

Acoustic Spectroscopy for Characterizing Heptane/H₂O/AOT Reverse Microemulsions

Thomas H. Wines,* Andrei S. Dukhin,† and Poniseril Somasundaran*

*Columbia University, 1140 Amsterdam Avenue, New York, New York 10027; and †Dispersion Technology Inc., 3 Hillside Avenue, Mt Kisco, New York 10549

Received January 8, 1999; accepted May 19, 1999

Acoustic spectroscopy was used to monitor the droplet size distribution in a classic three component system of heptane, water, and aerosol-OT (AOT). The size of the reverse microemulsion drops was varied by changing the molar ratio of water to AOT surfactant. The acoustic results for this transparent microemulsion were found to be in close agreement with literature results obtained with small angle neutron scattering and small angle X-ray scattering. The system was investigated well into the turbid region where microemulsion changes to macroemulsion. The droplet size distribution was found to shift to a bimodal form due to this transition. © 1999 Academic Press

Key Words: acoustic; microemulsion; reverse, Aerosol-OT; AOT; heptane; SANS; SAXS; PSD.

INTRODUCTION

The mixture of heptane with water and AOT is a classic three component system. It has been widely studied due to a number of interesting features it exhibits. This system forms stable reverse microemulsions (water in oil) without the complication introduced by an additional cosurfactant. Such a cosurfactant (usually alcohol) is required by many other reverse microemulsion systems. This simplification makes the alkane/water/AOT system a model for studying reverse microemulsions.

There have been many studies devoted to the characterization of these practically important systems. Reverse emulsion droplets have been used as chemical microreactors to produce nano-sized inorganic and polymer particles with special properties that are not found in the bulk form (1–5). These microemulsion systems have also been a topic of research for biological systems and the AOT head groups have been found to influence the conformation of proteins and increase enzyme activity (6–9). The unique environment created in the small water pools of swollen reverse micelles allows for increased chemical reactivity. The increase in surface area with the decrease in size of the droplets also can significantly increase reactivity by allowing greater contact of immiscible reactants.

There have been many attempts to measure the droplet size of this microemulsion. Several different techniques were used:

PCS (10–15), classic light scattering (12, 14, 16), SANS (17–19), SAXS (11, 20, 21), ultracentrifugation (9, 13, 16), and viscosity (11, 12, 14). It was observed that the heptane/water/AOT microemulsions have water pools with diameters ranging from two nanometers up to thirty nanometers. The water drops are encapsulated by the AOT surfactant so that virtually all of the AOT is located at the interface shell. The size of the water droplets can be conveniently altered by adjusting the molar ratios of water to surfactant designated as R ($[H_2O]/[AOT]$). At low R values ($R \leq 10$) the water is strongly bound to the AOT surfactant polar head groups and exhibits unique characteristics different from bulk water (16). At higher water ratios, ($R > 20$), free water is predominant in the swollen reverse micellar solutions, and at approximately $R = 60$, the system undergoes a transition from a transparent microemulsion into an unstable turbid macroemulsion. This macroemulsion separates on standing into a clear upper phase and a turbid lower phase.

The increase in droplet size and phase boundary can also be achieved by raising the temperature up to a critical temperature of 55°C. In addition this system has been found to exhibit an electrical percolation threshold whereby the conductivity increases by several orders of magnitude by either varying the R ratio or increasing the temperature (19, 20, 22, 23). Despite all these efforts, there still remain questions regarding the polydispersity of the water droplets, and few studies are available above the R value of 60 where a turbid macroemulsion state exists.

Acoustic Spectroscopy

Acoustic spectroscopy offers a new opportunity for characterizing these complicated systems. This technique has the advantage of being applicable to turbid emulsions where other methods such as light scattering will not work. Dilution of such systems can indeed alter their physical properties. Acoustic spectroscopy is also sensitive enough for characterizing *polydispersity*. There have been many successful application of this technique to regular emulsions (24–27). However, acoustic characterization of microemulsions for drop size and polydispersity has not been reported.



