preparation of solutions

Stock solutions of 2.00% w/w HPMC and 1.00% w/w NaCMC were prepared by dispersing proper weights of HPMC and NaCMC in water at 80 °C and 20 °C, respectively, by gentle stirring. The stock solutions were left for 24 h at room temperature, prior to further use. Stock solution of 7% w/v SDS was prepared by dispersing proper weight of SDS in bidistilled water at 20 °C.

Binary mixtures of HPMC and SDS were prepared by mixing required weights HPMC and SDS stock solutions with water. The mixtures were left for 24 h at room temperature prior to further use.

Binary mixtures of HPMC/NaCMC were prepared by mixing required weights of HPMC and NaCMC stock solutions to obtain HPMC/NaCMC mass ratio of 0.7/0.3. The mixtures were left for 24 h at room temperature prior to further use. Ternary mixtures of HPMC/NaCMC/SDS were prepared by addition of appropriately diluted stock solution of SDS to 24-h old HPMC/NaCMC binary mixture. The ternary mixtures were composed of 0.7% w/w HPMC, 0.3% w/w NaCMC and desired SDS concentration (0.00–2.00% w/w).

2.3. Preparation of emulsions

22.22% w/w stock emulsions of sunflower oil in a binary HPMC/SDS mixture (continuous phase) were prepared by homogenization (Ultraturrax T-25, Janke-Kunkel, Germany) during 3 min at 4700 rpm, $T = 25$ °C. Binary mixtures were composed of 0.8% w/w HPMC (expressed on the continuous phase mass) and SDS of various concentrations. Final emulsion was obtained by careful addition (drop by drop) of 10 g of 2.4% w/w NaCMC solution into 90 g of the stock emulsion placed on a magnetic stirrer. Depending on SDS concentration, the addition of NaCMC induces coacervate formation in the continuous phase. The coacervate deposits at the surface of emulsified oil droplets, which results in formation of oil-containing microcapsules with a coacervate shell. In this way 20% w/w O/W final emulsions were obtained. Continuous phases of the final emulsions were ternary HPMC/NaCMC/SDS mixtures, composed of 0.7% w/w HPMC, 0.3% w/w NaCMC, and 0.00–2.00% w/w SDS, expressed on the continuous phase of a final emulsion. In further text term 'emulsion' refers to the final emulsion.

2.4. Creaming

Emulsions were poured in 10 ml measuring cylinders immediately after preparation, and left at room temperature to test their creaming behavior. Emulsions separate in an emulsion cream (top) and an emulsion serum (bottom) layer. Changes in a creaming index, H, were visually monitored over 70 days. The creaming index is defined as follows:

$$H = \frac{\upsilon_{\text{serum}}}{V} \times 100 \tag{1}$$

where υ_{serum} is volume of serum; V is volume of emulsion.

Relative volume of cream in an emulsion, υ, is given by the following equation:

$$\upsilon = 100 - H \tag{2}$$

In some of the prepared emulsions a sediment of coacervate at the bottom of measuring cylinder was formed. Relative volume of the coacervate sediment in an emulsion, υ_c, is given by the following equation:

$$v_c = \frac{v_{co}}{V} \times 100 \tag{3}$$

where v_{co} is volume of coacervate phase.

2.5. Rheometry

Rheological measurements were carried out by RS600 HP rheometer (ThermoElectron, Germany). Cone-plate geometry was used (d = 60 mm, $\varphi = 1^\circ$). Flow curves of following systems were obtained: supernatants of 48-h old, phase separated, ternary HPMC/NaCMC/SDS mixtures; 48-h old ternary HPMC/NaCMC/SDS mixtures (when concentration of SDS was <0.15% and >1.00%); and serums of 48-h old, creamed emulsions. The examined systems were found to be shear thinning. Obtained experimental data were fitted with the following Cross equation (Steffe, 1996):

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (K\dot{\gamma})^m} \tag{4}$$

where η is viscosity [Pa]; $\dot{\gamma}$ is shear rate [s^{-1}]; η_0 is zero-shear viscosity [Pa]; η_∞ is infinite shear viscosity [Pa]; K is constant with the dimensions of time; m is a dimensionless constant. Zero-shear viscosities, η_0, of investigated systems were determined by fitting experimental data with the equation. Fit quality was evaluated by the coefficient of correlation, which was always better than 0.995.

