Preparation of microcapsules containing different contents of different kinds of oils by a segregative coacervation method and their characterization

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Abstract: Microencapsulation of different oils was performed using a segregative coacervation method. In order to microencapsulate, 20 % oil-in-water (O/W) emulsions were prepared in a continuous phase consisting of a 1 % mixture of hydroxypropylmethylcellulose (HPMC)/sodium carboxymethylcellulose (NaCMC) mass ratio (0.7/0.3) and various concentrations (0, 0.35 and 1 %) of the anionic surfactant sodium dodecylsulfate (SDS). Various interactions between the components occur in the continuous phase of emulsions, which influence the structure and properties of the adsorption layer around the oil droplets. The formed HPMC/SDS complexes in the presence of NaCMC molecules undergo segregative phase separation and form a coacervate which adsorbs onto the oil droplets, forming the wall of the microcapsules. Sunflower oil, pumpkin seed oil and a mixture of sunflower and linseed oil were used as the core material. Microcapsules in the solid form were obtained by spray drying the emulsions. The stability of the emulsions, the particle size and particle size distribution of the emulsions and suspensions of microcapsules and the oil content of the microcapsules were determined. The influence of the oil kind on the properties of the microcapsules was also investigated. It was found that at 0.35 % SDS, a coacervate layer around the oil droplets forms a stabile, compact microcapsules wall, which prevents oil extraction. The kind of oil influences the properties of the emulsions and microcapsules, which is important in the selection of oils for microencapsulation by this method.

Keywords: microencapsulation; coacervation; segregation; emulsions; oil content.

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INTRODUCTION

Microencapsulation is an effective method to wrap a liquid and/or a solid material by polymers and has extensive potential applications in the fields of food, pharmaceutics, cosmetics, pesticides, biotechnology, catalysis and many other areas.[1] Recently, microencapsulation techniques were adopted for the production of polymer-coated nanoparticles for electronic paper application[2] or for the production of electrorheological fluids.[3] The reason for microencapsulation of food ingredients is to protect sensitive food components, improve the stability of reactive or volatile additives (such as vitamins, flavors, *etc*.), mask unpleasant taste and flavor of certain ingredients, incorporate time-release mechanisms into the formulation or simply convert liquids to solid.[4,5] In recent years, the controlled release concept of encapsulated ingredients at the right time and in the right place has increased more and more.[6] Microencapsulated medical plant extracts can be used as supplements in functional food. Such microcapsules can improve the effectiveness of food designed for a health diet and for a food targeted to certain risk groups.

Among different techniques for microencapsulation of functional food ingredients, coacervation (phase separation) is the most common one applied in the food industry.[7] The term coacervation was suggested for the first time by Bungenberg de Jong[8] to explain the phenomenon of phase separation in a macromolecular system in which two phases are formed. Simple coacervation refers to phase separation brought about by reducing the solubility of a polymer by changing the temperature, adding non-solvents or "salting-out" by electrolytes, while complex coacervation or "associative" phase separation involves the addition of another oppositely charged macromolecule.[1,9,10] As a consequence, the system demixes into two phases: a solvent-rich phase containing a very small amount of polymer and a polymer-rich phase – coacervate. "Segregative" phase separation occurs due to the thermodynamic incompatibility of two polymers, which results in system demixing into two phases, each phase rich with one of the two polymers.[11]

In microencapsulation processes by a coacervation method, the material to be encapsulated is emulsified or dispersed in a solution of a polymer, and by changing the temperature, pH value or adding another polymer or non-solvent, coacervation can be induced, where the coacervate deposits at the surfaces of the dispersed particles and forms a thin coating. After further treatment, in order to solidify the polymeric wall, microcapsules can be obtained and separated from the system.[5,12,13] The coacervation method of microencapsulation was recently adopted for coating nanoparticles for electronic paper application. The most commonly used wall materials in microencapsulation by coacervation processes are proteins, gums, carbohydrates and various synthetic polymers.[5,7]