Acoustic spectroscopy of heterogeneous systems operates within a frequency range from 1 to 100 MHz. The frequency dependence of the attenuation coefficient is the normal experimental output of the acoustics. This frequency spectrum can be converted to the particle size distribution.

The above-mentioned conversion procedure is based on a theory of the sound propagation through the dispersed system. A theory created by Epstein and Carhart (28) and Allegra and Hawley (29) ("ECAH" theory) was developed for dilute systems where particle-particle interaction can be neglected. The ECAH theory can be applied even for characterizing concentrated emulsions because the predominant acoustic attenuation loss is thermal in nature. Thermal losses have been found to be almost insensitive to particle-particle interaction due to relatively thin thermal layers where the particles start to affect each other. This mechanism dominates attenuation of ultrasound in emulsions and this permits characterization of concentrated systems in an unperturbed state, without any dilution.

MATERIALS

Aerosol-OT (AOT, dioctyl sulfosuccinate sodium salt) was obtained from Sigma (SigmaUltra grade, 99% purity by thin layer chromatography, < 0.1% insolubles). The AOT was dissolved in methanol (Sigma, HPLC grade, 99.9% purity) with activated charcoal (Sigma, 100–400 mesh, previously rinsed in 18 megohm-cm water), then filtered through a 0.45 micrometer nylon membrane, and placed in a roto-vap to evaporate off the methanol under vacuum. This left a waxy white solid that was stored under vacuum for at least 48 h prior to use. This procedure generally follows the guidelines in the literature (30–32).

The water used in this study was semiconductor grade with a resistance of 18 megohm-cm, and total oxidizable carbon (TOC) content of less than 1 part per billion. The water was purified by reverse osmosis, ozone, UV light, ion exchange resin, and 0.04 micrometer filtration. Upon contact with air, some carbon dioxide was absorbed, and this gave the water a pH of 6.5.

The reverse microemulsions were prepared by first making a 0.1 molar AOT in heptane solution (6.1 wt% AOT). The heptane was obtained from Sigma as HPLC grade (99+ % purity). Known amounts of 18 megohm-cm water were added to the AOT-heptane solution using a 1 ml total volume, graduated glass syringe and then shaken for 30 s in Teflon capped glass bottles. The shaking action was required to overcome an energy barrier to distribute the water into the nano-sized droplets, as it could not be achieved using a magnetic stirrer.

In all cases, the reported *R* values are based on the added water and were not corrected for any residual water that may have been in the dried AOT or heptane solvent. Karl Fischer analysis of the AOT-heptane solutions before the addition of

TABLE 1
Physical Properties of Water and Heptane at 25°C

	Heptane	Water
Density [g cm ⁻³] (ρ_p)	0.68	0.997
Sound speed [m s ⁻¹] (c_p)	1153	1497
Specific heat [J g ⁻¹ K ⁻¹] (C_p)	2.29	4.179
Thermal conduction [mW cm ⁻¹ K ⁻¹] (τ_p)	1.3	6.1
Thermal expansion [K ⁻¹ 10 ⁴] (β_p)	12.1	2.07
Intrinsic losses [α_p/f^2] [dB cm ⁻¹ Mhz ⁻²]	0.00442	0.00217

water resulted in a *R* value of 0.4. This amount was considered to be negligible.

Acoustic spectroscopy of emulsions requires input of the thermodynamic properties of the liquid phases. These properties are listed in Table 1.

EXPERIMENTAL

A combined acoustic and electroacoustic spectrometer DT-1200 developed by Dispersion Technology, Inc. was used here (33). This instrument has two separate sensors for measuring acoustic and electroacoustic signals independently.

Both sensors use the pulse technique. The acoustic sensor measures attenuation frequency spectrum and group sound speed. The acoustic sensor has two piezoelectric crystal transducers. The gap between the transmitter and the receiver can be changed in steps. In default it changes from 0.15 up to 20 mm in 21 steps. The basic frequency of pulse changes in steps as well. In default it changes from 3 to 100 MHz in 18 logarithmic steps. The number of pulses collected for each gap and frequency is automatically adjusted in order to reach a target signal-to-noise ratio. The acoustic sensor measures group sound speed at one chosen frequency using the change in transit time of the pulse vs the gap. The instrument automatically adjusts the pulse sampling depending on the value of the sound speed, which is necessary to eliminate artifacts such as excess attenuation at low frequencies.

