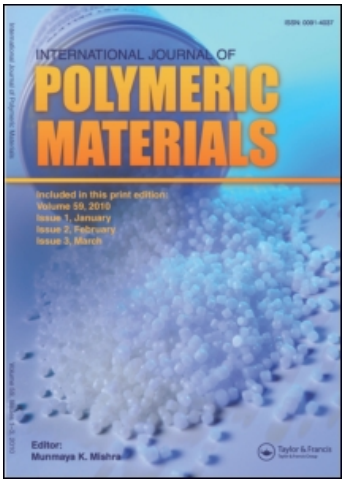

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Transmission Electron Microscopy Observations of Micelle Structure in a Vinyl Acetate-based Microemulsion

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Transmission Electron Microscopy Observations of Micelle Structure in a Vinyl Acetate-based Microemulsion

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One of the biggest challenges in studying micro-emulsions is the precise determination of the spatial structure of their micelles, to the extent that very scarce literature is available on this subject. In this work, a study of the various preparation techniques for the Transmission Electron Microscopy (TEM) analysis of a micro-emulsion of the vinyl-acetate/water/surfactant system is presented. The results indicate that the preparation method is a determining parameter if meaningful results are to be obtained.

Keywords: Micro-emulsions; micelles; vinyl-acetate transmission electron microscopy

INTRODUCTION

Most of the available studies to investigate micellar and micro-emulsion systems are scattering techniques: light scattering [1–4], small-angle neutron scattering [5–10], and X-ray scattering [11–13]. However, these techniques only provide specific features of a micro-emulsion. For instance, by these techniques, one can obtain the size of

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the droplets, but not their shape and micellar distribution. Electron microscopy is about the only technique by which the colloidal microstructure can be analyzed by direct visualization, along with the corresponding micellar distribution.

There exists great interest in many research areas to observe the structure of colloids, emulsions, sol, and gels. The observation of spatial structure in these complex fluids by electron microscopy poses particular problems since common methods of preparing samples for TEM observation, such as dessication and chemical fixation, can alter their structure. Other methods, such as freeze-fracture or replication techniques are difficult or time-consuming and only show the fracture surface.

Cryo-electron microscopy has long been regarded as a appropriate method for preserving the specimen in a state closer to its native state. Frozen aqueous solutions are the medium in which microemulsions are observed, but it is necessary to obtain thin layers of frozen aqueous solutions in the vitreous state. The traditional techniques for preparing liquids and colloidal dispersions for cryo-TEM can be summarized as follows:

Frozen double-film technique: it consists in trapping a thin layer of liquid between two very thin polymer films, then mount the sandwich on a grid and freeze it in a cryo stage [14, 15]. In this technique the radiation damage to the frozen sample with distilled water between two Formvar films, is strong [16, 17] and some authors have used cellulose nitrate films (collodion) [18].

Cryo-vitrification with freezing ethane at high cooling rate. It is utilized to prevent crystallization where a thin sample is plunged into liquid ethane to prevent crystallization, transferred under liquid nitrogen and finally inserted into TEM [19, 20, 21].

Other freezing methods, such as spraying into liquid nitrogen or jetting a liquid cryogenic against the specimen are summarized in Ref. [22].

EXPERIMENTAL

A set of micro-emulsions of the ternary system of dodecyltrimethyl ammonium bromide/vinyl/acetate/aqeous solution of 0.25 M NaBr

(DTAB/VA/solution) with different compositions were studied [23], as described in Table I.

A drop of each micro-emulsion was deposited on a clean 400 mesh copper specimen-supporting grid, coated with a very thin carbon film. Most of the excess liquid was removed with clean drying paper and then frozen with vapors of liquid nitrogen. Later on the sample was immersed into liquid nitrogen. The grid, kept under liquid nitrogen, is then transferred into the cryo-specimen holder and inserted in the microscope (a JEOL 100 CX, analytical configuration) for observation.