In recent years, hydroxypropylmethylcellulose (HPMC), a water soluble, non-ionic cellulose derivative, has been widely used in food products.[14] The presence of hydroxypropyl and methyl groups renders the cellulose molecules hydrophobic and makes them surface active.[15] The hydroxypropyl and methyl groups represent potential sites for adsorption of low molar mass surfactants, such as sodium dodecylsulfate (SDS), which results in the formation of a polymer–surfactant complex. This is of practical interest in dispersed systems, since such interactions affect the structure of the adsorption layer around oil droplets. It was shown in a previous investigation[16] that HPMC–SDS interactions affect the emulsion stability and adsorption layer formation. Since, the HPMC/SDS complex bears a net negative charge and behaves like a polyelectrolyte, the addition of an oppositely charged polyelectrolyte, such as sodium carboxymethylcellulose (NaCMC), causes electrostatic repulsion and "segregative" phase separation.[17] The system separates into an HPMC/SDS complex-rich phase, *i.e.*, coacervate and a NaCMC-rich phase, *i.e.*, supernatant.[18] This is a method of coacervate formation by thermodynamic incompatibility where one polyelectrolyte is actually a polymer–surfactant complex, formed through the interaction. If coacervation occurs in the continuous phase of an emulsion, it results in the adsorption of the coacervate around oil droplets and microcapsules wall formation.

The aim of the present work was to investigate the influence of coacervate formation in the continuous phase of emulsions in the system HPMC/SDS/ /NaCMC on wall formation around oil droplets, *i.e.*, microencapsulation, as well as on the properties of the microcapsules. In addition, the influence of the kind of oil on the properties of the microcapsules was investigated. Different properties of emulsions and microcapsules, such as stability, particle size and particle size distribution, redispersibility in water and encapsulation efficiency, were determined.

EXPERIMENTAL

Materials

Hydroxypropylmethylcellulose (HPMC), (trade name Methocel K4M CR, methoxyl content: 22.7 %, hydroxypropyl content: 8.9 %), pharmaceutical grade, was obtained from Colorcon Ltd., England. The viscosity average molecular mass was M_v = 91500 g/mol, determined at 20 °C, and the critical overlap concentration c^* = 0.127 %. Sodium carboxymethylcellulose (NaCMC), DS = 0.77, purity >96 %, was obtained from "Milan Blagojević" Lučani, Serbia. The viscosity average molecular mass was M_v = 116000 g/mol, determined at 25 °C, and the critical overlap concentration c^* = 0.187 %. Sodium dodecylsulfate (SDS), purity > 99 %, was obtained from Merck, Germany. As core materials, sunflower oil ("Sunce", Sombor, Serbia), pumpkin seed oil ("Banat", Nova Crnja, Serbia) and a mixture of cold pressed linseed/sunflower oil (mass ratio 0.2:0.8) were used. Cyclohexane was obtained from "Kemika", Zagreb, Croatia.

Preparation of the solutions

Stock solutions of HPMC and NaCMC were prepared at concentrations of 2.56 % (w/w) and 2.4 % (w/w), respectively, by dispersing the required amount of HPMC and NaCMC in bidistilled water at 80 °C (above the gel point of HPMC, which is approximately 70 °C) and 20 °C, respectively, by gentle stirring. The stock solutions were left for 24 h at room temperature before further use. A stock solution of SDS was prepared at a concentration of 7 % (w/v). Bidistilled water was used as the solvent.

Preparation of the emulsions

Stock emulsions of different oils 22.22 % (w/w) in a binary mixture HPMC/SDS (continuous phase) were prepared by homogenization using an Ultraturrax T-25 (Janke & Kunkel, Germany) at 4700 rpm for 3 min. The emulsification temperature was 25 °C. Binary mixtures were composed of 0.8 % w/w HPMC (based on the mass of the continuous phase) and various concentrations of SDS. The final emulsion was prepared by careful addition (drop by drop) of 10 g of a 2.4 % w/w NaCMC solution into 90 g of the stock emulsion stirred on a magnetic stirrer. In this way, 20 % w/w oil-in-water (O/W) final emulsions with continuous phases composed of a 1 % mixture HPMC/NaCMC (mass ratio 0.7:0.3) and SDS (0, 0.35 and 1 % SDS) were obtained.

