Predicting the Effect of Nonionic Surfactants on Dispersed Droplet Radii in Submicron Oil-in-Water Emulsions

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A novel theoretical model which describes the mass mean radius of oil droplets in an oil-in-water emulsion is described. A modified form of the Langmuir adsorption isotherm is used to account for nonlinear adsorption of surfactant to an oil–water film and its effect on interfacial tension and oil droplet radius. On the basis of this model, the mass mean oil droplet radius may be related to bulk surfactant concentration for a nonionic surfactant. An analysis of the mineral oil–Triton X405–water system shows that aqueous solutions of Triton X405 against mineral oil behaved in accord with the proposed model. γ_m, the maximum interfacial tension lowering by Triton X405, was estimated to be 20.9 dyne/cm. A surfactant specific apparent constant (B) which relates the rate constant for adsorption to the interface to the rate constant for desorption from the interface into the aqueous bulk was estimated as 5.44E4 cm^3/g. The pressure across the curved interface, δP, was estimated as 1.05E6 dyne/cm^2. The theoretical model appears to be consistent with experimentally observed oil droplet radii and is considered to be an accurate representation of the mechanics of dispersed droplet radii under conditions of moderate load of nonionic surfactant.

KEY WORDS: submicron emulsions; fine emulsions; droplet size; emulsion theory; microfluidization.

INTRODUCTION

Emulsions are dispersions of two immiscible liquids. A fine or submicron emulsion has been defined as an emulsion which possesses a dispersed phase mean droplet diameter under 1 μm (1,2). Some physical and chemical factors which govern the characteristics of a fine emulsion are emulsification technique, phase volume ratio, and surfactant type(s) and concentration(s) (3).

Fine emulsions typically have greater stability to physical degradation processes than their equivalent coarse emulsions. Therefore, these systems have a distinct advantage over conventional coarse emulsions in situations where physical stability is critical.

The application of technologies such as hyperhomogenization and microfluidization to the production of fine emulsions has been discussed elsewhere (4,5). The predominate emulsification forces generated by these technologies include high shear (laminar flow), turbulence (inertial force), and cavitation (vapor bubble implosion). These forces act simultaneously to reduce mean droplet size of the dispersed phase. Processes which oppose and occur simultaneous to emulsification are dispersed droplet aggregation and coalescence and phase inversion. These competing processes are driven by the underlying thermodynamic instability of emulsions.

The phenomenology of oil–water interfaces, surfactants, and their mutual relationships as they affect the physical properties of emulsions has not yet been fully established. Central to this is the dependence of radius of the dispersed globules on bulk surfactant concentration. Empirical log linear relationships have been successfully used to correlate these variables (6). While these efforts may be useful, they do not address the mechanism of surfactant induced droplet size reduction.

Recently, a nonempirical approach to prediction of mass mean droplet radius for a submicron emulsion containing *low loads* of nonionic surfactant was described (7). The shortcoming of this model was the constraint that the surfactant load be low. This condition was required since it was assumed that essentially all surfactant be preferentially adsorbed to the oil–water interface.

In this study, the Langmuir adsorption isotherm is applied to oil–surfactant–water interfacial thermodynamics (8). Combining this theory with LaPlace's equation for the thermodynamics of expanding or contracting spherical films, a nonempirical relationship describing the dependence of mean oil droplet radius on bulk surfactant concentration is realized. The relationships proposed herein are evaluated for a model system consisting of mineral oil–Triton X405–water.

THEORY

A form of the Langmuir adsorption isotherm (9) has been applied to the surface as well as the oil–water interfacial tension lowering induced by surfactant adsorption (8). For a single surfactant species adsorbed in accordance with a Langmuirian model,

$$\gamma^0 - \gamma = \frac{B\gamma_m C_e}{1 + BC_e} \qquad (1)$$

where γ^0 (dyne/cm) is the oil–water interfacial tension of the pure interface, γ (dyne/cm) is the interfacial tension in the presence of a surfactant at a specified concentration, γ_m (dyne/cm) is a constant and reflects the maximum interfacial tension lowering when monolayer adsorption is complete, and C_e (gm/cm^3) is the aqueous phase concentration of surfactant. B (cm^3/g) is an apparent constant which is equal to the ratio of the kinetic rate for interfacial adsorption to the kinetic rate for interfacial desorption of surfactant. This equation assumes that adsorbed surfactant forms a monolayer and that *quasi*-equilibrium conditions are present. Additional assumptions and conditions are given elsewhere (8).

