JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 949 - 951

Microscopic observation of ferrofluid droplet formation from a cylindrical channels membrane

V. BĂDESCU*, R. BĂDESCU[a]

National Institute of Research and Development for Technical Physics, Iasi, 700050, Romania

[a] Technical University "Gh. Asachi", Department of Physics, Iasi, 700050, Romania

Real-time microscopic observations of the membrane emulsification process of some ferrofluids were performed using a polycarbonate membrane module and an optical microscope video system. The droplet growth and the processes of detachment from the membrane cylindrical pores were analyzed via visual images taken during the experimental runs. The work also describes the influence of the continuous phase flow field structure and of flow velocity, as well as the applied magnetic field during membrane emulsification.

(Received November 2, 2006; accepted February 28, 2007)

Keywords: Ferrofluid, Emulsion, Membrane, Optical observation

1. Introduction

Microencapsulation of inorganic submicrometer particles with polymer walls have been extensively investigated in order to include novel composite lattices, dispersions, and particulates into coating materials, film formation, toners, cosmetic, biological and medical applications. In the medical areas, they can be used as drug carriers and as particles for clinical diagnosis [1]. Delivery of chemotherapeutic agents to desired target sites for the treatment of localized disease with a minimum of systemic side effects constitutes one of the major challenges of chemotherapy. Although particulate drug-carrier systems might be useful against some diseases in the reticulo-endothelial system or lungs, only limited means are available to direct it efficiently to other selected sites in the body.

In recent years a great number of works showed that magnetically responsive polymer microspheres that contain terapeutic agents and colloidal magnetite could be selectively targeted to the subcutaneous targets by utilizing externally applied magnetic fields [2,3]. Also, since ferrofluid emulsions showed a degree of magnetic response, it was possible to retain and immobilize a large amount of the drugs trapped in the blood capillaries under the applied magnetic field [4,5]. Ferrofluids are colloidal suspensions of superparamagnetic nanometer sized particles in a suitable liquid carrier [6,7]. Emulsions are colloidal systems constituted of droplets of a liquid dispersed in another immiscible one. Depending on the application for which the emulsion is tailored, water is the constituent of the external continuous phase (direct oil-in-water (o/w) emulsion) or the internal dispersed phase (reverse water-in-oil (w/o) emulsion).

The ferrofluid emulsions have two major practical applications: firstly, their microscopic droplets can constitute the precursors for obtaining magnetic microcapsules by polymerization or other procedures; secondly, thei microdroplets are themselves carriers for therapeutic agents. Emulsions with 0.1–100 μm droplet sizes are commonly prepared using colloid mils, rotor–stator systems, high-pressure homogenizers and ultrasonic homogenizers. Turbulent or cavitational flow in the dispersing regime of these emulsification devices breaks up one of two immiscible fluids into smaller droplets, which disperse in a continuous phase fluid. The average size and the size distribution of these droplets is of critical importance, as they determine the ability of the emulsion to prevent coalescence and how appropriate it is for the intended use. For successful application in these fields, it is necessary to control the droplet size of monodispersed emulsions. In the use of magnetic microparticles as supports in diagnostics or as carriers for delivering drugs it is important to control their size and size distribution because each of these factors can have a great effect on molecule and cell adsorbtion or on drug release, respectively.

Membrane emulsification has received much attention over the last 15 years as a potential technique for preparing emulsions with narrow size distribution [8-10]. The emulsion is formed by forcing the dispersing phase to transform into a continuous phase by passing through the membrane pores. Porous glass and ceramic membranes with uniform pores have been used in membrane emulsification on laboratory and industrial scales. These porous membranes yield relatively uniform emulsions with droplet sizes of 0.3-30 μm under suitable operating conditions. In addition, membrane emulsification that applies small shear stress and low energy input is available for preparing emulsions that contain shear-sensitive materials.

In the optimization of membrane emulsification process it is important to understand how emulsion droplets grow and detach from the membrane pores. We developed a micro-visualization system of membrane emulsification composed of a hydrophilic polycarbonate membrane with cylindrical pores and an optical microscope video system. The objective of our study was to observe and characterize the ferrofluid emulsification through a membrane with cylindrical pores. Also, we aimed at investigating the influences o some fundamental process parameters such as the continuous phase transverse flow velocity and the applied magnetic field on the membrane ferrofluid emulsification.

2. Experimental

An organic ferrofluid was prepared by us and used as the dispersed phase. As continuous phase we used a solution of 0.3 wt.% sodium dodecyl sulfate (SDS) in distilled water.