Viscoelastic properties of coacervate phase separated from ternary HPMC/NaCMC/SDS mixture were determined by oscillatory measurements. The amplitude sweep method was used (Steffe, 1996). The oscillating frequency was 1 Hz. Plateau values of elastic, G' [Pa], and viscous modulus, G'' [Pa], were determined from the linear viscoelastic region. Relative contribution of viscous to elastic component of the investigated systems was evaluated by means of the tan δ value, Eq. (5):

$$\tan\delta = \frac{G''}{G'} \tag{5}$$

2.6. Powder of microcapsules

Emulsions were spray dried 24 h after preparation by Mini Spray Dryer "Buchi 190", Switzerland, in order to obtain microcapsules in a powder form. Inlet and outlet temperature was 170 °C and 110 °C, respectively. Scanning electron microscopy of spray dried microcapsules was performed by JSM-6460, JEOL, Japan.

Cyclohexane was used to extract sunflower oil from powder of microcapsules. Apart from sunflower oil, neither of microcapsule's components is soluble in cyclohexane. Extraction of sunflower oil was achieved by dispersing 1 g of microcapsules in 100 ml of cyclohexane, which was then left for 40 min on a magnetic stirrer to ensure complete extraction. Kinetics of extraction was checked. It was found that no change in sunflower oil concentration in the cyclohexane extract takes place after 15 min from the onset of extraction. Dispersion of microcapsules in the cyclohexane extract was filtered (Sartorius SM11358, pore size 0.1 μm), and concentration of sunflower oil in the cyclohexane extract was determined by a spectrophotometric measurement (Hewlett Packard 8452A Diode Array, USA) of absorbance at 234 nm. Relative mass of extracted sunflower oil, m_r, was calculated as

$$m_r = \frac{m_o}{m_m} \tag{6}$$

where m_o is mass of extracted oil, m_m is mass of oil-containing microcapsules.

2.7. Dispersion properties

Droplet size and droplet size distribution of emulsions and suspension of microcapsules in water was determined by microphotography. Optical microscope ("Carl Zeiss", Jena, Germany) was used. Software package Q-win was employed to process the images and to determine droplet size. Volume to surface mean diameter, d_{32}, and standard deviation, σ, were determined:

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{7}$$

$$\sigma = \sqrt{\frac{\sum n_i (d_i - d_{32})^2}{\sum n_i}} \tag{8}$$

where d_i is droplet diameter; n_i is number of droplets.

3. Results and discussion

3.1. Viscoelastic properties of coacervate formed in ternary HPMC/NaCMC/SDS mixture

Ternary mixture composed of 0.7% HPMC, 0.3% NaCMC and various SDS concentrations phase separates in coacervate and a supernatant when SDS concentration is between 0.15% and 1.00%. Phase separation takes place when SDS concentration is higher than CAC, i.e. when HPMC–SDS complex is formed which is thermodynamically incompatible with NaCMC (Katona et al., 2008a; Sovilj & Petrović, 2007). The coacervate is rich in HPMC–SDS complex, and supernatant is rich in NaCMC. Viscoelastic properties of coacervate are influenced by SDS concentration in the ternary mixture (Fig. 1). On increasing SDS concentration tan δ firstly decreases, indicating more solid-like behavior of coacervate. This is due to the fact that the more SDS in the mixture, the more SDS molecules are bound via hydrophobic association to HPMC molecules, which supports intermolecular cross-links between HPMC macromolecules in the coacervate phase. At 0.25% SDS tan δ reaches minimum value. At this concentration of SDS tan δ is smaller than 1, and the elastic properties dominate the viscous ones. The coacervate phase is compact and HPMC–SDS complex forms a firm network throughout the separated phase. Further increase in SDS concentration

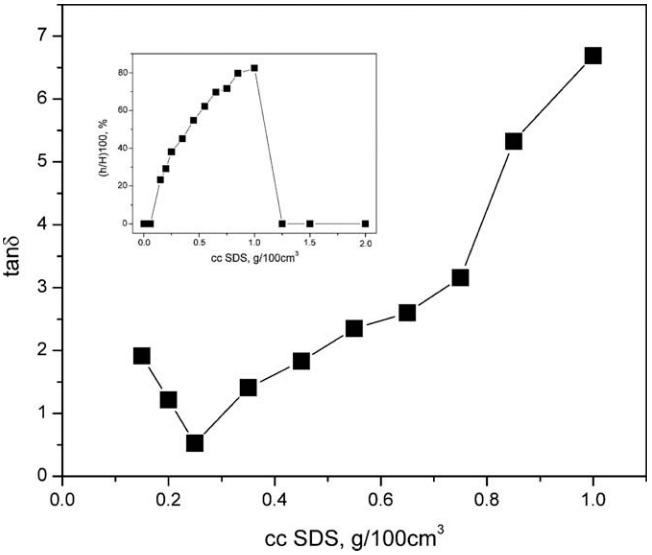

Fig. 1. Influence of SDS concentration in the ternary HPMC/NaCMC/SDS mixture on viscoelastic properties of coacervate. Relative volume of coacervate in the ternary mixture as a function of SDS concentration is given as the insert.