A single attenuation spectrum is measured using default conditions in about 5–10 min. Measurement can be sped up by changing setup parameters and successive measurements on the same sample made even faster.

A special analysis program is used to calculate the particle size distribution (PSD) from the attenuation spectrum. This program tests lognormal, bimodal, and modified lognormal (34) particle size distributions and uses error analysis in order to search for the best PSD. The goal of the optimization procedure is to minimize the error in the theoretical fit of the experimental attenuation spectrum.

The precision and accuracy of the acoustic spectrometer has been tested with several different systems (35). For the system of BCR silica quartz (12 wt%) in ethanol, the precision of the particle sizing is about 1%. The accuracy of the median particle

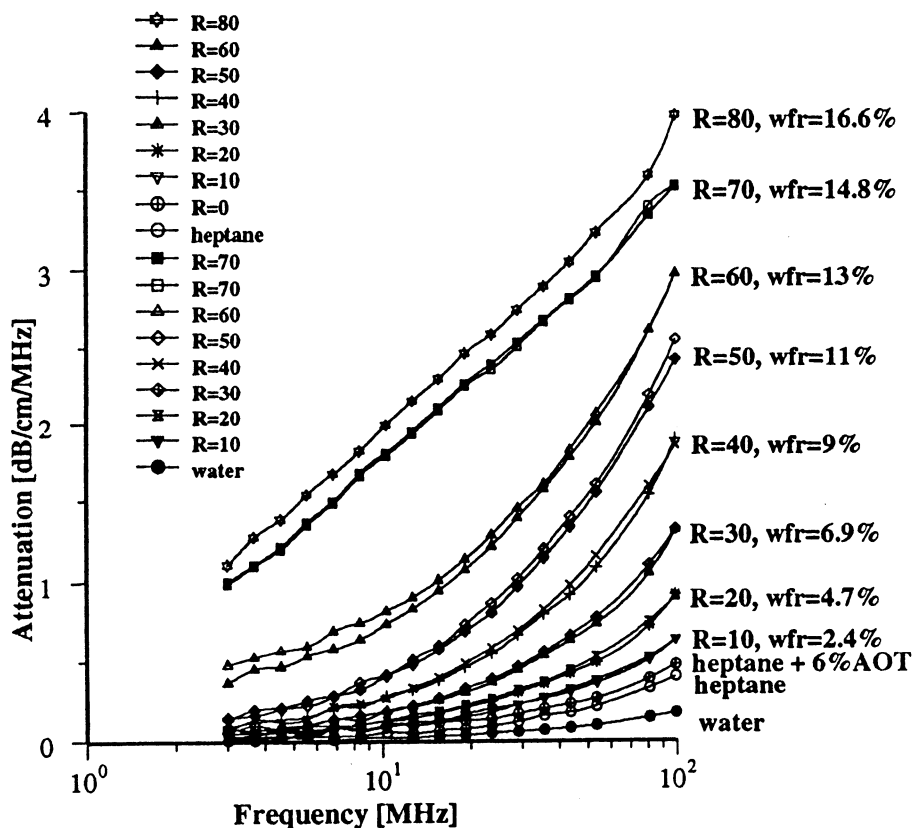


FIG. 1. Acoustic attenuation spectra measured for a water/AOT/heptane system for different water to AOT ratios R .

size is about 1% and the particle size distribution width about 5%. It is expected that similar precision and accuracy will hold for other dispersed systems as long as the particle size is not too close to the limits of detection for acoustics which is about 10 nanometers on the low side and 10 micrometers on the high side.

The total sample volume required is about 100 ml and a special magnetic stirrer is used to prevent sedimentation and provide mixing of reagents during titration. This was found to be effective for keeping the macroemulsion in a constant state of dispersion and for preventing the formation of any localized thermal gradient for both micro- and macroemulsions. Temperature and pH are also monitored using the probes in the equipment.

