

The Droplet Size in Oil-External Microemulsions Using the Membrane Diffusion Technique

The hydrodynamic radii of the microemulsion droplets in dilute oil-external microemulsions was determined by the membrane diffusion technique employing cylindrical-pore Nuclepore membranes of 500-Å pore radius and 5-μm thickness. The cell constant of the diffusion cell was calibrated by measuring the diffusion coefficient of inverted Aerosol OT micelles in octane and of SDS micelles in 0.15 M NaCl brine. For the present system, the hydrodynamic radii of the microemulsion droplets were found to be about 150 Å, in reasonable agreement with those determined by light scattering, quasi-elastic light scattering, and ultracentrifugation measurements.

The membrane diffusion technique as introduced by Northrop and Anson (1) has been used to determine the hydrodynamic size of micelles (2, 3). In a steady-state diffusion process, the diffusion coefficients of micelles can be easily determined by measuring the surfactant concentrations in each cell compartment across the membrane as a function of time. One of the major limitations of this technique is that the adsorption or entrapment of micelles in tortuous membrane pores may significantly reduce the permeability of the membrane in the course of diffusion. This limitation can be overcome by employing membranes with cylindrical pores (4). The objective of the present study was to establish the validity of this technique for determining the hydrodynamic radii of oil-external microemulsion droplets. The results are compared with those obtained using light scattering, quasi-elastic light scattering, and ultracentrifugation measurements.

EXPERIMENTAL

Materials

Single-phase, oil-external microemulsions were prepared using a petroleum sulfonate (TRS 10-410, mol wt = 418, Witco Chemical Co.), isobutanol (IBA, 99.9% pure), dodecane (99% pure, Chemical Samples Co.), and 1.5% NaCl brine. The brine/surfactant ratio was 2 ml/g. A concentrated microemulsion was prepared by titrating a surfactant-oil-brine mixture (1:10:2, w/w) with IBA to transparency and subsequently adding an extra 0.03 g IBA per gram of surfactant. The concentrated microemulsion was then diluted by its external phase (0.97% IBA in dodecane for the present system as determined by the alcohol titration method (5)). The samples were filtered through 0.2-μm sterile filters for light-scattering studies.

Membrane Diffusion

In the present study, cylindrical-pore membranes (Nuclepore Corp.) of 500-Å pore radius and 5-μm thickness were employed. The 1-in.-diameter mem-

brane was mounted on a dialysis cell (Technilab Co.) which was modified such that it could be locked by a screw cap from the outside. This modification was made to ensure that no pressure gradient across the membrane built up when the cell compartment was closed. The cell was first filled with the solvent (or the external phase of microemulsion) by a syringe in one compartment. Then moderate suction was applied to the other compartment to slowly displace the air within the membrane pores until the other side of the membrane was wetted by the solvent. Subsequently, each compartment was aspirated, rinsed, and refilled with solutions of suitable concentrations. The concentration should be made as low as possible to avoid possible solute interactions but high enough to allow accurate concentration measurements. Initially a thin glass stirrer was put into each cell compartment to ensure adequate mixing in the bulk solution, but it was found that this procedure was unnecessary and was eliminated. The cell was then put on a rotating tumbler at a speed of 24 rpm. After suitable time elapsed, the samples were taken out by syringe and their surfactant concentrations were analyzed by a two-phase, two-dye titration method (6). The diffusion coefficient, D , was calculated according to the following expression (3):

$$KD = \frac{1}{2\Delta t} \ln \frac{\Delta C_0}{\Delta C}, \quad [1]$$

where K is the cell constant, ΔC_0 and ΔC are the initial and final concentration differences, and Δt is the elapsed time for diffusion.

Light Scattering, Quasi-Elastic Light Scattering, and Ultracentrifugation

Light-scattering turbidity was examined by a Wood photometer using unpolarized light at 5460 Å. Quasi-elastic light scattering was measured using an argon ion laser at 5140 Å and the output from the photomultiplier was analyzed by a Malvern digital autocorrelator through 99 channels. The method of cumu-

TABLE I
Diffusion of AOT Micelles in Octane^{a,b}

C_0 (moles/liter)	C'_0 (moles/liter)	Δt (min)	KD (10^{-4} sec ⁻¹)	K (cm ² /r)
0.119	0	84	1.62	57.5
0.119	0	140	1.57	55.8
0.119	0.01	175	1.59	56.4
0.058	0	48	1.51	53.7
0.058	0	48	1.57	55.8
0.058	0.01	38	1.49	53.0
0.058	0.01	69	1.60	56.8

^a $D = 2.81 \times 10^{-6}$ cm²/sec at 23°C (11).

