Micro-encapsulation by complex coacervation: influence of surfactant[†]

KS Mayya, A Bhattacharyya and J-F Argillier*
Institut Français du Pétrole, 92852 Rueil-Malmaison Cedex, France

Abstract: Paraffin oil has been encapsulated using complex coacervation of gelatin and Arabic gum in the presence of a surfactant. Addition of an oppositely charged surfactant to a polyelectrolyte markedly increases the yield of the process. We report a two-layer encapsulation of paraffin oil, based on a primary layer of interface active polyelectrolyte–surfactant complex, followed by a second layer of the conjugate polyelectrolyte–polyelectrolyte complex. Surfactant concentration has been found to be a crucial parameter to obtain good quality microcapsules and optimal yield. This confirms the importance of formulation aspects when looking for optimization of these techniques of micro-encapsulation.
© 2003 Society of Chemical Industry

Keywords: microcapsules; microencapsulation; coacervation; polyelectrolyte–surfactant complexes

INTRODUCTION

Micro-encapsulation can be considered as a method of wrapping small individual particles in protective coatings, designed to protect, separate, help in storage, handling or controlled release of the active material. Such microcapsules may be produced by a host of techniques, like simple or complex coacervation, phase separation, interfacial polymerization, etc. One of the best studied systems in complex coacervation is the gelatin–acacia system.[1] Although much of the literature was confined to patent literature until 1970,[2] the procedure for preparation of gelatin–acacia microcapsules is now well established.[3,4] The primary reasons for using gelatin and Arabic gum as wall material are their abundance and biodegradability. The fact that the charge on gelatin is pH-dependent makes this method of preparation of microcapsules extremely pH-dependent[5] and hence easy to control. Fine tuning of all the parameters involved is extremely important, for small variations can lead to changes in the quality and quantity of the final product. Several authors have exploited this technique for encapsulation of solids and liquids.[6–8] The first important report was by Green *et al*[3a] for application of microcapsules in 'carbon less' copying paper. Detailed reports of the study on micro-encapsulation using complex-coacervation of the gelatin-acacia system is mainly attributed to Luzzi and Gerraughty.[4]

An important factor determining the micro-encapsulability of a particular core material is the amount of polyelectrolyte that can be adsorbed on the droplet surfaces before or during coacervation. Several authors[6,7,9] have used surfactants to increase encapsulation. The increase in encapsulation is usually interpreted in terms of improved wettability of the coacervate. In this study, we propose another interpretation based on a two-step process: formation of a primary surfactant/polyelectrolyte complex at the paraffin/water interface, followed by the deposition of a two-polyelectrolyte complex coacervate.

EXPERIMENTAL

Materials

We have used gelatin A (GE), obtained from Sigma, and Arabic gum (AG), obtained from the University of Rouen. GE is an acid-processed gelatin with an isoelectric point close to 9. It is positively charged below its isoelectric point. AG is negatively charged throughout the pH range. Paraffin wax with the specifications (melting point 28 °C, relative density 0.789 at 15 °C, and 17–20 carbon atoms in the alkyl chain) was obtained from Condea Augusta. Sodium dodecyl sulfate (99%) was obtained from Prolabo (France) and was used as received. Gluteraldehyde was obtained from Aldrich. Water used was purified Millipore Milli-Q with a resistivity above 18.2 Ωm.