RESULTS AND DISCUSSION

Figures 1–6 contain the micrographs for the different proportions of the ternary micro-emulsion systems. All of them show different shapes and sizes of the micro-emulsion vesicles. Figure 1 correspond to sample A (Tab. I), showing esferical vesicles between 59 nm – 130 nm immersed within the matrix. We had difficulties to focus properly this structure, probably because a specimen-supporting grid coated with carbon film was used, which produces a thin layer onto the material. Figure 2 corresponds to sample B and shows many bubbles ranging 20 nm – 100 nm supported in the matrix. Figure 3 (sample C), prepared onto an uncoated grid, shows now irregularly-structured vesicles including some spherical shapes ranging 50 nm – 160 nm. In this micrograph a good contrast was easily achieved. Figure 4 (sample D), shows structures with irregular shapes between 70 nm – 130 nm. Figure 5 (sample E) presents the micro-emulsion like homogenous particles of different sizes between 140 nm – 350 nm, were single phases

TABLE I Composition of microemulsion

Sample	*DTAB*	*VA*	*Solution*
A	4.9	2.0	93.1
B	9.8	2.0	88.2
C	9.5	5.0	85.5
D	18.8	6.0	75.2
E	38.0	5.0	57.0
F	32.0	20.0	48.0

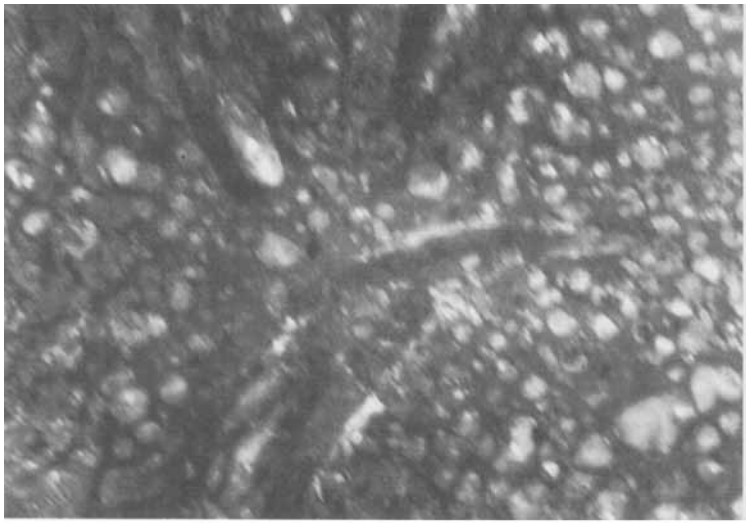

FIGURE 1 Sample A DTAB/VA/solution (4.9/2.0/93.1).

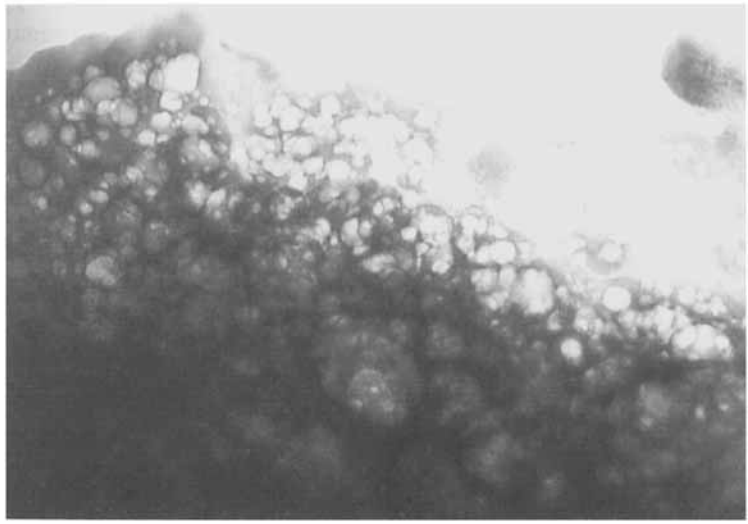

FIGURE 2 Sample B DTAB/VA/solution (9.8/2.0/88.2).

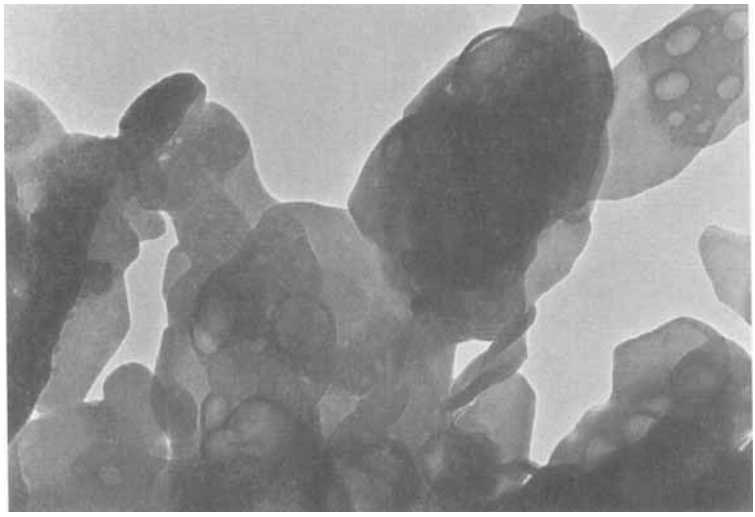

FIGURE 3 Sample C DTAB/VA/solution (9.5/5.0/85.5).