^b C_0 and C'_0 are the initial surfactant concentrations in each cell compartment.

^c $\bar{K} = 55.6 \pm 1.64$ cm².

lants (7) was used to analyze the autocorrelation function of the scattered-light intensity from which one can calculate the translational diffusion coefficient (8–10). Ultracentrifugation was performed in a Beckman Model E analytical ultracentrifuge with Schlieren optics. The rotor speed was 20,400 rpm. All experiments were performed at 23°C.

RESULTS

The cell constant was determined using the Aerosol OT inverted micelles in octane or sodium dodecyl sulfate micelles in 0.15 M NaCl brine as shown in Tables I and II. The diffusion coefficients of these systems were taken from the literature (11, 12). The average K was found to be 55.6 (Table I) or 53.6 (Table II). The difference between these two values is within experimental error. It is interesting that the cell constant is independent of the solvent used (oil or brine) or the type of diffusing micelles (inverted or normal).

TABLE II
Diffusion of SDS Micelles in 0.15 M NaCl^{a,b}

C_0 (moles/liter)	C'_0 (moles/liter)	Δt (min)	KD (10^{-5} sec ⁻¹)	K (cm ² /r)
0.069	0.01	51	5.30	54.7
0.069	0.01	70	4.90	50.6
0.069	0.01	86	5.30	54.7
0.069	0.01	133	5.47	56.4
0.069	0.01	139	4.99	51.5

^a $\bar{D} = 9.69 \times 10^{-7}$ cm²/sec at 25°C (12).

^b C_0 and C'_0 are the initial surfactant concentrations in each cell compartment.

^c $\bar{K} = 53.6 \pm 2.43$ cm².

TABLE III
Diffusion of Oil-External Microemulsions^{a,b}

C_0 (moles/liter)	C'_0 (moles/liter)	Δt (min)	D (10^{-7} cm ² sec ⁻¹)
0.0548	0.00782	610	0.99
0.0548	0.00782	730	1.04
0.0548	0.00782	1257	0.97
0.0548	0.00782	1380	0.94
0.0548	0.00782	1520	1.10
0.0548	0.00782	1780	1.04
0.068	0.0113	480	1.15
0.068	0.0113	950	0.95
0.068	0.0113	1300	1.01

^a System: TRS 10-410/IBA/dodecane/1.5% NaCl brine, brine/surfactant = 2 ml/g.

^b C_0 and C'_0 are the initial surfactant concentrations in each cell compartment.

^c $\bar{D} = 1.02 \pm 0.07 \times 10^{-7}$ cm²/sec, $R_h = kT/6\pi\eta\bar{D} = 150$ Å.

Table III shows the results for the oil-external microemulsions prepared from the petroleum sulfonate, IBA, dodecane, and 1.5% NaCl brine system. Taking $K = 55.6$ the average diffusion coefficient was found to be 1.02×10^{-7} cm²/sec. The hydrodynamic radius was then calculated to be 150 Å using the Stokes–Einstein equation for spherical particles. The effect of concentration (13–15) on the diffusion coefficient appears to be negligible as there is no systematic variation of the results with respect to the initial concentration differences or the elapsed time for diffusion.

Figure 1 shows the light-scattering turbidity as a function of the concentration of the dispersed phase. ^c The turbidity increases linearly with the concentration of dispersed phase within the range of measurements. Thus, the second virial coefficient of osmotic pressure is zero and the average molecular weight is equal to $\pi/H(c - c_0)$ (18), where H is an optical constant of the solution ($H = 32\pi^2 n^2 (dn/dc)^2 / 3N_A \lambda_0^4$, $n \approx 1.42$, $dn/dc = -0.0134$, and $H = 2.24 \times 10^{-6}$ mole cm²/g² in the present study). The average

¹ The concentration of the dispersed phase was calculated on the basis that the microemulsion droplets consist of 0.22 g IBA, 2.016 g brine (1.5% NaCl, $\rho = 1.008$ g/ml), and 0.407 g dodecane per gram of surfactant. The 0.22 g IBA is the amount of the interfacial alcohol molecules as determined from Bowcott and Schulman's titration method (5). The 0.407 g dodecane is the equimolar amount of oil molecules assumed to penetrate into the interfacial surfactant–alcohol film. It has been shown that the penetration of oil molecules into the interfacial film is necessary for the stability of oil-external microemulsions (16, 17).