EXPERIMENTAL PROTOCOL

Measurements were made starting with the pure water and heptane and then the AOT-heptane sample with no added water ($R = 0$). The sample fluid was removed from the instrument cell and placed in a glass bottle with a Teflon cap. Additional water was titrated and the microemulsion was shaken for 30 s before being placed back into the instrument cell. The sample cell contained a cover to prevent evaporation

of the solvents. The samples were visually inspected for clarity and rheological properties for each R value. These steps were repeated for increasing water weight fraction or R ratios up to $R = 100$. At $R \geq 60$ the microemulsions became turbid. At $R > 80$, the emulsions became distinctly more viscous.

The weight fractions of the dispersed phase were calculated for water only without including the AOT. Each trial run lasted approximately 5–10 min with the temperature varied from 25–27°C. A separate microemulsion sample for $R = 40$ was made up a few days prior to the first study. For the $R = 70$ sample, a second acoustic measurement was made with the same sample used for the first study. The complete set of experiments for water, heptane, and the reverse microemulsions from $R = 0$ to 100 was repeated to evaluate the reproducibility.

RESULTS AND DISCUSSION

Attenuation spectra measured in the first run up to $R = 80$ are presented in Fig. 1. The results for $R = 90$ and $R = 100$ are not reported because they were found to vary appreciably. As the water concentration is increased, the attenuation spectrum rises in intensity and there is a distinct jump in the attenuation spectrum from $R = 50$ to $R = 60$ in the low

frequency range. This discontinuity is also reflected in the visual appearance as at $R = 60$ the system becomes turbid. The smooth shape of the attenuation curve also changes at $R > 60$. The stability and reproducibility of the system was questioned due to the irregular nature of the curve so the experiment at $R = 70$ was repeated and gave almost identical results. An additional experiment was run at $R = 40$ for a separate microemulsion prepared a few days earlier. This showed excellent agreement with the results for freshly titrated microemulsion.

For R values >70 , an increase in the viscosity and a decrease in the reproducibility of the attenuation measurement were observed. This could be due to the failure of the model for this system as a collection of separate droplets at high R values.

A second set of experiments was run to check the reproducibility. The results of both sets of experiments up to $R = 70$ are given in Fig. 1. It can be seen that the error related to the reproducibility is much smaller than the difference between attenuation spectra for the different R values. This demonstrates that the variation of attenuation reflects changes in the sample properties of water weight fraction and droplets size. The sound attenuation at R values above 70 were not as reproducible, but did give the same form of a bimodal distribution as the best fit for the experimental data.

The two lowest attenuation curves correspond to the attenuation in the two pure liquids: water and heptane. This attenuation is associated with the oscillation of liquid molecules in the sound field. If these two liquids are soluble in each other, the total attenuation of the mixture would lie between these two lowest attenuation curves. But it can be seen that the attenuation of the mixture is much higher than that of the pure liquids. The increase in attenuation, therefore, is due to this heterogeneity of the water in the heptane system. The extra attenuation is caused by motion of droplets, not separate molecules. The scale factor (size of droplets) corresponding to this attenuation is much higher than that for pure liquids (size of molecules).

The current system contains a third component—AOT. A question arises on the contribution of AOT to the measured attenuation. In order to answer this question, measurements were done on a mixture of 6.1 wt% AOT in heptane ($R = 0$). It is the third smallest attenuation curve in Fig. 1. It is seen that attenuation increases somewhat due to AOT. However, this increase is less than the extra attenuation produced by water droplets. The small increase in attenuation is attributed to AOT micelles. Unfortunately thermal properties of the AOT as a liquid phase are not known and the size of these micelles could not be calculated.