brings about the increase in tan δ values. Namely, at higher SDS concentrations more SDS is bound to HPMC chains, leading to an increase in the osmotic pressure of the coacervate phase, due to the counterions that follow the bound surfactant molecules, which result in osmotic swelling and consequently increases relative volume of coacervate phase, insert in Fig. 1 (Sjöström & Piculell, 2001; Sovilj & Petrović, 2007). This, combined with an electrostatic repulsion between increasingly charged HPMC–SDS complexes, results in progressive loss of physical cross-links between HPMC molecules and a decrease in number of elastically active chains. Finally, at 1.25% SDS no phase separation is observed. When SDS concentration is higher than PSP, individual HPMC molecules are fully solubilized with SDS and the osmotic pressure is sufficiently large so that the HPMC–SDS complex becomes completely soluble in the ternary mixture (Katona et al., 2008a; Sovilj & Petrović, 2007).

3.2. Properties of emulsions stabilized with coacervate

Twenty percent emulsions of sunflower oil in ternary HPMC/NaCMC/SDS mixtures were prepared. Composition of the emulsions was such that formation of coacervate of different viscoelastic properties is expected to take place in continuous phases of emulsions. Deposition of coacervate at the surface of oil droplets and stability of deposited coacervate was investigated.

3.2.1. Rheological investigation

Prepared emulsions separate in emulsion cream (top) and emulsion serum (bottom) as a result of sedimentational instability. Zero-shear viscosities of emulsion serums (48 h after emulsion preparation) and supernatants of corresponding ternary HPMC/NaCMC/SDS mixtures (48 h after the ternary mixture preparation) were determined and compared (Fig. 2). The three regions shown in Fig. 2, i.e. pre-coacervation (no formation of coacervate), coacervation (coacervate is formed) and post-coacervation region (no formation of coacervate), refer to the ternary HPMC/NaCMC/SDS mixture. Viscosity of emulsion serums is influenced by composition and governing interactions between components of the serum, where various HPMC–NaCMC–SDS interactions are known to significantly affect viscosity of a solution (Katona et al., 2008a, 2008b; Sovilj & Petrović, 2007). Viscosities of emulsion serums and supernatants of corresponding ternary mixtures in the coacervation region overlap (Fig. 2). This indicates similar composition and thus alike governing interactions among components in the two examined systems. It indirectly shows that coacervate phase is formed in the emulsions, and that it is adsorbed at surface of creamed droplets. The only exception in the coacervation region is emulsion where concentration of SDS is 1.00%. Here, viscosity of emulsion serum is substantially higher than viscosity of the ternary mixture supernatant, suggesting that all or some of the coacervate remains unadsorbed, which increases viscosity of the emulsion serum. The increased viscosity of emulsion serums is observed up to 1.50% of SDS (post-coacervation region), indicating presence of unadsorbed coacervate. It should be noted that there is no formation of coacervate in the ternary mixtures when SDS concentration is >1.00% (Fig 1), since HPMC–SDS complex becomes solubilized at such a high concentration (Katona et al., 2008a; Sovilj & Petrović, 2007). This suggests that solubilization of HPMC–SDS complex in emulsions takes place at higher nominal SDS concentrations than it is the case in the ternary HPMC/NaCMC/SDS mixtures, which is attributed to the fact that during the stock emulsion preparation some portion of free SDS molecules adsorbs to the oil/water interface and stabilize dispersed oil droplets. Consequently, concentration of SDS in continuous phase of emulsions is lower than the nominal one. When concentration of SDS is 2.00% viscosities of the serum and the supernatant are again the same (Fig. 2), which is due to the fact that at sufficiently high SDS concentrations full solubilization of HPMC–SDS complex takes place. When full solubilization of the complex occurs viscosity of the ternary HPMC/NaCMC/SDS mixtures is only slightly changed on change in SDS concentration (Sovilj & Petrović, 2007). Therefore, even if there is some difference in SDS concentration in the continuous phase of emulsion and the corresponding ternary mixture, once the HPMC–SDS complex becomes fully soluble in continuous phases of emulsions, viscosities of emulsion serums and corresponding ternary mixture supernatants becomes again approximately the same. On the other hand, in the pre-coacervation region (Fig. 2), viscosity of emulsion serum is lower than viscosity of the ternary mixture, due to the fact that in this region there is no HPMC–SDS complex formation, no coacervation, and emulsified oil droplets are stabilized mostly with adsorbed, surface active HPMC macromolecules (Kulicke, Arendt, & Berger, 1998). The adsorption decreases concentration of HPMC macromolecules in continuous phase of emulsion which results in decreased viscosity of emulsion serum. In the like manner, binding of NaCMC to the adsorbed HPMC via hydrogen links (Alvarez-Lorenco et al., 2001) might decrease NaCMC concentration in the continuous phase, and result in additional decrease in viscosity.

