Colloid & Polymer Science Colloid Polym Sci 272:1295–1299 (1994)

Synthesis of magnetic DDAB vesicles

C. Menager and V. Cabuil

Laboratoire de Physicochimie Inorganique, URA CNRS, Structure et Réactivité des Systèmes Interfaciaux, Université Pierre et Marie Curie, Paris, France.

Abstract: The synthesis of magnetic vesicles is described. The vesicles are constituted by didodecyldimethylammonium bromide and have a diameter of about 1 μm. An aqueous magnetic fluid, constituted by charged magnetic nanoparticles dispersed in water without surfactant, is encapsulated in the vesicles with a volume fraction in particles that may range up to 10%. The first step of the encapsulation is the synthesis of a multiple emulsion the intermediate oily phase being evaporated to obtain the DDAB bilayer. The magnetic vesicles thus synthesized align and change shape when a magnetic field is applied.

Key words: Magnetic fluids – magnetic vesicles – encapsulation

Introduction

Incorporation of magnetic particles in self-assemblies of tensioactive molecules has been described in some particular cases. Magnetic particles have been introduced in nematics in order to orient them [1]. Synthesis of ferrosmectics constituted by surfactant-coated magnetic particles confined in the cyclohexane phase of the system cyclohexane/water/sodium dodecyl sulfate/pentanol has been recently reported [2–4].

Synthesis of magnetic liposomes has been reported by several authors. De Cuyper describes the synthesis of magnetoliposomes constituted by magnetic nanoparticles coated by a bilayer of phospholipids [5, 6]. Fendler describes the incorporation of surfactant-coated magnetite particles in DODAC vesicles [7]. Mann [8, 9] describes the synthesis of magnetite particles in situ in small vesicles. Usually, the synthesis of magnetic vesicles is proposed for immunomagnetic separation [10]

The aim of this work is to produce intermediate size magnetic vesicles (diameter ranging from 0.1 to 1 microns), containing an ionic magnetic fluid [11], with an important volume fraction in magnetic particles (10%). We have chosen to entrap the magnetic fluid in didodecyldimethyl ammonium bromide vesicles.

Materials

i) The ionic magnetic fluid

The ionic magnetic fluid is constituted by cationic maghemite particles (γ-Fe_2O_3) dispersed in water. Magnetite particles are synthesized according to Massart's procedure [12], then oxidized to maghemite by ferric nitrate in nitric acid medium. These particles have a mean diameter of about 9 nm. They carry positive surface charges, the surface charge density being of the order of 0.2 C/m^2 [11], with the associated counterions beieng nitrate anions. By dispersion in deionized water, they form a stable magnetic colloidal dispersion (ferrofluid), which is acid (pH $<$ 4). The volume fraction in particles in such a dispersion may range from 0 to 10%. Stability is ensured by screened electrostatic repulsions. Ionic strength is thus reduced as much as possible, but free nitric acid always stays in solution. The maximum concentration of free acid is 0.2 mol/l.

ii) The DDAB vesicles

DDAB (didodecyldimethyl ammonium bromide) is a double-chain cationic surfactant which swells spontaneously in presence of water at room temperature. The binary system water/DDAB has been described by M. Dubois [13] and presents in the diluted regime a domain of vesicles for a weight concentration in DDAB of the order of 0.2%.

Preparation of magnetic vesicles

Many procedures may be used to encapsulate magnetic fluids in vesicles, but the only way to perform a theoretical total encapsulation (i.e., to introduce inside the vesicles a magnetic fluid without decreasing the volume fraction in particles) is to use the multiple emulsion procedure described in refs. [14–16].

This is schematized in Fig. 1. The aqueous solution to be encapsulated is dispersed in an oily phase in order to get a water-in-oil emulsion (W/O). This emulsion is then mixed with an excess of water to get a multiple emulsion W/O/W. Vesicles are obtained by removing the oily phase from the microscopic oil spherules containing smaller water droplets inside. The oily phase is thus choosen with a low boiling point (for example a mixture of ether/cyclohexane), in order that it can be eliminated at low temperature. The two layers of surfactants that were separated by the oil layer then form the bilayer of the vesicles.

In the case of magnetic fluids, the operative mode we used is the following one.

The oily phase is a mixture of ether (1.25 ml) and cyclohexane (0.25 ml). DDAB (2% in weight) is solubilized in this phase. The aqueous acidic magnetic fluid, whose volume fraction in particles may range up to 10%, is added (0.02 ml) at room temperature to the oily phase under ultrasonic agitation. The emulsion thus obtained (0.75 ml) is introduced slowly (in 20 s) in water (15 ml). The ether-cyclohexane mixture is evaporated at 45–50 °C under a nitrogen stream, the flask being kept in a warm water bath under magnetic stirring to keep the spherules suspended. The complete evaporation of the ether/cyclohexane mixture is indicated by a noticeable decrease of turbidity and lasts about 30 min.