The particle size distributions corresponding to the measured attenuation spectra are presented in Figs. 2a and 2b. It can be seen that the distribution becomes bimodal for $R \geq 60$ that coincides with the onset of turbidity. It is to be noted that such a conclusion could not easily be arrived at with other techniques. There is a feature of this system, however, that can be

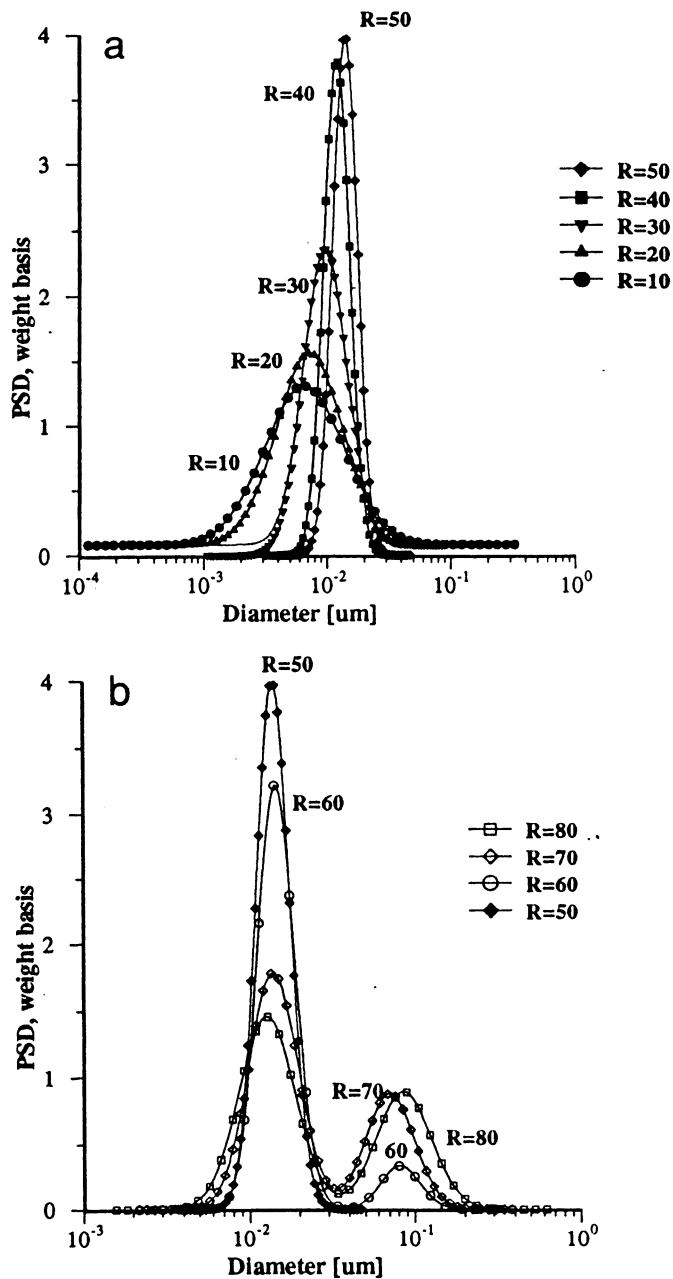


FIG. 2. Drop size distribution for varying R [H₂O]/[AOT] from (a) 10 to 50 and (b) 50 to 80.

compared with independent data from literature: mean particle size increases with R almost in a linear fashion. This dependence becomes apparent when mean size is plotted as a function of R as in Fig. 3.

It is seen that mean particle sizes measured using acoustic spectroscopy are in good agreement with those obtained independently using the neutron scattering (SANS) and X-ray scattering (SAXS) techniques (6, 11, 17) for R values ranging from 20 to 60. A simple theory based on equi-partition of water