Preparation of microcapsules

The standard procedure[4] of micro-encapsulation by complex coacervation of gelatin–Arabic gum was used, except for the addition of surfactant during emulsification. The method involved the following steps:
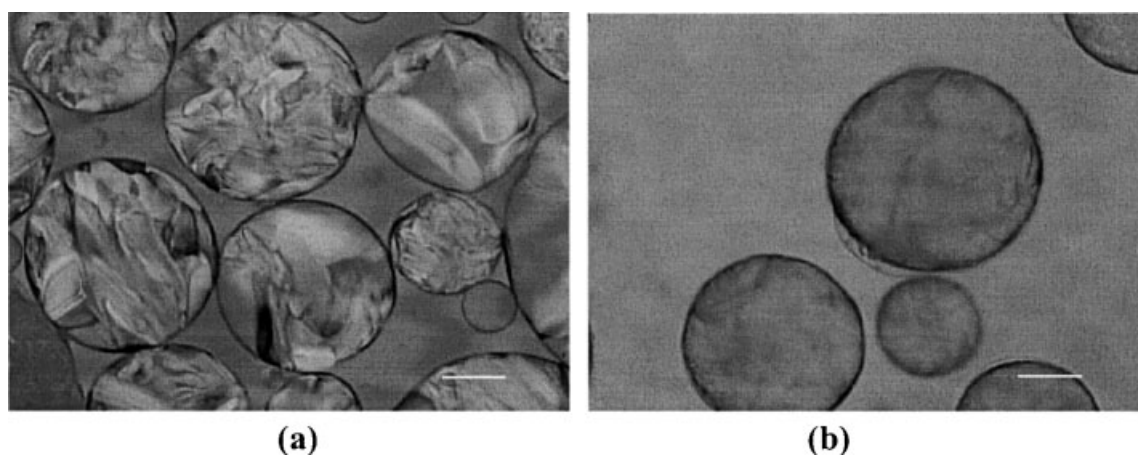

Figure 1. Optical microscope images of (a) emulsion droplets and (b) capsules obtained without using SDS. The bar represents 50 μm.

— preparation of 100 ml of 1% GE and AG solutions
— adjustment of pH to 6.5
— dispersion of 15 ml (11.34 g) paraffin in the GE solution, at 45 °C ie above the gelation temperature of gelatin (40 °C)
— drop-wise addition of the solution of the other polyelectrolyte into the dispersion
— adjustment of pH to 4.5, to induce coacervation. Stirring for 1 h
— cooling the system to 8 °C, addition of cross-linking agent (gluteraldehyde) to induce reticulation
— adjustment of pH to 9, system stirred for 12 h.

The mixture obtained was centrifuged and precipitates were found to settle at the top and bottom of the container. The precipitate at the top contained the capsules. It was separated and washed with water. Then it was washed with chilled isopropanol to dehydrate the walls of the capsule and air-dried at room temperature. A free-flowing powder with particles physically adsorbed to each other was obtained.

Capsule characterization

In order to characterize the capsules and optimize the procedure, various parameters have been studied, in particular the effect of surfactant concentration. The microcapsules were characterized by optical and scanning electron microscopy (SEM). Microcapsule yield (Y) was determined from the mass of the capsules obtained as a function of the total mass of ingredients used. Encapsulation efficiency (Er), ie the percentage of paraffin present in the capsules, was determined from differential scanning calorimetry (DSC) studies. Samples weighing 5–10 mg were cooled from 80 °C to −40 °C at the rate of 2 °C min^{-1} in sealed capsules in a stream of helium in the oven of a 2920 Modulated DSCTA Instruments (H69).

The surface tension behaviour of the SDS/GE system was studied using a pendant drop apparatus. A bubble of air of volume 10 μl was suspended in the solution and its profile monitored using a digital CCD camera interfaced to a PC. The surface tension was determined from this profile using the fundamental Laplace equation.[10]

RESULTS AND DISCUSSION
Capsules without surfactants

GE and AG have a natural surface activity. Hence it is possible to form microcapsules starting from an oil-in-water emulsion at a temperature higher than the melting point of paraffin, even in the absence of surfactants. Optical microscope images of the emulsion droplets and the capsules are shown in Fig 1. The pictures have been taken at 20 °C, below the melting point of paraffin, with a polarizer to show the crystallization of the paraffin. The procedure gives $Er = 87\%$ and $Y = 41\%$. SEM pictures (Fig 2) have been obtained on fractured capsules in slushed nitrogen and show the membrane the thickness of which is about 1 μm.