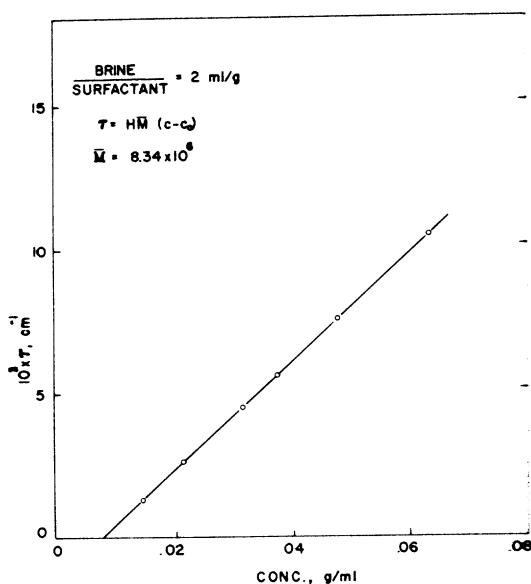


FIG. 1. Light-scattering turbidity of oil-external microemulsions as a function of the concentration of the dispersed phase c .

molecular weight of the droplet was then calculated to be 8.34×10^6 g/mole. The apparent density of the microemulsion droplet, ρ_p , was determined to be 1.001 g/ml by pycnometer² (19). The radius³ of the microemulsion droplet was then calculated to be 149 Å using the measured molecular weight and density values. Quasi-elastic light scattering gave a hydrodynamic radius of 169 Å with a variance of 0.08. Therefore, the results obtained using light scattering and quasi-electric light scattering are in reasonable agreement with the membrane diffusion results.

The sedimentation coefficient (S) data are shown in Fig. 2 as a plot of $[-\log S]$ vs $[-\log(1 - \phi)]$, where ϕ is the volume fraction of dispersed phase ($= c/\rho_p$), following the theoretical treatment of Maude and Whitmore (20) for the concentration dependence of sedimentation coefficients. A straight line was obtained and the sedimentation coefficient at infinite

² The apparent density of the microemulsion droplet ρ_p was calculated according to the expression (19): $(d\rho/dc)_{c \rightarrow 0} \approx 1 - \rho_s/\rho_p$, where ρ_s is the density of the solvent (external phase of the oil-external microemulsions).

³ The depolarization of the scattered light at 90° was found to be 0.009 and the intrinsic viscosity was found to be 2.7, indicating that these oil-external microemulsions consist of spherical particles. The excellent agreement in hydrodynamic radii obtained using different techniques also supports this thesis.

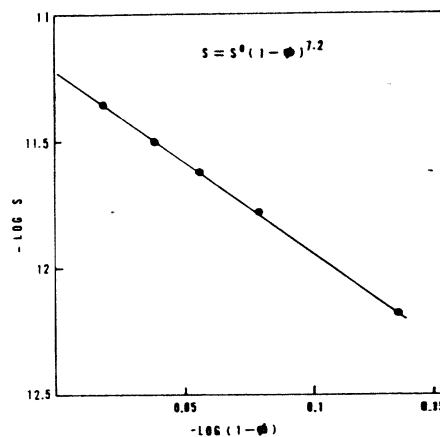


FIG. 2. Sedimentation coefficient of oil-external microemulsions as a function of the volume fraction of the dispersed phase $\phi (= c/\rho_p)$. The Maude and Whitmore expression (20): $S = S^0(1 - \phi)^a$, S^0 is the sedimentation coefficient at infinite dilution.

dilution S^0 was determined. The hydrodynamic radius by ultracentrifugation $[=(9\eta S^0/2\Delta\rho)^{1/2}]$ was calculated to be 125 Å. This smaller value could be due to the pressure effect on the viscosity of oil (20) and or the simplifications made in the approximate expression for the apparent particle density (18); a 7% decrease of the apparent density would increase the hydrodynamic radius from 125 to 150 Å.

In summary, the membrane diffusion technique can be successfully applied to determine the hydrodynamic radius of dilute oil-external microemulsions using 500-Å-pore-radius and 5- μ m-thick Nuclepore membranes. The cell constant of this membrane was found to be nearly independent of the solvent as determined from the diffusion coefficients of SDS micelles in 0.15 M NaCl brine or inverted AOT micelles in octane. The hydrodynamic radius of oil-external microemulsion droplets thus determined is in reasonable agreement with those obtained using light scattering, quasi-elastic light scattering, and ultracentrifugation measurements.

ACKNOWLEDGMENTS

This work was supported by NSF-RANN, ERDA, and Department of Energy Grant EW-78-S-19-0008 and a consortium of 25 major oil and chemical companies. The authors are grateful to Professor E. Gulari of the Department of Chemical Engineering at the University of Michigan for performing quasi-elastic light-scattering measurements and to Professor P. W. Chun of the Department of Biochemistry and Molecular Biology at the University of Florida for performing the ultracentrifugation experiments.

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Received February 25, 1980; accepted June 2, 1980