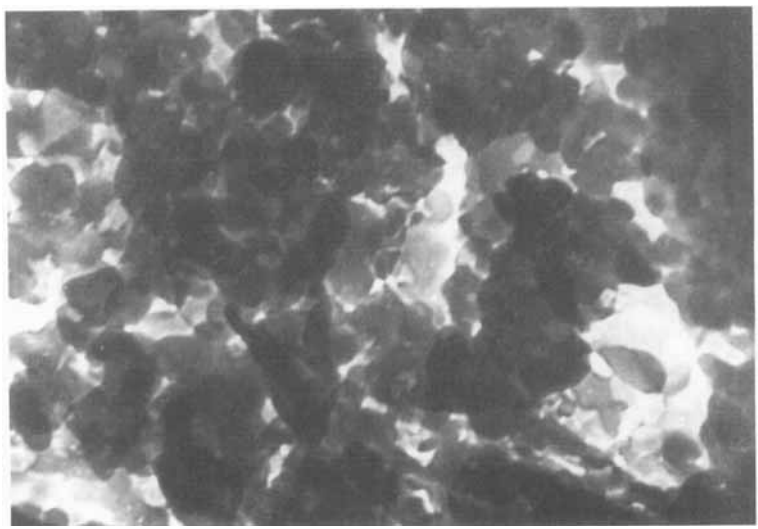

FIGURE 4 Sample D DTAB/VA/solution (18.8/6.0/75.2).

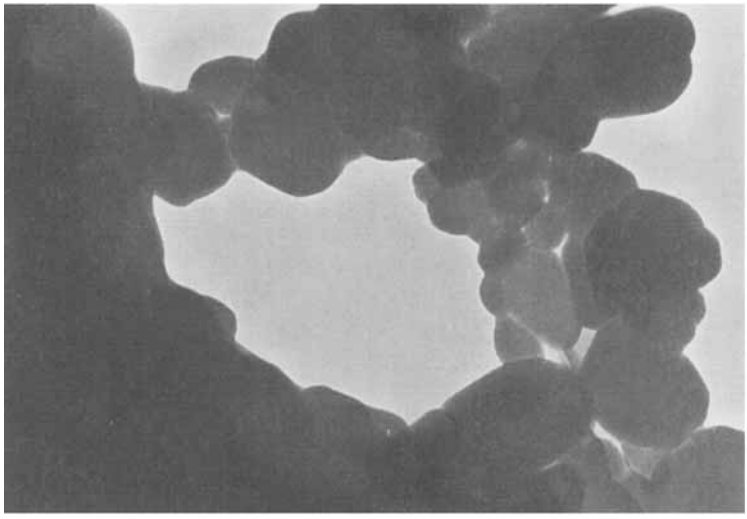

FIGURE 5 Sample E DTAB/VA/solution (3.80/5.0/57.0).

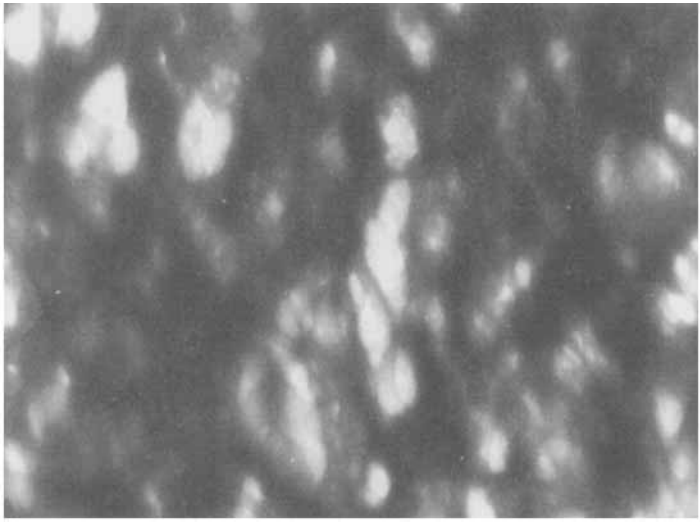

FIGURE 6 Sample F DTAB/VA/solution (32.0/20.0/48.0).

are observed. Figure 6 (sample F) shows some spherical irregular porous films, with the pores ranging from 70 nm to 250 nm.

