

Encapsulation of emulsion drops

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INTRODUCTION

Microencapsulation is the process, in which colloidal particles or droplets are being coated by shells of various materials to obtain capsules. The number of processes used to produce microcapsules continues to grow. The layer-by-layer adsorption of polyelectrolytes (PE) is considered as a convenient method to obtain microcapsules' shells on colloidal cores (Shchukin 2003, Voigt 1999). Solid particles (polystyrene latex, silica, CaCO₃) are most often used as cores for formation of capsules, which may contain some active ingredient. Alternatively the solid core can be dissolved to leave the hollow shell, which can be then refilled with the desired composition (Shchukin 2003, Voigt 1999). For example Sivakumar et al. (2008) proposed the two-step procedure to produce capsules with liquid core. They used solid template to produce monodisperse polyelectrolyte multilayer capsules and then after dissolving solid core they filled capsules with oil. In that way they obtained monodisperse emulsions encapsulated with polyelectrolyte multilayers with the size in the range of a few micrometers. However, the disadvantages of the method of sacrificial core can be traces of the destructed core trapped in the capsule and/or low efficiency of loading of the active substance into the hollow shells (Grigoriev 2008, Sukhorukov 2004).

Use of emulsions droplets as liquid cores gives possibility to encapsulate oil soluble active components in one step process with control of size and shell properties of capsules and that opens perspectives for their application in many fields such as: cosmetic, medicine, pharmacy and food industry (Caruso 2000). In our paper we propose two methods of formation of submicron liquid core capsules with polyelectrolyte multilayer shells. These methods are schematically depicted in Fig.1.

MATERIAL AND METHODS

The polyelectrolytes used in our studies were: polycations – poly(diallyldimethylammonium) chloride PDADMAC (MW ~ 100000 to 200000), poly(fluorescein isothiocyanate allylamine hydrochloride) PAH* (MW ~ 70000), chitosan CHIT (MW ~medium), poly-L-lysine hydrobromide PLL (MW 15000-30000) and polyanions - polysodium 4 – styrenesulfonate PSS (MW~ 70000), alginate sodium salt ALG (MW ~ 90000), Poly-L-glutamic acid sodium salt PGA (MW 15000-50000). All polyelectrolytes, docusate sodium salt AOT ≥99%, octane 98%, 3-(2-Benzothiazolyl)-7-(diethylamino)coumarin Coumarine-6 98%, TEOS (Tetraethyl orthosilicate), APS ((3-Aminopropyl)triethoxysilane), DTSACI (Dimethyloctadecyl[3-trimethoxysilyl]propyl]ammonium chloride), TWEEN80 (polyoxyethylenesorbitan monooleate) hydrochloride acid, sodium chloride were obtained from Sigma-Aldrich. Chloroform cz.d.a. was purchased from POCH Gliwice. All materials were used without further purification. The distilled water used in all experiments was obtained with the three-stage Millipore Direct-Q 3UV purification system.

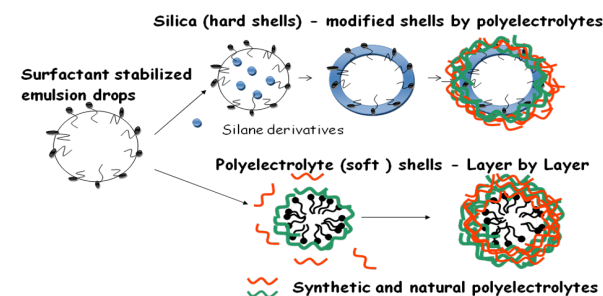


Figure 1 Scheme of formation nanocapsules with silica shells (on top) and nanocapsules stabilized by interfacial complex AOT/PDADMAC and building up PE multilayers (on bottom).

Size (hydrodynamic diameter) of emulsion droplets and capsules was determined by DLS (Dynamic Light Scattering) using Zetasizer Nano Series from Malvern Instruments with the detection angle of 173° in optically homogeneous square polystyrene cells. All measurements were performed at 25°C. Each size was obtained as average one from three runs with least 10 measurements. The zeta potential of emulsion's droplet was measured by the microelectrophoretic method using Malvern Zetasizer Nano ZS apparatus. Each value was obtained as an average from three subsequent runs with at least 20 measurements.