Stability test

For the stability test, the emulsions were transferred into graduated cylinders and stored at room temperatures for 60 days. During storage, the emulsions separated into a cream layer at the top, and a transparent serum layer at the bottom of the cylinder. The total height of the emulsion, H_E, and the height of the serum layer, H_S, were measured during time. The extent of creaming was characterized by the creaming index, H, given by:[19]

$$H = 100\frac{H_S}{H_E} \tag{1}$$

The higher creaming index, H, the worse is the emulsion stability.

Spray drying of the emulsions

The emulsions were spray dried in a Mini Spray Dryer (Büchi 190, Switzerland), whereby microcapsules in the form of a powder were obtained. The drying parameters during the process, such as air flow, aspiration and feeding were controlled to keep 150 °C inlet and 100 °C outlet temperature.

Determination of the particle size and particle size distribution

Particle size and particle size distribution of the emulsions and suspensions of microcapsules in water were determined by the microscopic image analysis technique, using "QWin" software (Leica).[20] The volume–surface mean diameter, d_{vs} / μm, and standard deviation, σ / / μm, were calculated.

Encapsulation efficiency

The encapsulation efficiency was determined by extraction of the encapsulated oil with cyclohexane. Microcapsules (1 g) were dispersed in 100 ml of cyclohexane and left for 40 min on a magnetic stirrer. The samples were then filtered and the amount of released oil was determined spectrophotometrically, at 234 nm for the sunflower oil and the mixture of linseed/sunflower oil, and at 274 nm for the pumpkin seed oil, using a Hewlett Packard 8452A Diode Array spectrophotometer.

RESULTS AND DISCUSSION

Deposition of coacervate at the surface of the oil droplets in the emulsions

Since the emulsions were prepared by dispersing the oils in continuous phases consisting of HPMC molecules or HPMC–SDS mixtures, to which NaCMC molecules were subsequently added, various interactions occurred in the continuous phase of the emulsions, *i.e.*, HPMC–NaCMC, HPMC–SDS, and HPMC–SDS––NaCMC, which could affect the properties of the emulsions and the obtained microcapsules.

The interactions between HPMC and SDS molecules were previously investigated by various methods: conductometry, viscometry and rheology.[16,18,21,22] It was shown that binding of the SDS molecules onto the HPMC molecules starts with a hydrophobic interaction mechanism when the surfactant concentration reaches the critical aggregation concentration (*CAC*). The interaction causes an increase in viscosity and after reaching the maximum, when a three-dimensional network with a negative net charge had been created, the viscosity decreases with increasing SDS concentration until the end of interaction, *i.e.*, at an SDS concentration called the polymer saturation point (*PSP*). After *PSP*, the viscosity remains constant and is lower than the viscosity of the pure HPMC solution.[16,21]

The addition of the anionic polymer NaCMC to an emulsion having HPMC//SDS complexes in the continuous phase results in electrostatic repulsion between the same charged groups of the NaCMC molecules and HPMC/SDS complexes, which leads to phase separation and coacervate formation. The formed coacervate deposits around the oil droplets. A schematic diagram of the procedure for emulsion preparation with a coacervate layer around the oil droplet, *i.e.*, microcapsule formation, is presented in Fig. 1.

The results of previous investigations[15,16] showed that, depending on the mass ratio of the components in the HPMC/SDS/NaCMC system, complexes with different structures were obtained, which influence the properties of the adsorption layer around the oil droplets and, hence, microcapsules with different wall properties could be expected.

In the present study, a 1 % solution of HPMC/NaCMC mass ratio 0.7:0.3 was chosen, which gives a coacervate having the largest volume in the presence of SDS.[17,18] The concentrations of SDS were 0, 0.35 and 1 %, which cover different regions of HPMC–SDS interaction. With 0 % SDS in the continuous phase of emulsion, only the complex HPMC/NaCMC is present and there is no coacervate formation. With 0.35 % SDS, the HPMC/SDS complex in the continuous phase forms the most entangled negatively charged network, and after addition of NaCMC molecules, the polymer–polymer incompatibility results and the continuous phase separates into an HPMC/SDS complex-rich phase, the coacervate, and a NaCMC-rich phase, the supernatant.[18] The formed coacervate adsorbs at the oil droplets surface forming a compact polymer layer. With 1 % SDS, the in-