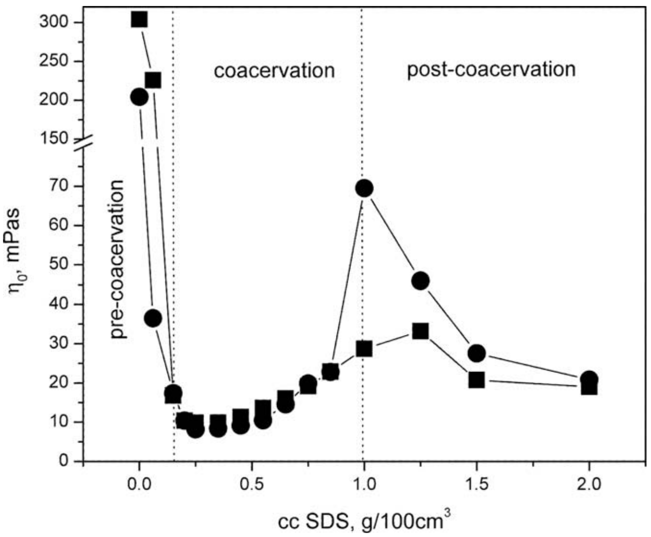

Fig. 2. Comparison of viscosities of emulsion serums (●) and corresponding ternary HPMC/NaCMC/SDS mixtures supernatants (■), 48 h after preparation.

3.2.2. Creaming investigation

Photograph of 14-day-old emulsions stored in graduated cylinders is shown in Fig. 3a. Apart from the cream layer (top) and the emulsion serum (bottom) in none of 14-day-old emulsions a sediment of coacervate was visible at the bottom of graduated cylinders. This indicates that coacervate is adsorbed at the surface of the creamed oil droplets.

Influence of SDS concentration on relative volume of the cream in emulsion, v, 48 h and 70 days after emulsion preparation is shown in Fig. 3b. For both of the two curves v firstly increases with the increase in SDS concentration, then reaches maximum value, and finally decreases. Maximum in v occurs at 1.00% and 0.55% of SDS for the 48 h and the 70 days curve, respectively. The increase in v is attributed to increased volume of the adsorbed coacervate phase at creamed oil droplets, where insert in Fig. 1 shows that coacervate volume in the ternary HPMC/NaCMC/SDS mixture (of the same composition as is continuous phase of the creamed emulsion) increases with an increase in SDS concentration with a

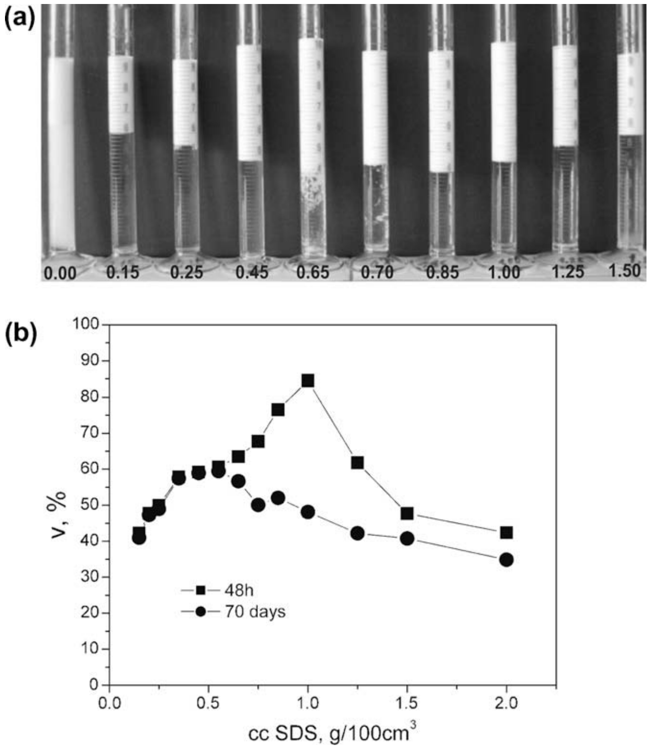

Fig. 3. (a) Photograph of 14-day-old emulsions stored in graduated cylinders. The numbers indicate concentrations of SDS in emulsions. (b) Influence of SDS concentration on relative volume of cream in emulsions 48 h and 70 days after emulsions preparation.