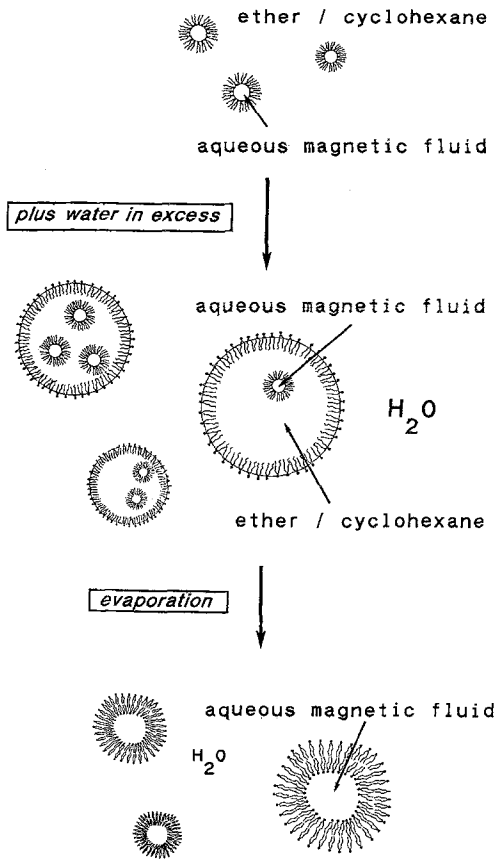


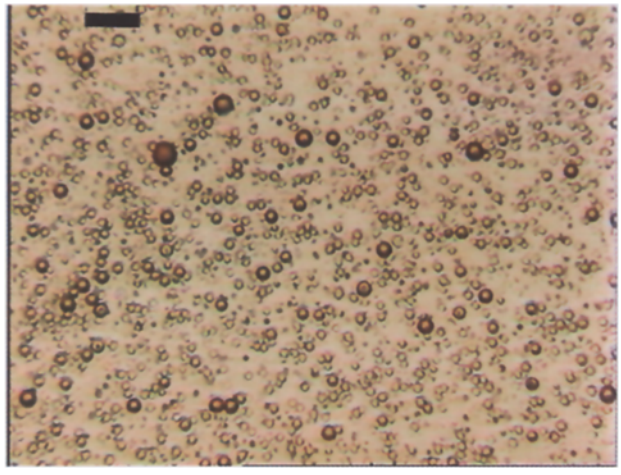
Fig. 1. Outline of the preparation of magnetic vesicles.

Characterisation

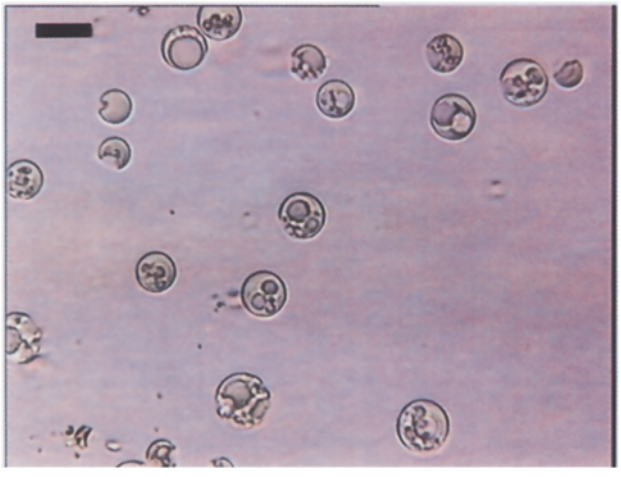
Methods

Each step of the synthesis is controlled by optical microscopic observation to check if the magnetic fluid is really confined, first in the droplets of the emulsion, second in the vesicles. The magnetic fluid has a characteristic orange color and thus may be easily located in the preparation.

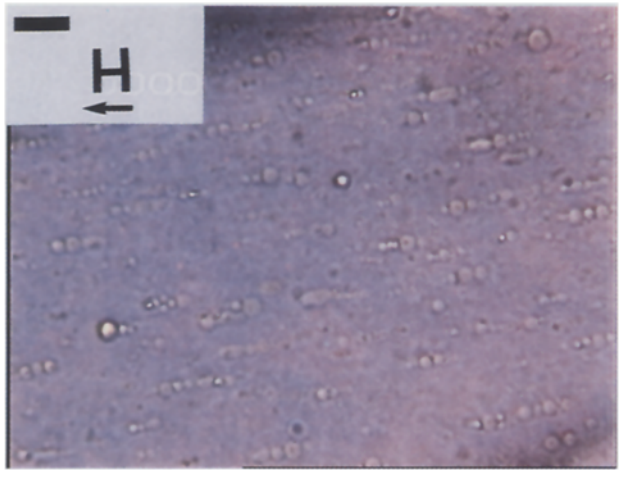
Negative stain electron microscopy is performed according to the procedure described in ref. [16] : A drop of the solution of vesicles is deposited on the microscope grid initially covered by a carbon film. Two minutes are allowed for the vesicles to attach to the film and the excess of solution is drawn off and replaced with a drop of a solution of uranyl acetate (2% in weight). After 5 min the excess of colorant is drawn off in order



a



b



c

to get a thin film of heavy metal in which the vesicles are embedded.