Influence of surfactant

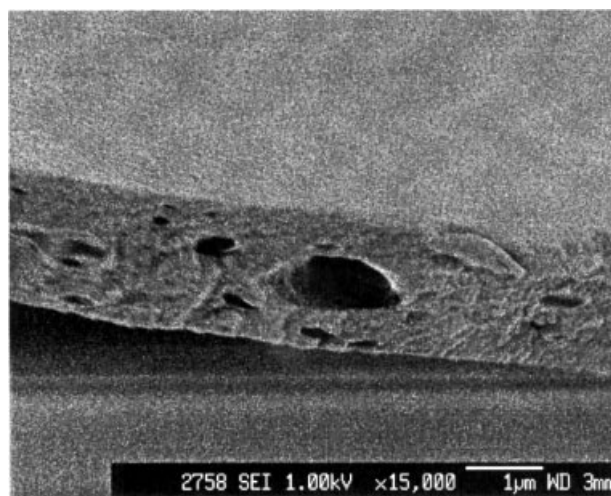In order to improve the encapsulation efficiency and

Figure 2. SEM picture of capsules fractured in slushed nitrogen: the picture exhibits the membrane structure.
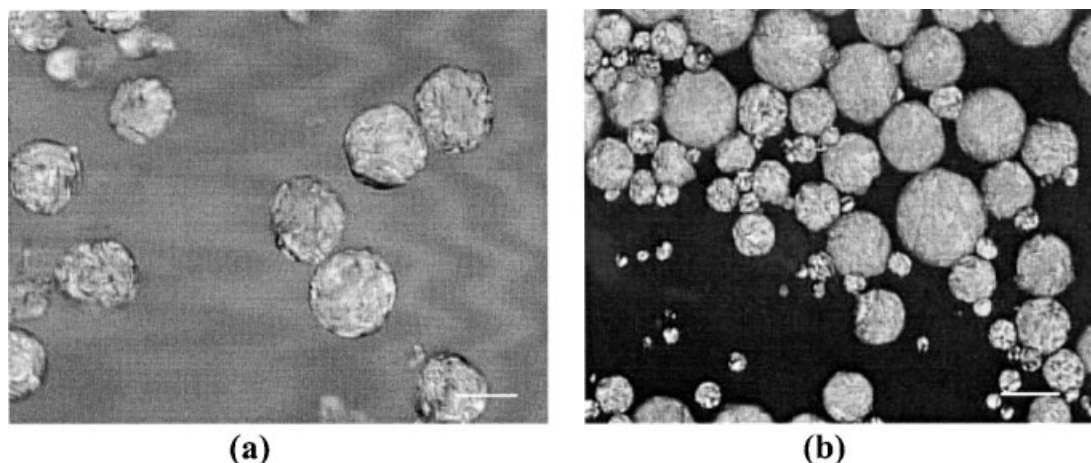
Figure 3. Optical microscope images of (a) emulsion droplets and (b) capsules obtained with 1 mM SDS. The bar represents 50 μm.

yield of the process, we studied the effect of adding an oppositely charged surfactant in GE solution at pH 6.5. The same procedure as described above was used except that SDS at various concentrations was added to the GE solution before adding paraffin. The concentration of surfactant was far less than its critical micellar concentration (CMC) of 8 millimoles litre^{-1} at 45 °C. Figure 3 shows the emulsion droplets solidified at room temperature and the capsules. Not much difference is noticed on adding SDS, except that the average particle size is lower. This is expected as a classical effect of surfactant on emulsion size distribution. However, there are significant improvements in *Er* (91%) and *Y* (62%).