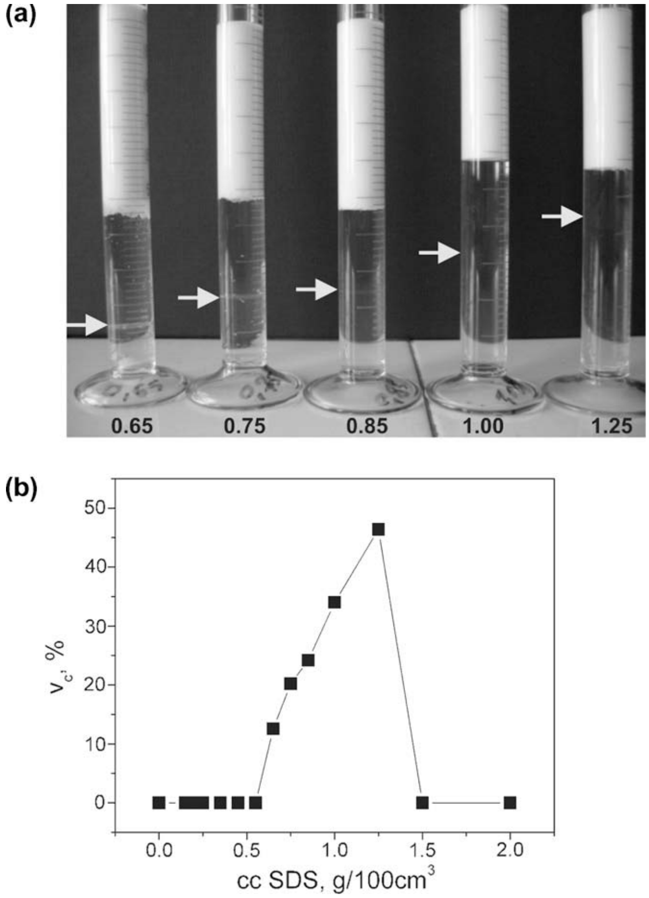

Fig. 4. (a) 50-day-old emulsions (0.65–1.25% SDS) stored in graduated cylinders. Apart from the cream layers and the serums, coacervate phase at the bottom of the cylinders can be noticed. The numbers indicate concentrations of SDS in emulsions. (b) Relative volume of unadsorbed coacervate phase, v_c, in 50-day-old emulsions as a function of SDS concentration.

maximum at 1.00% SDS. This is supported by rheological measurements shown in Fig. 2, which indicates that during first 48 h after emulsion preparation coacervate phase remains adsorbed at oil drops in the cream layer of all emulsions where SDS concentration is between 0.15% and 0.85%. In emulsion with 1% SDS, rheological measurements show increased viscosity of the emulsion serum, which indicates presence of unadsorbed coacervate in the serum (Fig. 2). Therefore, large relative volume of the cream in 48-h old emulsion with 1% SDS is attributed to slow creaming rate, which results from increased viscosity of emulsion serum and small droplet size (Fig. 7). However, performed experiments does not exclude that some portion of coacervate remains adsorbed at the surface of oil droplets in 48-h old emulsion with 1% SDS, which can also contribute to large relative volume of the cream.

In emulsions with SDS concentration up to the 0.55% relative volumes of cream determined after 48 h and 70 days overlap (Fig. 3b), showing that there are no further structural and compositional rearrangements in the cream layers already 48 h after preparation of the emulsions. On the other hand, for emulsions where SDS concentration is >0.55% a considerable difference in v of the 48 h and the 70-day-old emulsions is observed. For this concentration range the v of 70-day-old emulsions is significantly decreased when compared to the 48-h old emulsions. The decrease is due to sedimentation of desorbed coacervate from oil droplets. Sediment of coacervate phase at the bottom of measuring cylinders is observed in sufficiently old emulsions with 0.65–1.25% of SDS (Fig. 4a). Coacervate sediment is transparent and the phase boundary is indicated only by a tiny, turbid region (denoted by the arrows in Fig. 4a). The size of the turbid region decreases on increasing SDS concentration, and the sediment is more and more difficult to observe by naked eye. Relative volume of unadsorbed coacervate phase in 50-day-old emulsions, v_c, as a function of SDS concentration is shown in Fig. 4b. The increase in v_c with an increase in SDS concentration is observed. The small decrease in relative volume of emulsion cream in 70-day-old emulsions where SDS concentration is >1.25% (where no coacervate is formed) (Fig. 3b) is attributed to slow, cream layer compaction process during which structure of the cream equilibrates. The initial volume fraction of droplets in the cream layer is lower than the maximum, the closed-packed case, and it undergoes further compaction with time until it becomes a uniform layer at the maximum volume fraction (Becher, 2002; Friberg, Larsson, & Sjöblom, 2004; Robins, 2000).