To prepare fluorescently labeled emulsion cores, oil soluble fluorescent dye Coumarine-6 was dissolved in octane or chloroform (0,1mg/ml) prior to emulsification. Images of fluorescently labeled capsules/cores were taken with a Carl Zeiss Observer D1 microscope with TIRF illumination.

Core preparation: Liquid cores for polyelectrolyte capsules were prepared by dissolution of AOT in octane (360g/l) and mixed it with PDADMAC solution in NaCl of the ionic strength (0.015 M). The concentration of PDADMAC solution was 2 g/l.

Capsules with silica shells were prepared by emulsification of chloroform containing silane derivatives, TEOS, APS or DTSACI in combination with evaporation technique.

Shells formation: Silica shells were formed by polymerisation reaction (hydrolysis and polycondensation) of silane derivatives at the interface. Progress of hydrolysis, i.e. shell formation, were followed by NMR spectroscopy. Spectra were obtained using a Varian VXR S 300 MHz and Varian GEMINI 300 MHz instruments. The volume of 0,7ml of the solution was used in the NMR-tube. C₆D₆ in a capillary was used to lock the instrument. First spectra were taken 15 minutes after preparing sample.

PE multilayers were constructed by layer-by-layer technique using the saturation method (Guzey 2006).

RESULTS AND DISCUSSION

For preparation of the emulsion of capsule cores, 0.1 ml of octane solution with 360 g/dm³ of AOT was added to 2 g/dm³ of aqueous PDADMAC solution during continuous mixing. We obtained the emulsion stabilized by AOT/PDADMAC surface complex with the average drop size around 200nm with polydispersity index 0.2 (Fig. 2.), which was stable over several weeks. Zeta potential of emulsion droplets was 73 ± 8mV.

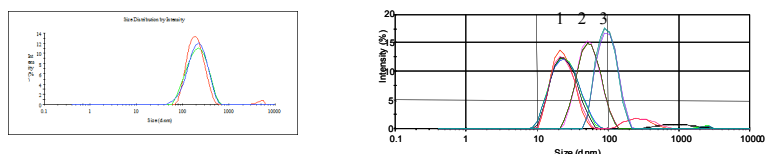


Figure 2. Left -Typical size distribution of emulsion drops - octane/AOT-PDADMAC/water measured by DLS (three runs with least 10 measurements). Right - Example of size distribution of chloroform emulsions containing TEOS, stabilized by TWEEN80 with average drop size 1- 20 nm, 2- 50 nm and 3 –100 nm, produced at various weight ratio between oil and surfactant

Chloroform emulsions containing silane derivatives were prepared by continuous mixing of all components by magnetic stirrer for one night (in case of the smallest emulsion chloroform was allowed to evaporate during mixing). As the result emulsion containing TEOS, APS or DTSACl, stabilized if it was necessary by Tween 80 (5%), were obtained. Figure 2 shows the size distribution of the emulsions droplets measured by DLS. Emulsion in the range 20 – 200 nm were obtained by using various weight ratios between chloroform and surfactant.

Progress of hydrolysis of silane derivatives during shell formation was followed by NMR spectroscopy. Since Si-NMR spectra were ambiguous, we proposed the alternative way to characterize the hydrolysis of silica sources by analyzing the H-NMR peak from alcohols. Alcohol is a product of the hydrolysis of TEOS, APS and DTSACl. Progress of the reaction was monitored in three various condition: basic pH~10, acidic pH~3 and natural (natural—without any additions). We have found that acidic condition is favorable for TEOS hydrolysis, basic conditions are favorable for DTSACl hydrolysis while in the APS case hydrolysis is very fast in all conditions. Since DTSACl containing capsules were made without addition of surfactant, we chose them as cores for PE multilayer build up. Their average size was 100nm and zeta potential 22mV. We visualized the emulsion of capsules' cores by dissolving fluorescent dye – Coumarine-6 in the oil phase. Figure 3 shows the intensive fluorescence inside the droplets, which were deposited at surface of microscopic slide for a) capsules with silica shells made from DTSACl and b) capsules stabilized by AOT/PDADMAC complex. It gives direct evidence of formation of liquid emulsion droplets containing hydrophobic compound.

