## Encapsulation of Water-in-Water (W/W) Emulsions inside Polyelectrolyte Capsules

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Water-in-water (W/W) emulsions are dispersions of one aqueous phase, forming droplets, into another aqueous phase [1-4]. These emulsions can be prepared in Aqueous Two-Phase Systems (ATPS), in which phase segregation occurs because of thermodynamic incompatibility between two hydrophilic components, mainly due to differences in hydration between the two water-soluble components [2,3]. Therefore, W/W emulsions can be prepared by applying agitation in aqueous biphasic systems, without oil and without surfactant. It is known that Water-in-Water emulsions can be stabilized by particles able to adsorb at the W/W interface [5], forming Pickering emulsions. These fat-free dispersions can be highly interesting for food and drug delivery applications.

In the present work, W/W emulsions were prepared using a highly charged anionic polyelectrolyte (either sodium alginate or sodium carboxymethyl cellulose, NaCMC), mixed in aqueous solution with a lowly charged globular protein (bovine serum albumin, BSA). These combinations of macromolecules showed phase separation, forming ATPS, and their phase behaviour was studied. BSA-in-alginate and BSA-in-NaCMC water-in-water emulsions were formed and characterized. Such emulsions showed to be relatively stable, which was attributed to the high viscosity of either alginate or NaCMC aqueous phases.

These W/W emulsions were introduced inside capsules, by dropping emulsions into a third aqueous solution, which contained a multivalent cation ( $Ca^{2+}$  or  $Fe^{3+}$ ). The anionic polyelectrolytes (either alginate or NaCMC) formed ionic complexes with  $Ca^{2+}$  or  $Fe^{3+}$ , producing capsules that contained W/W emulsions in the interior. These capsules can have a smooth surface (made of polyelectrolyte-cation complexes) and a highly porous interior (formed by the presence of W/W emulsion droplets). Fig. 1 shows a scheme of capsules (a); the visual aspect of capsules formed with  $Fe^{3+}$  (b); and illustrative examples of Scanning Electron Microscopy images of capsules, (c) and (d). The porous structure of dried capsules (Fig. 1d) was characterized by nitrogen sorption, confirming the macroporous nature. These porous capsules might have interesting applications in encapsulation of active components (drugs, fragrances, etc.), and various possibilities are being evaluated.



Fig. 1. (a) Scheme of encapsulated W/W emulsions; (b) Example of freshly formed capsules; (c) SEM image of a partly fractured capsule; and (d) Example of the macroporous interior of a freeze-dried capsule.

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References

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