It should also be noted that coacervate sediment is observed in 1.25% SDS emulsion (Fig. 4a) though at such a high SDS concentration in corresponding ternary HPMC/NaCMC/SDS mixture HPMC molecules are completely solubilized with SDS and no coacervation takes place. This suggests, in agreement with rheological measurements shown in Fig. 2, that solubilization of HPMC–SDS complex in continuous phase of emulsions takes place at somewhat higher nominal SDS concentrations when compared to the ternary HPMC/NaCMC/SDS mixture.

Investigation on kinetics of creaming was carried out in order to determine time during which coacervate remains adsorbed at the surface of emulsified droplets. Dependence of the creaming index, H, on the creaming time of emulsions having different concentrations of SDS (0.15%, 0.65%, 0.75%, and 2.00%) is shown in Fig. 5a. The obtained dependence for 0.15% and 2.00% SDS emulsions is typical for fully flocculated emulsions. In fully flocculated emulsions, creaming does not start immediately after pouring an emul-

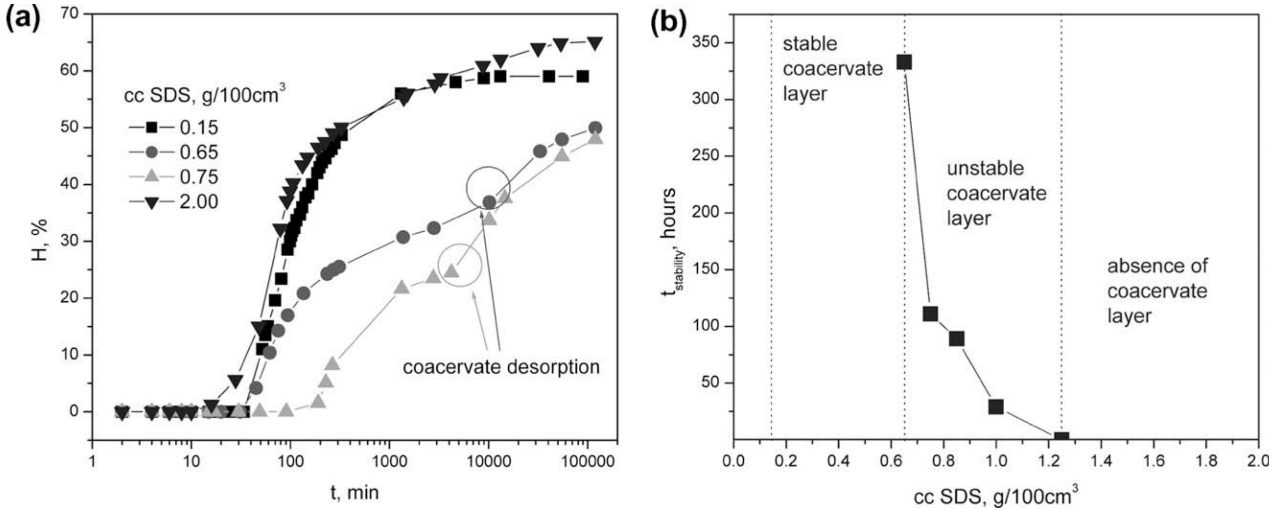

Fig. 5. (a) Characteristic curves of creaming kinetics. Concentration of SDS is 0.15%, 0.65%, 0.75%, and 2.00%. (b) Influence of SDS concentration on stability of adsorbed coacervate layer at emulsified oil droplets.

sion in a measuring cylinder, but only after certain delay time, during which the creaming index is zero (Manoj, Fillery-Travis, Watson, Hibberd, & Robins, 1998; Robins, 2000). Flocculation was observed (by microscopy) in all emulsions apart from 0.00% and 0.06% of SDS (not shown). Once the creaming is established, the creaming index start to increase in time at approximately constant rate (Fig. 5a). When most of the drops reach the top of the container, an emulsion cream is formed which undergoes slow compaction process (Becher, 2002; Robins, 2000). During the compaction process change in *H* with time is only slight, and ultimately *H* reaches certain constant value. Such a creaming behavior is observed for all investigated emulsions where SDS concentration was <0.65% and >1.00% and is illustrated in Fig. 5a by the 0.15% and 2.00% creaming curves.