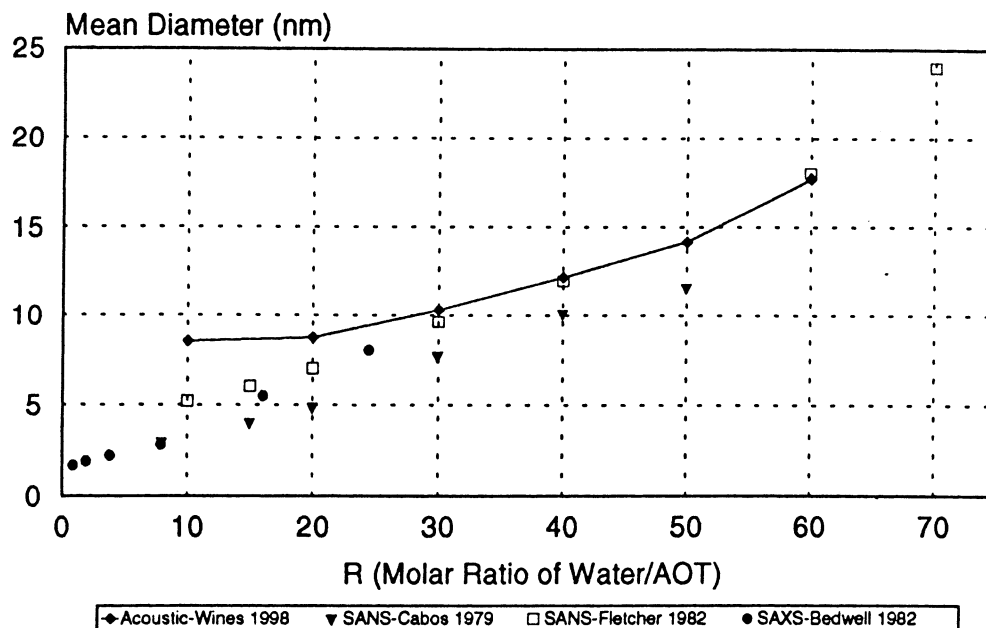


FIG. 3. Comparison of mean droplet size measured using acoustic spectroscopy, neutron scattering, and X-ray scattering.

and surfactant (36) can reasonably explain the observed linear dependence.

At $R = 10$ the acoustic method gave a slightly larger diameter than expected. This could be due to the constrained state of the "bound water" in the swollen reverse micelles. The water under these conditions may exhibit different thermal properties than the bulk water used in the particle size calculations. Also at the low R values ($R \leq 10$ or $\leq 2.4\%$ water), the attenuation spectrum is not very large as compared to the background heptane signal. The contribution of droplets to the attenuation spectrum then may become too low to be reliably distinguished from the background signal coming from heptane molecules and AOT micelles.

CONCLUSIONS

Acoustic spectroscopy is well able to characterize the microemulsion's droplet size distribution. The mean droplet size measured using acoustic spectroscopy agrees well with those from small angle neutron scattering and small angle X-ray scattering measurements. These three different techniques yield the same linear dependence of the mean droplet size on the AOT-to-water ratio.

ACKNOWLEDGMENTS

The authors acknowledge the support of the National Science Foundation IUCRC for Separation Using Selective Solubilization in Adsorbed Polymer Surfactant Aggregates (Grant CTS-96-32479).