CONCLUDING REMARKS

In spite that some authors mention that liquid nitrogen freezing induces crystallite formation, these can also be formed by electron irradiation. However, the alternative procedure presented here allows to avoid both effects and achieve good observations of the microemulsions, as the images shown have demonstrated. In any case, the role of the preparation route when performing TEM morphological studies is a key parameter to consider when interpreting the observations.

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References

[1] Huang, J. S. and Kim, M. W. (1981). *Phys. Rev. Lett.*, **47**, 1462.
[2] Rodriguez-Guadarrama, A., Mendizabal, E., Puig, J. E. and Kaler, E. W. (1993). *J. Appl. Polymer Sci.*, **48**, 775.
[3] Tartaglia, P., Ducros, E., Chabrat, P., Rouch, J. and Chen, S. H. (1993). *J. Phys. IV*, **3**, 249.
[4] Rouch, J., Safouane, A., Tartaglia, P. and Chen, S. H. (1989). *J. Chem. Phys.*, **90**, 3756.
[5] Atkinson, P. J., Grimson, M. J., Heenan, R. K., Howe, A. M., Mackie, A. R. and Robinson, H. (1988). *Chem. Phys. Lett.*, **151**, 494.
[6] Eastoe, J., Robinson, B., Steytler, D. C. and Dore, J. C. (1990). *Chem. Phys. Lett.*, **166**, 153.
[7] Chen, S. H., Ku, C. Y., Rouch, J., Tartaglia, P., Cametti, C. and Samseth, J. (1993). *J. Phys. IV*, **3**, 143.
[8] Abillon, O., Lee, L. T., Langevin, D. and Wong, K. (1991). *Physica A*, **172**, 209.
[9] Kotlarchyk, M., Chen, S., Chen, H., Huang, J. S. and Kim, M. W. (1984). *Phys. Rev. A*, **29**, 2054.
[10] Kotlarchyk, M., Chen, S., Chen, H. and Huang, J. S. (1983). *Phys. Rev. A*, **28**, 2054.
[11] Schulman, H., Stockenius, W. and Prince, L. M. (1959). *J. Phys. Chem.*, **63**, 1677.

[12] Kaler, E. W., Bennet, K. E., Davis, H. T. and Scriven, L. E. (1983). *J. Chem. Phys.*, **79**, 5673.
[13] Auvray, L., Cotton, J. P., Ober, R. and Taupin, C. (1984). *J. Phys. (Paris)*, **45**, 913.
[14] Talmon, Y., Davis, H. T., Scriven, L. E. and Thomas, E. L. (1979). *Rev. Sci. Intrum.*, **50**, 698.
[15] Talmon, Y. and Miller, W. G. (1978). *J. Collid Interphace, Sc.*, **6**, 284.
[16] Dubochet, J., Chang, J.-J., Freeman, R., Lepault, J. and McDowall, A. W. (1982). *Ultramicroscopy*, **10**, 55.
[17] Dubochet, J., Lepault, J., Freeman, R., Berriman, J. A. and Homo, J.-C. (1982). *J. Microscopy*, **128**, 219.
[18] Talmon, Y. (1984). *Ultramicroscopy*, **14**, 305.
[19] Bailey, J., Bellare, J. R. and Mecartney, M. L. (1988). *Mat. Res. Soc. Symp. Proc.*, **115**, 69.
[20] Bellare, J. R., Sheehan, J. G., Davis, H. T. and Scriven, L. E. (1988). *Mat. Res. Soc. Symp. Proc.*, **115**, 75.
[21] Adrian, M., Dubochet, J., Lepault, J. and McDowall, A. W. (1984). *Nature*, **308**, 32.
[22] Robards, A. W. and Wilson, A. J. (1996). In: Procedures in Electron Microscopy, Jon Wiley & Sons. Eds. Centre for Cell and Tissue Research University of York, UK **2**, N°**16**.
[23] López, G., private communication.