In emulsions where SDS concentration was between 0.65% and 1.00%, an 'instability region' in the creaming curves is observed. The instability is characterized by a sudden and unexpected increase in creaming index in the compaction region, circled in Fig. 5a. For the same set of emulsions where the instability is detected a sediment of coacervate at the bottom of the measuring cylinders is observed some time after the instability took place (Fig. 4a). Onset of the instability region indicates beginning of coacervate desorption, and is used to determine stability of the adsorbed coacervate layer, i.e. the time during which the coacervate is adsorbed at the droplets surface (Fig. 5b). Three distinct regions can be observed with respect to stability of the adsorbed coacervate layer formed around the droplets (Fig. 5b). These are region of stable coacervate layer (coacervate is adsorbed at the droplets surface during the course of the experiment), region of unstable coacervate layer (desorption of coacervate takes place after certain period), and region where the coacervate layer is absent (there is no adsorption/formation of coacervate at all). Stability of adsorbed coacervate layer is governed by HPMC–SDS complex properties. On increasing SDS concentration more SDS is bound to HPMC chains, which increases solubility of the complex in the ternary HPMC/NaCMC/SDS mixture. Therefore, adsorption of coacervate (i.e. HPMC–SDS complex) is more difficult when SDS concentration in emulsions is increased. For largest concentrations of SDS, coacervate is either sufficiently soluble in the continuous phase so that it is unable to adsorb at droplets surface, or there is no formation of coacervate at all due to full solubilization of HPMC–SDS complex.

3.3. Properties of spray dried microcapsules

The investigated emulsions were spray dried in order to obtain free-flowing powder of oil-containing microcapsules. SEM image of microcapsules obtained from emulsion with 0.35% SDS is shown in Fig. 6. The image represents typical visual appearance of spray dried microcapsules. No difference in visual appearance of microcapsules obtained from emulsions having different concentration of SDS was observed by scanning electron microscopy.

Dispersion properties of suspension of microcapsules in water and of corresponding emulsions are compared (Fig. 7). At low SDS concentrations mean diameter of microcapsules and emulsified droplets overlap. At higher concentrations of SDS, d_{32} of microcapsules becomes larger than of emulsified droplets. The largest difference is observed for smallest emulsion droplets. We attribute the difference in droplet diameter to the fact that during the spray draying process small microcapsules are carried by the air current out of the cyclone and does not reach the collecting vessel.

Fig. 8 shows influence of SDS concentration in emulsion on the relative mass of extracted oil from spray dried microcapsules. Relative mass of extracted oil changes with SDS concentration, indi-

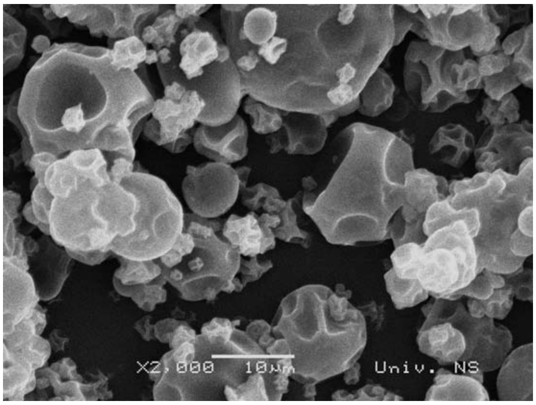

Fig. 6. SEM image of powder of microcapsules obtained by spray drying of 0.35% emulsion.

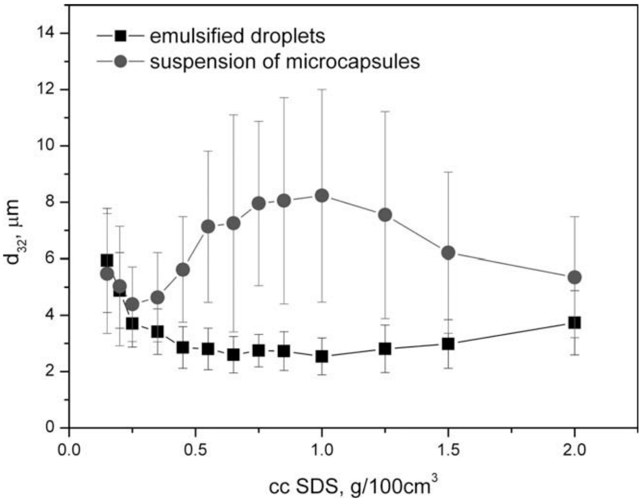

Fig. 7. Comparison of dispersion properties of microcapsules suspension and corresponding emulsions. The bars indicate standard deviations.