REFERENCES

1. Wilcoxon, J. P. and Williamson, R. L., in "Material Research Society Symposium Proceedings: Macromolecular Liquids" (C. R. Safinya, S. A. Safran, and P. A. Pincus, Eds.), Vol. 177. Materials Research Society, Pittsburgh, 1990.
2. Candau, F., in "Material Research Society Symposium Proceedings: Macromolecular Liquids" (C. R. Safinya, S. A. Safran, and P. A. Pincus, Eds.), Vol. 177. Materials Research Society, Pittsburgh, 1990.
3. Motte, L., Lebrun, A., and Pileni, M. P., *Progr. Colloid Polym. Sci.* **89**, 99 (1992).
4. Ichinohe, D., Arai, T., and Kise, H., *Synth. Metals* **84**, 75 (1997).
5. Schubert, K. V., Lusvardi, K. M., and Kaler, E. W., *Colloid Polym. Sci.* **274**, 875 (1996).
6. Menger, F. M., and Yamada, K., *J. Am. Chem. Soc.* **101**, 22, 6731 (1979).
7. Chatenay, D., Urbach, W., Cazabat, A. M., Vacher, M., and Waks, M., *Biophys. J.* **48**, 893 (1985).
8. Timmins, G. S., Davies, M. J., Gilbert, B. C., and Caldararu, H., *J. Chem. Soc. Faraday Trans.* **90**, 18, 2643 (1994).
9. Kabanov, A. V., *Makromol. Chem., Macromol. Symp.* **44**, 253 (1991).
10. Crupi, V., Maisano, G., Majolino, D., Ponterio, R., Villari, V., and Caponetti, E., *J. Mol. Struct.* **383**, 171 (1996).
11. Bedwell, B., and Gulari, E., in "Solution Behavior of Surfactants" (K. L. Mittal, Ed.), Vol. 2. Plenum Press, New York, 1982.
12. Gulari, E., Bedwell, B., and Alkhafaji, S., *J. Colloid Interface Sci.* **77**, 1, 202 (1980).
13. Zulauf, M., and Eicke, H.-F., *J. Phys. Chem.* **83**, 4, 480 (1979).
14. Eicke, H.-F. in "Microemulsions" (I. D. Rob, Ed.), p.10. Plenum Press, New York, 1982.
15. Nicholson, J. D., Doherty, J. V., and Clarke, J. H. R. in "Microemulsions" (I. D. Rob, Ed.), p. 33. Plenum Press, New York, 1982.
16. Eicke, H.-F., and Rehak, J., *Helv. Chim. Acta* **59**, 8, 2883 (1976).
17. Fletcher, P. D. I., Robinson, B. H., Bermejo-Barrera, F., Oakenfull, D. G., Dore, J. C., and Steytler, D. C. in "Microemulsions" (I. D. Rob, Ed.), p. 221. Plenum Press, New York, 1982.
18. Cabos, P. C., and Delord, P., *J. Appl. Cryst.* **12**, 502 (1979).

19. Radiman, S., Fountain, L. E., Toprakcioglu, C., de Vallera, A., and Chieaux, P., *Progr. Colloid Polym. Sci.* **81**, 54 (1990).
20. Huruguen, J. P., Zemb, T., and Pileni, M. P., *Progr. Colloid Polym. Sci.* **89**, 39 (1992).
21. Pileni, M. P., Zemb, T., and Petit, C., *Chem. Phys. Lett.* **118**, 4, 414 (1985).
22. Sager, W., Sun, W., and Eicke, H.-F., *Progr. Colloid Polym. Sci.* **89**, 284 (1992) 284.
23. Safran, S. A., Grest, G. S., and Bug, A. L. R. in "Microemulsion Systems" (H. L. Rosano and M. Clause, Eds.), p. 235. Marcel Dekker, New York, 1987.
24. Dukhin, A. S., and Goetz, P. J., *Langmuir* **12**, 21, 4998 (1996).
25. McClements, J. D., *Colloids Surf.* **90**, 25 (1994).
26. McClements, J. D., *Adv. Colloid Interface Sci.* **37**, 33 (1991).
27. Dukhin, A. S., and Goetz, P. J., *Langmuir* **12**, 19, 4334 (1996).
28. Epstein, P. S., and Carhart, R. R., *J. Acoust. Soc. Am.* **25**, 3, 553 (1953).
29. Allegra, J. R., and Hawley, S. A., *J. Acoust. Soc. Am.* **51**, 1545 (1972).
30. Zhou, Z., Hilfiker, R., and Eicke, H.-F., *Progr. Colloid Polym. Sci.* **89**, 66 (1992).
31. Kotlarchyk, M., Chen, S.-H., Huang J. S., and Kim, M. W., *Phys. Rev. A* **29**, 4, 2054 (1984).
32. Kitahara, A., Kobayashi, T., and Tachibana, T., *J. Phys. Chem.* **66**, 363 (1962).
33. Dukhin, A. S., and Goetz, P. J., US Patent, Pending.
34. Irani, R. R., and Callis, C. F., "Particle Size: Measurement, Interpretation and Application." Wiley, New York, 1971.
35. Dukhin, A. S., and Goetz, P. J., in "Handbook of Ultrasonic and Dielectric Characterization Techniques for Suspended Particles" (V. A. Hackley and J. Texter, Eds.), p. 77. American Ceramic Society, Westerville, 1998.
36. Oakenfull, D., *J. Chem. Soc. Faraday I* **76**, 1875 (1980).