Figure 4 shows the quantity of microcapsules recovered as a percentage of the total mass of ingredients used (*Y*) as a function of the SDS concentration. The SDS concentration has been expressed in mM with respect to the final solution containing both polyelectrolytes. As can be seen, there is a maximum in the yield at 1.5 mM, after which the yield decreases
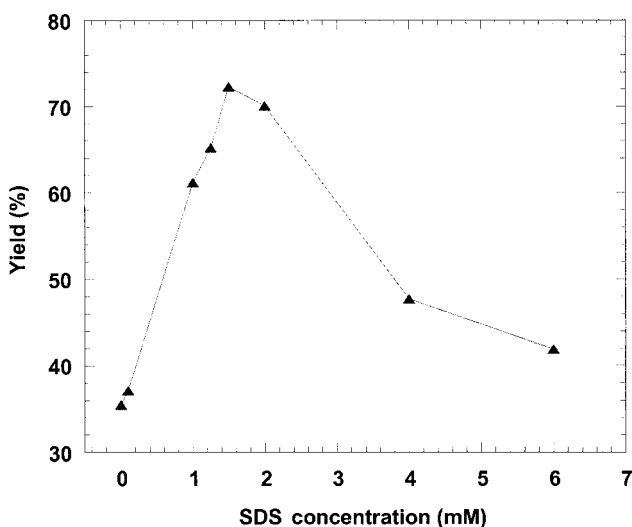
rapidly. This is in agreement with results using sodium dodecylbenzyl sulfonate.[11]

In order to understand the interactions between GE and SDS we studied the surface tension of the system using a pendant drop apparatus. GE concentration was maintained at 1% by weight, and the SDS concentration was varied from 0.01 to 100 mM. The pH was maintained at 6.5 and the temperature at 45 °C. The results, as shown in Fig 5, are qualitatively similar to the results of Knox *et al.*[12] The surface tension of pure SDS solutions is also shown. As seen, at 0.01 mM, the surface tension remains almost that of water. It starts decreasing from 0.05 mM and reaches 38 mN m^{-1} at around 8 mM, which corresponds to the CMC.

On addition of GE, there is a lowering of surface tension to 57 mN m^{-1} for SDS concentrations as low as 0.01 mM. The surface tension for 1% pure gelatin is 65.25 mN m^{-1}. This indicates complex formation between SDS and GE at the surface which has a strong surface activity. The surface tension decreases

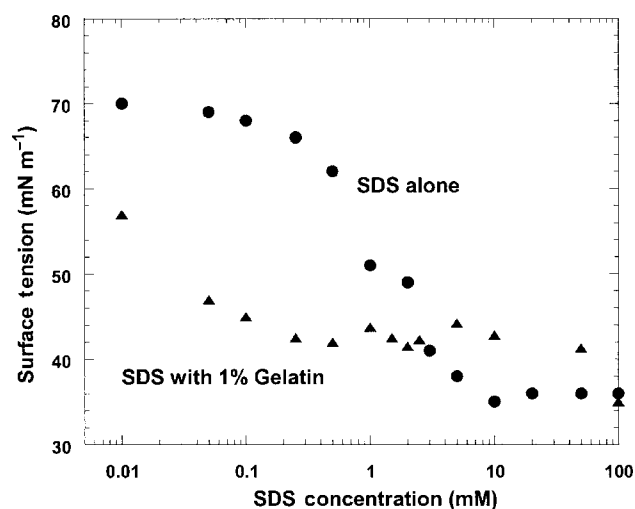**Figure 4.** The micro-encapsulation yield *Y* as a percentage as a function of SDS concentration.
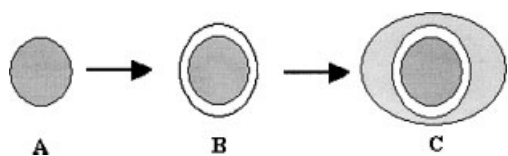

Figure 5. Surface tension of SDS gelatin system, as a function of SDS concentration at 45 °C.