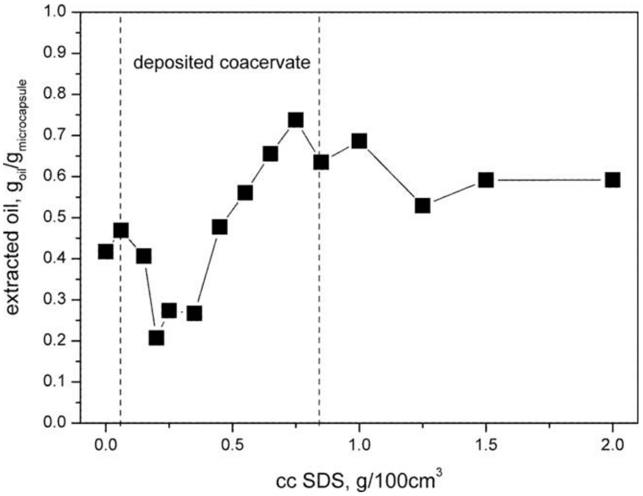

Fig. 8. Influence of SDS concentration on the relative mass of extracted oil from powder of microcapsules.

cating that shell properties of microcapsules are influenced by SDS concentration. It can be seen that the minimum in relative mass of extracted oil occurs at 0.20–0.35% SDS, implying the most compact structure of the shell. Further increase/decrease in SDS concentration in the 'deposited coacervate' region brings about increase in relative mass of extracted oil, which suggests less compact shell. We compare such an behavior of spray dried microcapsules, obtained from emulsified oil droplets stabilized with coacervate layer, with viscoelastic properties of coacervate present in a corresponding ternary HPMC/NaCMC/SDS mixture (of the same composition as is the composition of continuous phases of the investigated emulsions) (Fig. 1). It is to be expected that viscoelastic properties of coacervate deposited at the droplets surface change with SDS concentration in emulsion in a similar manner as the properties of coacervate in corresponding ternary HPMC/NaCMC/SDS mixture. In the ternary mixture tan δ of the coacervate is at minimum when SDS concentration is 0.25%, indicating most solid-like structure of the coacervate. On decreasing or increasing SDS concentration the coacervate becomes less compact, as was evidenced by increase in tan δ (Fig. 1). It is thus found that viscoelastic properties of coacervate correlates with the relative mass of extracted oil from spray dried microcapsules.

4. Conclusion

Interactions between HPMC–SDS complex and NaCMC in a ternary mixture composed of 0.7% HPMC, 0.3% NaCMC, and 0.00–2.00% SDS result in segregative phase separation and coacervate formation when SDS concentration is 0.15–1.00%. Viscoelastic properties of the coacervate depend on SDS concentration, and are governed by complex HPMC/NaCMC/SDS interactions. Coacervate with the most compact structure (i.e. with smallest tan δ) is obtained in the ternary mixture with 0.25% SDS.

Microencapsulation of sunflower oil was achieved by deposition of coacervate of different properties at O/W interface in emulsions. Deposition and stability of coacervate shell depend on HPMC/NaCMC/SDS interactions in the continuous phase. Coacervate shell was found to be most stable in 0.15–0.55% SDS emulsions, where coacervate is least solvated and where its structure is most compact. On increasing SDS concentration coacervate becomes less compact, more solvated, and it's adsorption to the O/W interface becomes more difficult. In emulsions with 0.65–1.00% SDS the coacervate shell is unstable and coacervate desorbs from surface of droplets with time, while if concentration of SDS is >1.00% there is no formation of coacervate shell around the oil droplets.

Emulsions were spray dried and powder of microcapsules was obtained. Relative mass of extracted oil from powder of microcapsules depends on SDS concentration, and correlates with viscoelastic properties of corresponding ternary HPMC/NaCMC/SDS mixture coacervate. Minimum in the amount of extracted oil was obtained for microcapsules with coacervate of most compact structure.

It was shown that investigation on rheological properties of coacervate formed in ternary HPMC/NaCMC/SDS mixture can be employed to predict structure of the adsorption layer around the dispersed oil droplets, which can be used for regulation of microcapsules shell's barrier properties.

Acknowledgements

This work was supported by Ministry of Science of the Republic of Serbia (Grant No. 20022). The authors are thankful to Colorcon Ltd. (England) for their generous gift of the HPMC sample.

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