teraction between HPMC and the SDS molecules is completed, the intermolecular network breaks down, the HPMC/SDS complex is solubilized with SDS and the formed coacervate layer is not compact.
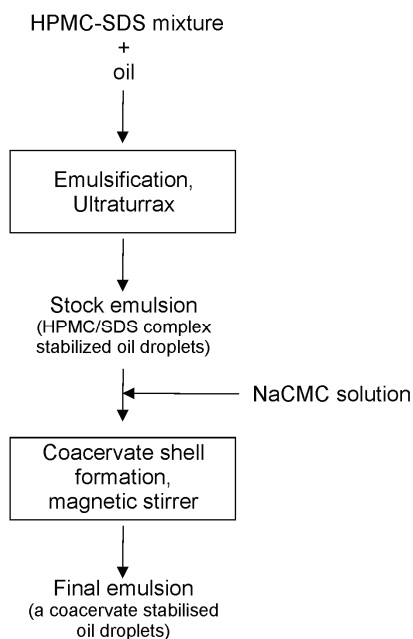

Fig. 1. Scheme of the preparation of coacervate stabilized emulsions.

Photographs of 20 % emulsions prepared with different kinds of oil at the chosen SDS concentrations after 24-h storage are shown in Fig. 2.
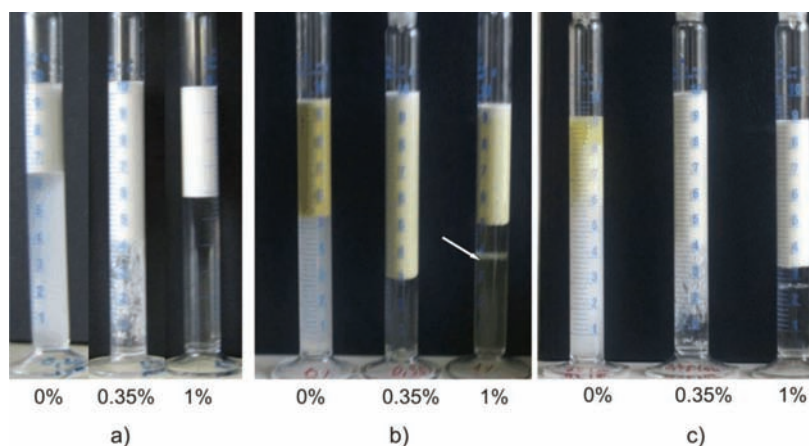

Fig. 2. Photographs of 20 % emulsions of a) sunflower oil, b) pumpkin seed oil and c) a mixture of linseed/sunflower oil (0.2/0.8) in a 1 % solution of HPMC/NaCMC (0.7/0.3) at the investigated SDS concentrations after 24 hours of storage.

It can be seen that in all emulsions, the highest volume of the cream layer was obtained at an SDS concentration of 0.35 %, *i.e.*, at the maximum coacervation. At this SDS concentration, the formed HPMC/SDS complex separated from the continuous phase after addition of NaCMC molecules and deposited around the oil droplets as a compact coacervate layer. Therefore, cream layers were formed immediately after preparation of the emulsions and the creaming index did not change with time, Fig. 3, except for the emulsion of the pumpkin seed oil. At the bottom of the cylinders, Fig. 2, there is no evidence of any coacervate sediment, indicating that all of the formed coacervate was adsorbed around the oil droplets, which contributes to the cream height, and thus the emulsions have the lowest creaming index, *H*, Fig. 3. The serum layers of the emulsions are clear, while in the emulsions of sunflower oil and mixture of linseed/ /sunflower oil some of the rest cream remains stuck to the wall at the lower part of the cylinders, Fig. 2.
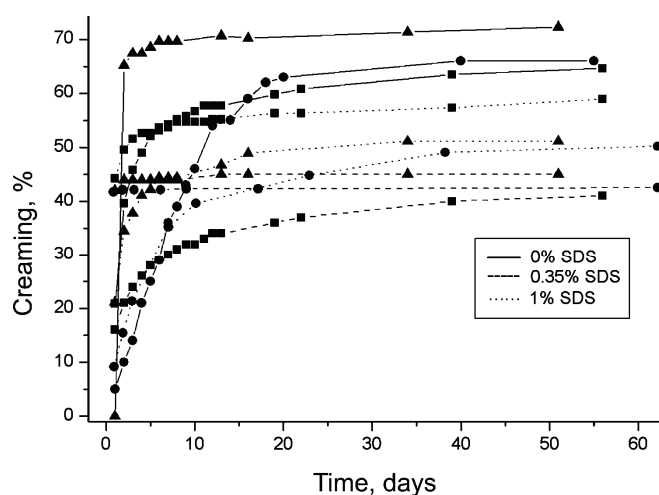