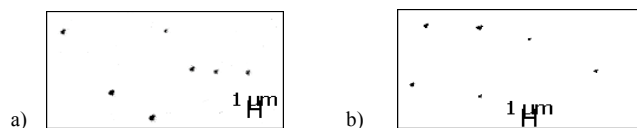


Figure 3 Fluorescence micrographs of capsules a) capsules with silica shells made from DTSACl and b) capsules stabilized by AOT/PDADMAC complex containing Coumarine-6 as oil soluble dye.

The formation of the multilayer polyelectrolyte shells on such prepared cores were performed by subsequent adsorption of polyelectrolytes from their solutions using the saturation method, i.e. without the intermediate rinsing step. The following polycation/polyanion pairs were selected to form PE shells: PDADMAC/ALG, PDADMAC/PSS, CHIT/PSS, CHIT/ALG PLL/PGA and

PAH*/PGA. Figure 4 illustrates examples of typical zigzag dependence of zeta potential of capsules on the adsorption of subsequent polyanion and polycation layers for silica capsules and capsules stabilized by interface complex AOT/PDADMAC. Shells formation was also visualized by using fluorescently labeled polycation poly(fluoresceinisothiocyanateallylamine hydrochloride).

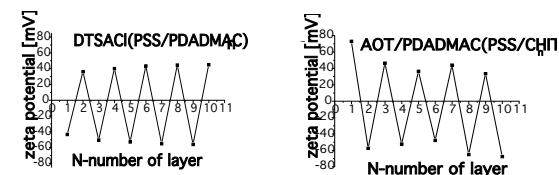


Figure 4 Variations of zeta-potential of PE coated emulsion droplets with number of polyelectrolyte layers for a) silica capsules (DTSACl) and b) capsules stabilized by interface complex AOT/PDADMAC.

CONCLUSIONS

We proposed two methods of formation of submicron, liquid core capsules with polyelectrolyte multilayer shells. In the first method, oil phase containing silane derivatives, TEOS, APS or DTSACl, is dispersed in the aqueous phase. Then, as the result of their hydrolysis and polycondensation the silica shell is formed around the emulsion droplets. This shell can be subsequently modified by formation of polyelectrolyte multilayer. The second method is based on the formation of emulsion stabilized by surface complex of oil soluble ionic surfactant and oppositely charged polyelectrolyte. This emulsion cores can be then encapsulated by layer-by-layer adsorption of polyelectrolytes using the saturation method. The average size of obtained emulsions/cores obtained by either method was in the range 20-300 nm and they were stable in the period of several weeks. For formation of shells we used several combinations of synthetic and natural polyelectrolytes. The average size of capsules obtained was in the range 100-300 nm. The capsules were stable in the period of several weeks. To demonstrate the possibility of encapsulation of hydrophobic compounds we enclosed oil-soluble dye, Coumarine-6, therefore, we showed that direct encapsulation of hydrophobic compounds in the liquid core, submicron capsules with polyelectrolyte shells of various composition is possible.

REFERENCES

- Caruso, F. et al. (2000) *Assembly of β -glucosidase multilayers on spherical colloidal particles and their use as active catalysts*. *Colloids Surf., A*, 169, 287-293.
- Grigoriev, D.O. et al. (2008) *Emulsion Encapsulation by Polyelectrolyte Layer-by-Layer Deposition on the Liquid Core*. *Langmuir*, 24, 999-1004.
- Guzey, D. et al. (2006) *Formation, stability and properties of multilayer emulsions for application in the food industry*. *Advances Colloid Interface Sci.* 128-130, 227-248.
- Shchukin, D. G. et al. (2003) *Smart Inorganic/Organic Nanocomposite Hollow Microcapsules*. *Angew Chem Int Ed Engl.*, 42, 4472-4475.
- Sivakumar, S. et al. (2008) *Monodisperse Emulsions through Templating Polyelectrolyte Multilayer Capsules*. *Chem. Matter.*, 20, 2063-2065
- Sukhorukov, G. B. et al. (2004) *Physical chemistry of encapsulation and release*. *Phys. Chem. Chem. Phys.*, 6, 4078-4089.
- Voigt, A. et al. (1999) *Membrane Filtration for Microencapsulation and Microcapsules Preparation by Layer-by-Layer Polyelectrolyte Adsorption*. *Ind. Eng. Chem. Res.*, 38, 4037-4043.