Magnetization curves of the suspensions of magnetic vesicles have been performed using a vibrating magnetometer (Foner) [17].

Results

Optical microscopy

The different steps of the synthesis of magnetic vesicles have been followed by optical microscopy (Fig. 2). Figure 2a corresponds to the first step of the synthesis, i.e., the synthesis of the emulsion of the aqueous magnetic fluid in a mixture of ether-/cyclohexane. The magnetic fluid appears as orange droplets in a colorless background. Figure 2b corresponds to the multiple emulsion: the droplets of magnetic fluids are inside larger droplets of oily phase, themselves dispersed in water. After evaporation of the oily phase, the double layers are formed and the vesicles synthesized. In the absence of an applied magnetic field, they appear as almost spherical orange droplets. When a magnetic field is applied, the droplets align along the direction of the field and some of them lose their shape and become elongated in the direction of the field (Fig. 2c).

Electron microscopy

Figure 3 is a typical electron micrograph of a preparation of magnetic vesicles. The vesicles appear as polydisperses spherules, with a diameter ranging from 0, 1 to 5 μm. The magnetic particles, identified by their electron diffraction, are well encapsulated inside the vesicles (Fig. 4).

Fig. 2. Optical micrographs magnification × 900: a) of the emulsion of the aqueous magnetic fluid (dark droplets) in a mixture cyclohexane/ether; b) of the multiple emulsion: the aqueous magnetic fluid appears as dark droplets inside the larger droplets which are constituted by the mixture cyclohexane/ether and are dispersed in water; c) of the final magnetic vesicles obtained after evaporation of the intermediate cyclohexane/ether phase: the magnetic fluid appears as darker than the outside water; These vesicles submitted to a magnetic field, align along the direction of the field and some of them change shape. The bar represents 10 μm.

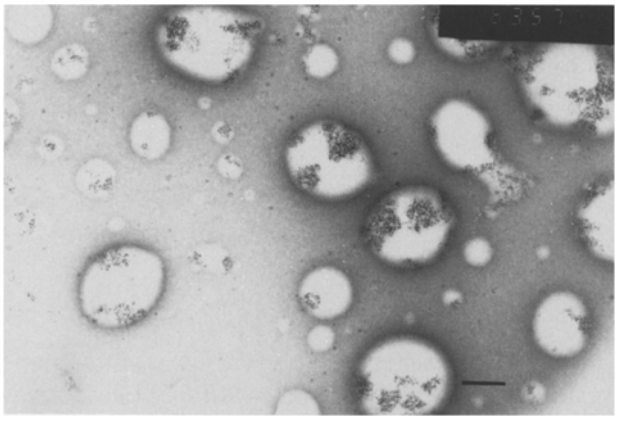


Fig. 3. Electron micrograph (negative stain) of a typical preparation of magnetic vesicles. The bar represents 0.3 μm.

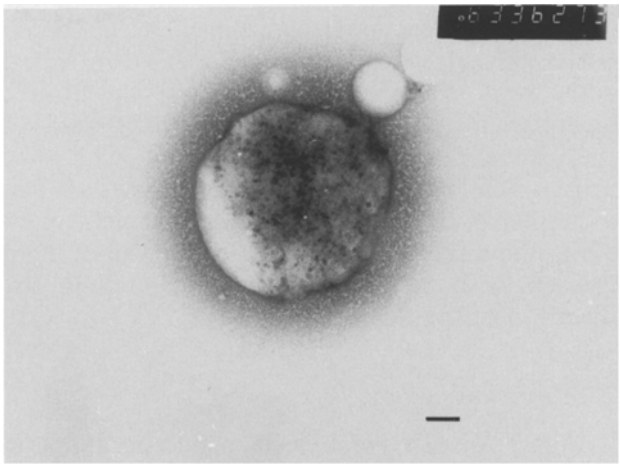


Fig. 4. Electron micrograph of a magnetic vesicle magnification. The bar represents 0.07 μm.