Fig. 3. Creaming index of 20 % emulsions prepared with different oils (■, pumpkin seed oil, ▲, linseed/sunflower oil (0.2/0.8), ●, sunflower oil) at the investigated SDS concentrations as a function of time.

Emulsions without SDS, *i.e.*, without a coacervate, exhibited typical sedimentation instability with a turbid serum layer due to the polydispersity of the emulsions and slow migration of the small oil droplets through the viscous continuous phase containing the HPMC/NaCMC complex.[18] The creaming indexes, *H*, of all emulsions with 0 % SDS were the highest and changed with time, Fig. 3. The emulsion of linseed/sunflower oil was found to be the least stable and separated in five days. In the emulsions of pumpkin seed oil and the mixture of linseed/sunflower oil without SDS, the cream layers were more intensely colored, compared to the corresponding cream layers of the emulsions with SDS, in-

dicating that in the absence of a coacervate shell, the adsorption layer around the oil droplets was thin. Therefore, the characteristic color of the used oils was visible.

At an SDS concentration of 1 %, the volume of the cream layer of emulsions was smaller, *i.e.*, the creaming index, *H*, was higher than that with 0.35 % SDS, indicating that the formed coacervate, which consisted of a solubilized HPMC/ /SDS complex, was partly desorbed from the oil droplets surface and was visible lower in the cylinders as a transparent sediment, arrow in Fig. 2. The creaming indexes of emulsions with 1 % SDS were between those with 0 and 0.35 % SDS and changed with time, Fig. 3, due to the slow process of desorption and stabilization of the adsorption layers in the emulsions.

It is evident that the thickness and the composition of the adsorption layers around the oil droplets depended on the SDS concentration, which suggests that microcapsules of different wall properties could be obtained after spray drying of the emulsions. In addition, the different appearance of the pumpkin seed oil emulsion with 0.35 % SDS and the linseed oil emulsion with no SDS, when compared to the corresponding sunflower oil emulsions, Fig. 2, indicates that the kind of oil also affects the properties of the adsorption layer and, hence, the properties of the emulsions and microcapsules.

Particle size distribution of the emulsions and suspensions of microcapsules

The prepared emulsions were spray dried and microcapsules in powder form were obtained. The particle size and particle size distribution of the emulsions and the suspensions of microcapsules in water were determined, Table I.

TABLE I. Parameters of the particle size distribution of the emulsions and suspensions of microcapsules in water

Parameter	Sunflower oil			Pumpkin seed oil			Linseed/sunflower oil (0.2/0.8)		
	c_{SDS} / %								
	0.00	0.35	1.00	0.00	0.35	1.00	0.00	0.35	1.00
	Emulsions								
d_{vs} / μm	20.53	3.42	2.54	11.0	3.36	3.10	7.61	5.52	5.30
σ / μm	5.49	0.81	0.66	4.37	0.79	0.86	3.56	2.56	3.06
	Suspensions								
d_{vs} / μm	4.14	4.63	8.24	5.88	6.56	7.79	7.81	4.94	10.42
σ / μm	1.83	1.58	3.77	2.83	2.93	3.54	3.48	1.71	4.52

It is evident that the presence of SDS significantly decreased the particle size in all emulsions. The best correlation, *i.e.*, the smallest difference in particle size distribution of the emulsions and the corresponding suspensions of microcapsules was obtained with SDS concentration of 0.35 %. At this SDS concentration, the formed HPMC/SDS complex was separated from the solution by addition of NaCMC and deposited on the surface of the oil droplets as a compact coacervate layer. This enabled microcapsules to be obtained with a stable wall and almost

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the same particle size as in the original emulsion, indicating that at this SDS concentration, the drying conditions had an insignificant effect on the particle size of the microcapsules. These microcapsules had a more uniform particle size distribution (lower standard deviation, σ) and a better redispersibility in water, compared to the microcapsules obtained with 0 and 1.0 % SDS. The microcapsules prepared without SDS and with 1 % SDS had significantly different mean diameters to those of the corresponding emulsions, as a consequence of wall instability under the employed drying conditions.