The ferrofluid synthesis was carried out at room temperature according to the following recipe. First, iron oxide nanoparticles were synthesized by coprecipitation from an acidic solution of ferrous and ferric chlorides using concentrated ammonia. Iron salts were used in an initial molar ratio $[Fe^{3+}]/[Fe^{2+}] = 2$ in order to avoid the formation of non-magnetic hydroxides such as $Fe(OH)_3$. When the pH of the medium was around 9, oleic acid was added to the dispersion under vigorous stirring. Then, by introducing kerosene in the medium, the hydrophobic modified iron oxide nanoparticles were extracted directly into the organic solvent. Finally, the organic ferrofluid was centrifuged at 14,000rot/min to eliminate aggregates and the supernatant was retained for characterization and emulsification.

The size distribution of magnetite particles in the obtained ferrofluid was determined by a dynamic light scattering method (DLS) and by magnetogranulometry analysis [11, 12]. The magnetization curve was obtained using a balance force method.

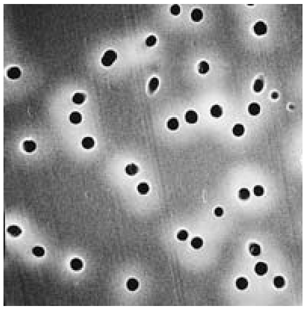

Fig.1. Scanning electron microscopy of a polycarbonate membrane.

The membranes used in the present work were from Nucleopore Co. This type of membrane is manufactured by irradiating a thin polycarbonate film in a field of α-particles and then chemically etching the film to produce essentially straight, circular pores that are nearly perpendicular to the membrane surface. The scanning electron microscopy image in Fig. 1 indicates that the polycarbonate membrane possesses uniformly sized cylindrical pores. These pores are distributed randomly though they sometimes overlap, creating larger pores.

The membrane emulsification system, schematically depicted in Fig. 2, consist of a membrane module, a syringe pump to feed the dispersed phase, a peristaltic pump to feed the dispersed phase, and the optical microscope video system. The emulsification process was visualized in real time through an acryl plate in the module and was recorded via optical microscope (Krües Optics, Germany) using a CCD videocamera (Sony DCR-HC85E) with a total magnification of 1000. A 25 mm diameter polycarbonate membrane was mounted in the membrane module between two flat acryl plates, using rubber spacers to form lower and upper chambers. The lower part was the disperse phase-feed camber and the upper part was the permeate camber. The membrane module has an effective membrane area of 1.75 cm^2 and the thickness of continuous phase fluid film in the upper chamber is approximately 500 µm. The membrane module is mounted coaxially in the center of a Helmholtz coil that can generate a magnetic field of up to 40 kA/m transverse to the membrane plane.

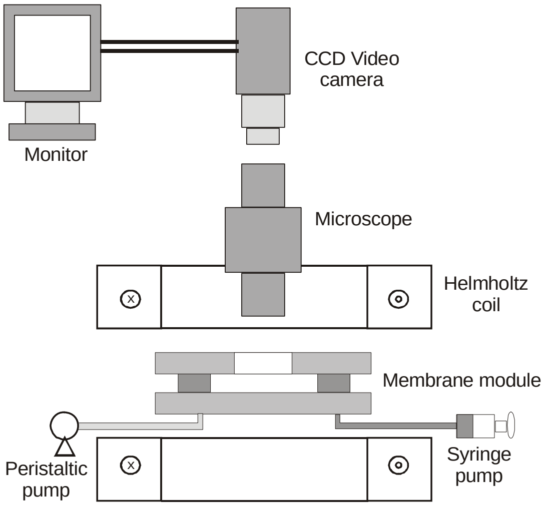

Fig. 2. Experimental setup for membrane emulsification.

3. Results and discussion

The magnetization of saturation for the obtained ferrofluid depends on the volume fraction of the magnetite which remains in suspension after the centrifugation process. Usually, the ferrofluids obtained after centrifugation were concentrated by evaporation under vacuum at room temperature. The magnetization of saturation of the tested ferrofluid was of 150 Gs (12 kA/m). The result of magneto-granulometric analysis for this ferrofluid is presented in Fig. 3. The particle size distribution is a lognormal function and the average size of the particles which states the magnetization of ferrofluid is 8.9 nm.

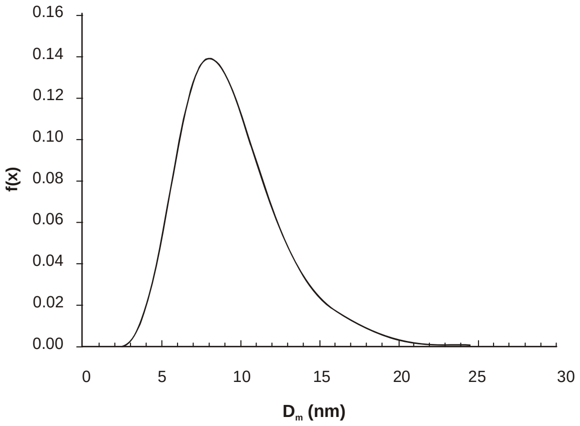

Fig. 3. The function of distribution of particle size determined by magnetogranulometric analysis of magnetization curve.