Magnetization curve

The magnetization curve of a magnetic fluid, constituted by magnetic particles without interactions, is of the Langevin type [17] with a saturation magnetization proportional to the concentration in magnetic particles, and a shape which is a function of the size distribution of the particles. The magnetization curve of the suspension of magnetic vesicles is compared to the magnetization curve of the magnetic fluid before encapsulation in Fig. 5. Even if low, the saturation magnetization of the vesicles is measurable and the shape of the curve is the same as the one for the initial magnetic fluid, indicating that the magnetic behavior of the latter is not modified by encapsulation.

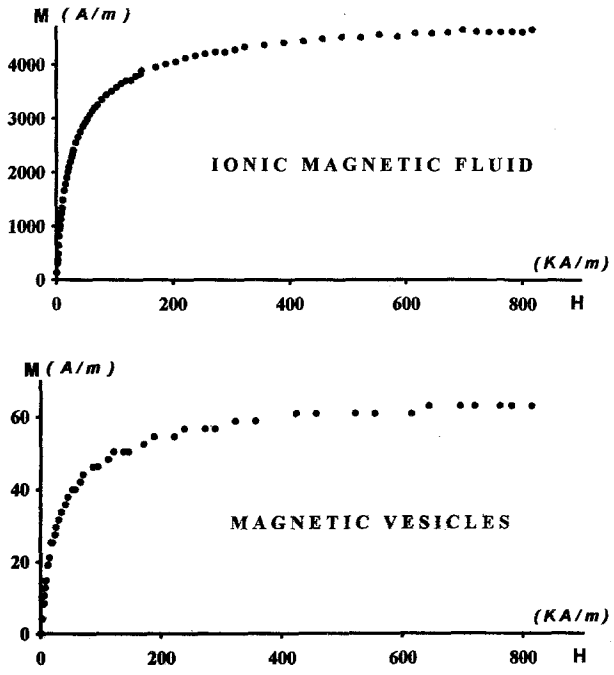


Fig. 5. Magnetization curves of the initial aqueous magnetic fluid (a) and of the corresponding suspension of magnetic vesicles (b).

Conclusion

We have proposed a procedure to encapsulate aqueous ionic ferrofluids in DDAB vesicles, and then produced magnetic vesicles with a diameter ranging from 0.1 to 5 μm, which are able to move and to become elongated when a magnetic field is applied. This procedure allows the confinement in the vesicles of magnetic solutions with a volume fraction in particles that may range 10%. The DDAB vesicles are rather rigid, and most of them are multilamellar. Nevertheless, the procedure may be extended to other systems in order to produce unilamellar systems and to study the deformation of magnetic vesicles.

Acknowledgements

The authors are greatly indebted to Monique Dubois and Thomas Zemb for helpful discussions. They also sincerely

thank M. Lavergne, who performed the electron micrographs in the Groupement Régional de Mesures Physiques (Université Pierre et Marie Curie).

References

1. Matuo CY, Tourinho FA, Figueiredo Neto AM (1993) J Magn Magn Mat 122:53–56
2. Fabre P, Casagrande C, Veyssie M, Cabuil V, Massart R (1990) Phys Rev Lett 64(5):539–542
3. Dabadie JC, Fabre P, Veyssie M, Cabuil V, Massart R (1990) J Phys Condens Matter 2:SA 291–SA 294
4. Fabre P, Ober R, Veyssie M, Cabuil V (1990) J Magn Magn Mat 85:77–81
5. De Cuyper M, Joniau M (1988) Eur Biophys J 15:311–319
6. De Cuyper M, Joniau M (1991) Langmuir 7:647–652.
7. Herve P, Nome F, Fendler JH (1984) J Am Chem Soc 106:8291–8292
8. Mann S, Hannington JP, Williams RJP (1986) Nature 324:565–567
9. Mann S, Hannington JP (1988) J. Colloid Interface Sci. 122(2):326–335
10. Grow DT, Sonti SV, Bose A, Raj K (1993) J Magn Magn Mat 122:343–348
11. Bacri JC, Perzynski R, Salin D, Cabuil V, Massart R (1990) J Magn Magn Mat 85:27–32
12. Massart R (1981) IEEE Trans Magn MAG-17:1247–1248
13. Dubois M, Zemb Th (1991) Langmuir 7:1352–1360
14. Kim S, Martin GM (1981) Biochim Biophys Acta 646:1–9
15. Kim S, Turker MS, Chi EY, Sela S, Martin GM (1983) Biochim Biophys Acta 728:339–348
16. New RRC (1990) in: Liposomes: a practical approach. IRL Press p 140
17. Bacri JC, Perzynski R, Salin D, Cabuil V, Massart R (1986) J Magn Magn Mat 62:36–46.

Received November 16, 1993;
accepted February 25, 1994

Authors' address:
Dr. V. Cabuil
Universite Pierre et Marie Curie
Laboratoire de Physicochimie Inorganique, casier 63
4, Place Jussieu
75252 Paris Cedex 05, France