Figure 6. Schematic diagram of the model of capsule formation. (A) oil droplet (B) oil droplet with primary layer, and (C) oil droplet with secondary layer.

with increasing SDS up to about 0.2 mM, after which it remains constant. This can be defined as the critical aggregation concentration (CAC).[13] Above this concentration, complexes are formed mainly in the bulk and are found to be insoluble in water, though they are formed of SDS and GE, which are soluble.[14] Surface tension starts decreasing again only after 50 mM, signifying the completion of complex formation, so that surfactant molecules can come to the surface.

Based on these results, we propose a model for the formation of the capsule wall, shown schematically in Fig 6. On adding the surfactant to the emulsion at very low concentration, there is a complexation between the oppositely charged polyelectrolyte and surfactant. This complex is insoluble and very surface active[14] and deposits at the droplet/water interface in the form of a primary layer as shown in Fig 6(B). This makes the oil droplet surface rich in GE. It is yet unclear why the optimum range for encapsulation yield is so narrow compared with the CAC to CMC plateau in surface tension values. This may be due to the large difference (factor of thousand) in the surface-to-volume ratio between oil-in-water emulsion droplets during encapsulation and air/water pendant drop interface during surface tension measurements. However, most of the GE keeps in solution and addition of the conjugate polyelectrolyte (AG) to the solution induces further complexation between the two polyelectrolytes. This complex grows on the primary layer surface as well as in the continuous phase, and finally deposits on the droplets, forming a secondary layer (Fig 6(C)).

CONCLUSION

Microcapsules of paraffin have been produced by complex coacervation of gelatin/Arabic gum in the presence of a surfactant. Various parameters have been studied, in particular the effect of the presence and concentration of the surfactant. Encapsulation yield increases from 35% to 70% in the presence of small quantities of an oppositely charged surfactant. The concentration of surfactant for optimum encapsulation efficiency (up to 91%) is in between the CAC and the CMC for SDS alone as seen from surface tension studies. We propose that the encapsulation efficiency is improved by forming a primary layer of surfactant–polyelectrolyte complex on the paraffin oil droplets prior to coacervation. In conclusion, we have proposed a two-layer model for the formation of microcapsules in the presence of a surfactant. Influence of paraffin quantity is being investigated as well as influence of a cationic surfactant with arabic gum.

REFERENCES
1 Benita S, *Microencapsulation: Methods and Industrial Applications*, Marcel Dekker, New York (1996).
2 Chem Tech Rev, No 73, *Microcapsules and Microencapsulation Techniques*, ed by Gutcho MH, Noyes Data Corporation, New Jersey (1976).
3 (a) Green BK and Schleiker L, *US Patent* 2 800 458 (1957);(b) Green BK and Schleiker L, *US Patent* 2 730 456 (1956).
4 Luzzi LA and Gerraughty RJ, *J Pharm Sci* **56**:634 (1967).
5 Bungenberg de Jong HG, *Colloid Science*, Vol II, ed by Kruyt HR, Elsevier, Chap X, p 339 (1949).
6 Madan PL, Madan DK and Price JC, *J Pharm Sci* **65**:1476 (1976).
7 Tirkkonen S, Turakka L and Paronen P, *J Microencapsulation* **11**:615 (1994).
8 Yoshizawa H, Uemura Y, Ijichi K, Hano T, Kawano Y and Hatate Y, *J Chem Engng Jpn* **29**:379 (1996).
9 Vinetsky Y and Magdassi S, *J Colloid Interface Sci* **89**:63 (1997).
10 Benjamins J, Cagna A and Lucassen-Reynders EH, *Coll Surf A Physicochem Engng Aspects* **114**:245 (1996).
11 Sovilj V, Djakovic L and Dokic P, *J Colloid Interface Sci* **158**:483 (1993).
12 Knox WJ Jr and Parshall TO, *J Colloid Interface Sci* **33**:16 (1970).
13 Goddard ED, *J Am Oil Chem Soc* **71**:1 (1994).
14 Asnacios A, Langevin D and Argillier J-F, *Macromolecules* **29**:7412 (1996).