The size distribution obtained by DLS showed an average size of the magnetic particles from suspension of ~20 nm. The larger average size determined by DLS for the tested ferrofluid can be attributed to a certain extent of flocculation of magnetite particles after centrifugation.

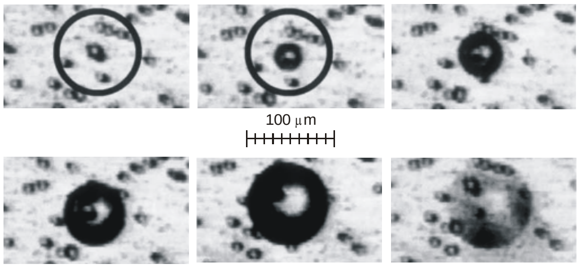

Fig. 4. Optical microscopic images of the membrane emulsification process for the ferrofluid/water (0.3% SDS) system.

Fig. 4 illustrates typical behavior of droplet formation on the polycarbonate membrane surface. The ferrofluid flux was set at a value of $3\times10^{-6}m^3/(m^2s)$ and the continuous–phase flow velocity at 0.020 m/s. The ferrofluid penetrates through a pore and starts growing as a droplet at the pore tip. The almost spherically shaped droplet continues to grow until it detaches under drag force imposed by continuous phase. The polycarbonate membrane yielded almost uniformly sized droplets from each pore, whereas the droplet size depended on the site of the pore. This indicates less monodispersity of the prepared O/W ferrofluid emulsion.

The continuous phase flow velocity is a process parameter tat can determines the drops characteristics with membrane emulsification. In our experiments, when the average flow velocity was increased from 0.025 to 0.050 m/s under a fixed ferrofluid flux of 130 $L/m^2/h$, the average droplet diameter decreased significantly up to a flow velocity of 0.03 m/s, and then remained almost constant.

An interesting observation in our experiment was the effect of the applied magnetic field. When a magnetic field is applied normal to the membrane surface, the ferrofluid drops detached as small average droplet diameter. For a flow velocity of the continuous phase in the range tested by us, an increase in magnetic field intensity from 8 kA/m to 40 kA/m resulted in nearly halved average droplet diameter. This effect can be attributed to an increase of contact angle at interface between ferrofluid and solid membrane in the aqueous continuous phase.

4. Conclusions

Microscopic observations of the membrane ferrofluid emulsification process enabled on one hand a better understanding of the characteristics of droplet formation from the membrane pores, and on the other hand of the importance of process parameters such has the continuous phase flow velocity and the applied magnetic field intensity.

Acknowledgements

This work was supported by the CERES 4 Program of the National Authority for Scientific Research, Romania.

References

[1] S. Slomkowski, T. Basinska, B. Miksa, Polym. Adv. Technol. **13**, 906 (2002).
[2] K O'Grady, J. Phys. D: Appl. Phys. **36,** R165 (2003).
[3] A. K. Gupta, M. Gupta, Biomaterials **26**(18), 3995 (2005).
[4] M. Akimoto, Y. Morimoto, Biomaterials **4**, 49 (1983).
[5] M. Akimoto, K. Sugibayashi, Y. Morimoto, J. Contr. Release **1**, 205 (1985).
[6] R. E. Rosensweig, Ferrohydrodynamics, Cambridge University Press, Cambridge, London, New York, (1985).
[7] B. Berkovski, V. Bashtovoi, (Ed.), Magnetic Fluids and Applications Handbook, Begel Haouse, New York, (1996).
[8] T. Nakashima, M. Shimizu, T. Ishikawa, Key Eng. Mater. **61/62**, 513(1991).
[9] V. Schröder, H. Schubert, Col. Surf. Physicochem. Eng. Aspects **152**, 103(1999).
[10] S. M. Joscelyne, G. Trägårdh, J. Food Eng. **39**, 59 (1999).
[11] R. W. Chantrell, J. Popplewell, S. W. Charles, IEEE Trans. Magn. **MAG-14**, 975 (1978).
[12] L. Vekas, M. Rasa, D. Bica, J. Colloid Interface Sci. **231**, 247 (2000).

---

[*] Corresponding author: bav02@phys-iasi.ro