The microphotographs of the sunflower oil emulsions, the microcapsules powders and the suspensions of the microcapsules in water, obtained at characteristic SDS concentrations, are presented in Fig. 4, while the particle size distributions of the sunflower oil emulsions and suspension of microcapsules in water are presented in Fig. 5.
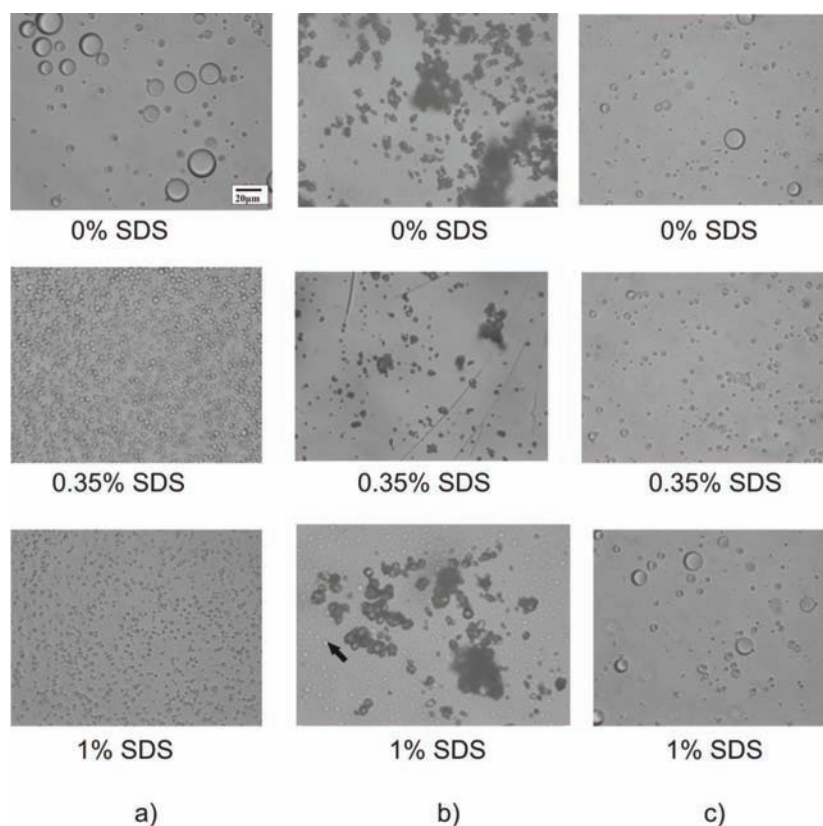

Fig. 4. Microphotographs of a) 20 % emulsions of sunflower oil in a 1 % solution of HPMC/NaCMC (0.7/0.3) at different SDS concentrations, b) the corresponding microcapsules powders and c) suspension of the microcapsules in water.
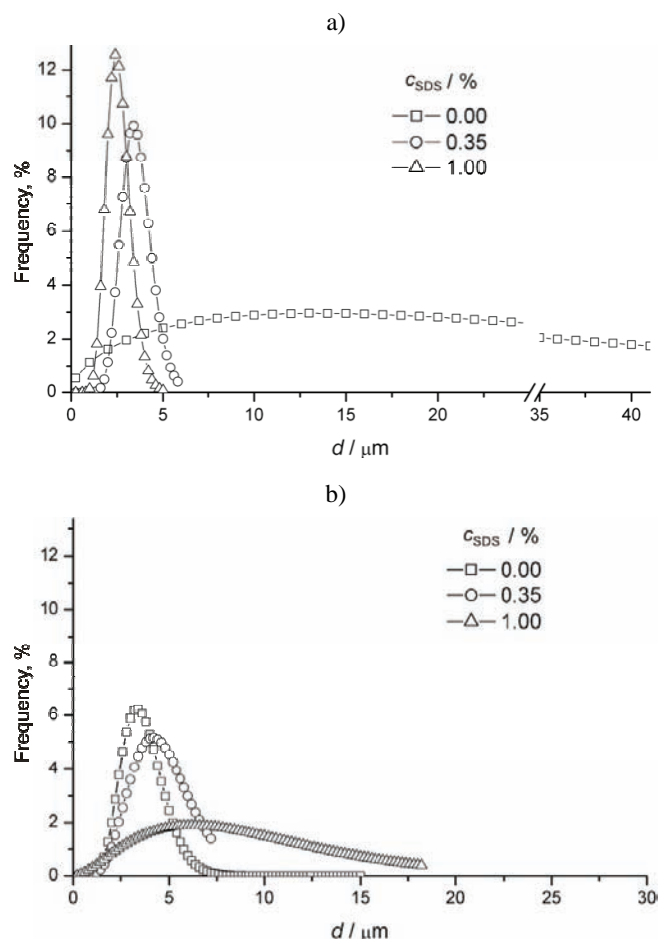
a)

b)

Fig. 5. Particle size distribution of a) emulsions and b) suspensions of the microcapsules
in water, obtained at the investigated SDS concentrations.

The microphotographs and the particle size distributions show that the emulsions without SDS contained large droplets and were more polydisperse when compared to the emulsions with SDS. A similar behavior was found for the other investigated emulsions. During the spray drying of the emulsions without SDS, the large oil droplets stick or crack and remain on the spray cylinder wall, which results in a decrease in particle size of the microcapsules and a change in particle size distribution, Fig. 5. The exception is the microcapsules with the oil mixture, Table I, which have almost the same particle size as the corresponding emulsion. This is due to the significantly smaller d_{vs} of the emulsion droplets containing the linseed/sunflower oil mixture and hence better stability during the drying process. The lower d_{vs} value could be a consequence of the higher level of poly-

unsaturated fatty acids in linseed oil,[23] which contributed to the emulsification efficiency of the HPMC molecules.

An increase in the size of the microcapsules, compared to the corresponding emulsion, is evident for the sample containing 1 % SDS, Fig. 5, because of coalescence of the oil leached from microcapsules during their redispersion in water. Namely, the microcapsules readily cracked during the manipulation as indicated by the presence of free oil droplets (arrow) in the microphotograph of the microcapsules powder, Fig. 4, which indicates the instability of the wall of the microcapsules. Only the suspension of microcapsules obtained at 0.35 % SDS had almost the same particle size and particle size distribution, Table I and Fig. 5, as the corresponding emulsion, i.e., firm and stable microcapsules walls which were resistant to the spray drying conditions.

Encapsulation efficiency

The encapsulation efficiency was determined spectrophotometrically after extraction of the oil from the microcapsules with cyclohexane. The results are presented in Fig. 6.
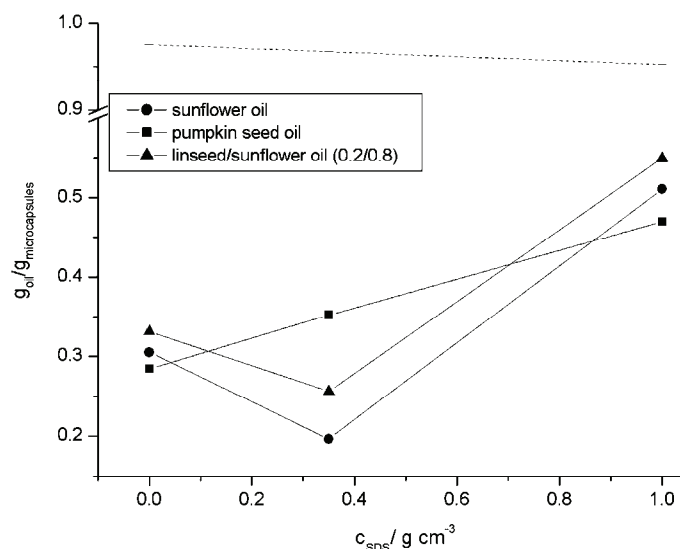

Fig. 6. Amount of oil extracted from the microcapsules as a function of SDS concentration and the theoretical amount of oil (---).

The lowest amount of extracted oil was found in the microcapsules containing sunflower and the mixture of linseed/sunflower oil (0.2/0.8) in the HPMC/ /SDS interaction region, i.e., at 0.35 % SDS. This is most likely a consequence of the presence of the compact, networked coacervate layer around the oil surface, which forms a stable microcapsules wall and hinders oil extraction. The largest

amount of extracted oil was found at SDS concentration of 1 %, which is in agreement with the proposed permeable structure of microcapsules wall. In comparison with the theoretical amount of oil present in the microcapsules, Fig. 6, the amount of extracted oil suggests that some oil was still present in all microcapsules after extraction, and that the permeability depends on the wall structure, *i.e.*, the presence of the coacervate around the oil droplets. The exceptions were the microcapsules of pumpkin seed oil where the amount of extracted oil increased with increasing SDS concentration, indicating that the presence of coacervate has no influence on the transport of oil through the wall. The reason for this could be presence of sterols in high percent in pumpkin seed oil, which can be adsorbed onto the oil droplets surfaces[24] and influence the permeability of the adsorption layer.

As the nature of the encapsulated oil influences the microencapsulation process and the properties of microcapsules, for a detailed explanation of the different behaviors of the used oils, information about their chemical composition is necessary. Therefore, the physico-chemical characteristics of oils should be considered as an important parameter of microencapsulation by the presented method.

CONCLUSIONS

Due to the interaction of the components in the continuous phase of emulsions consisting of HPMC, NaCMC and SDS molecules, the formed anionic complex HPMC/SDS deposits around the oil droplets as a coacervate in the presence of NaCMC molecules and forms the microcapsules wall. The properties of the walls of the microcapsules depend on the SDS concentration. At 0.35 % SDS, the formed coacervate layer is compact and enables the formation of stable microcapsules with entrapped oil, which is difficult to extract. In addition, the oil characteristics affect the stability of the coacervate layer. For the microencapsulation of different oils, knowledge of their components is important for predicting their influence on the microencapsulation efficiency by the coacervation method.

И З В О Д

ДОБИЈАЊЕ И КАРАКТЕРИЗАЦИЈА МИКРОКАПСУЛА КОЈЕ САДРЖЕ РАЗЛИЧИТЕ ВРСТЕ УЉА ПРИМЕНОМ МЕТОДЕ СЕГРЕГАТИВНЕ КОАЦЕРВАЦИЈЕ

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Формиране су микрокапсуле уљног садржаја методом коацервације сегрегативног типа. Континуална фаза 20 % (w/w) емулзија уља у води, У/В, састојала се од 1 % (w/w) смеше хидроксипропилметил-целулозе (HPCMC) и натријум-карбоксиметил-целулозе (NaCMC) масеног односа 0,7/0,3, уз присуство анјонске површински активне материје, натријум-додецил

сулфата (SDS) концентрација: 0, 0,35 и 1 мас. %. Наведене концентрације SDS омогућавају формирање различитих структура адсорпционих слојева око диспергованих капљица уља сегрегативном коацервацијом комплекса HPMC/SDS у присуству молекула NaCMC, што је утицало на формирање и особине микрокапсула. Као уљна фаза коришћено је сунцокретово уље, бундевино уље и смеша сунцокретовог и ланеног уља. Микрокапсуле у облику праха добијене су распршивањем емулзија у Spray Dryer-у. Одређивана је стабилност, величина и расподела честица емулзија и одговарајућих суспензија микрокапсула у води, као и проценат енкапсулираног уља екстракцијом. Показало се да се стабилан компактан слој коацервата око капи формира при 0,35 % SDS, који спречава екстракцију уља из микрокапсула. Такође, на особине емулзија и микрокапсула утиче и врста уља тако што поједине компоненте уља мењају структуру адсорпционог слоја око капи и њихову стабилност, о чему треба водити рачуна при избору уља за микрокапсулацију овом методом.

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