The LaPlace equation for the special case of spherical oil droplets as applied to oil-in-water emulsions (3,10) is

$$r = 2\gamma/\delta P \qquad (2)$$

where r (cm) is the oil droplet radius, γ (dyne/cm) is the interfacial tension of the curved oil–water interface, and δP

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(dyne/cm^2) is the pressure gradient across the interface. This equation may be derived from thermodynamic considerations of free energy and work as they apply to a spherical film.

Combining and rearranging Eqs. (1) and (2) yields

$$r = r_0 - \frac{2\gamma_m B C_e}{\delta P\,(1 + BC_e)} \tag{3}$$

where r represents the mass mean oil droplet radius of an emulsion system in the presence of a specific concentration of surfactant and r_0 (cm) represents the mass mean oil droplet radius of the same emulsion system with no surfactant present.

Equation (3) may be linearized by several means. As an example, solving for $r_0 - r$ yields

$$r_0 - r = \frac{2\gamma_m B C_e}{\delta P\,(1 + BC_e)} \tag{4}$$

Rearrangement of Eq. (4) gives

$$\frac{r_0 - r}{C_e} = \frac{2\gamma_m B}{\delta P\,(1 + BC_e)} \tag{5}$$

Taking the reciprocal of Eq. (5) and rearranging further results in

$$\frac{C_e}{r_0 - r} = \frac{\delta P}{2\gamma_m B} + \frac{\delta P}{2\gamma_m} C_e \tag{6}$$

where $\delta P/(2\gamma_m B)$ and $\delta P/(2\gamma_m)$ are apparent constants for a given oil–surfactant–water combination. Equation (6) predicts that a plot of $C_e/(r_0 - r)$ versus C_e should be linear with slope equal to $(\delta P/2\gamma_m)$ and an intercept of $\delta P/(2\gamma_m B)$.

Equation (6) eliminates conditions of low surfactant load and linear interfacial adsorption of surfactants as a prerequisite to theoretical explanation of surfactant effects on mass mean oil droplet radius in an oil-in-water dispersion. The limitation is that surfactants are required to be nonionic.

MATERIALS AND METHODS

Borosilicate glass apparatus and double-distilled water were used in all studies. All chemicals were reagent grade or ACS certified and were used as received. Further, all studies were conducted at 23°C.

Surface Tension Studies

Aqueous solutions of various concentrations of Triton X405 (Sigma) were prepared to give final concentrations from 0 to 8.82E-4 g/cm^3. Then 25 ml of solution was placed in a thermostated (23°C) sample beaker and allowed to stand for 30 min (11) to establish a surface tension equilibrium. A clean 5.985-cm Pt–Ir ring was lightly flamed, allowed to cool to 23°C, and placed on the solution surface. Surface tension was determined with a DuNouy Tensiometer (Fisher Surface Tensiomat) equipped with an electric arm lifting device. Apparent surface tension was taken as the average of three upward detachment readings within a 0.5-dyne/cm range.

Interfacial Tension Studies

Solutions of Triton X405 were prepared as described above. Then, 25 ml of solution was placed in the thermal sample beaker. Next 25 ml of light mineral oil (Fisher) was gently poured over the aqueous surfactant solution. The phases were allowed to remain in contact for 30 min to establish an interfacial tension equilibrium (11). The Pt–Ir ring was lowered to the interface and the apparent interfacial tension was determined with the tensiometer analogous to surface tension determination.

Fine Emulsion Studies

Mineral oil-in-water emulsions containing 10% mineral oil and various concentrations (0 to 2.76 g/100 cm^3 emulsion) of Triton X405 were prepared using microfluidization. Coarse emulsions were processed through a M110T Microfluidizer (modified high-pressure pump) thermostated to 23°C and set to an inlet air pressure of 60 psi. Emulsions were processed 5 vol cycles through the device, collected, and used immediately for particle size studies. Processing conditions were held constant such that mechanical droplet size minimization should be complete and observed changes in droplet distribution should reflect only the constituent ratios in the emulsion system (5). Particle size distributions were determined using a Nicomp 270 Submicron Particle Sizer (photon correlation spectroscopy).

RESULTS AND DISCUSSION

The Pt–Ir ring used for these studies was calibrated (Fisher Scientific). Calibration results indicate that the ratio of the ring radius to the wire radius is 53.6145 and the circumference of the ring is 5.985 cm. The densities (23°C) of pure water and pure Triton X405 were determined to be 1.00 and 1.10 g/ml, respectively. The density of air was taken as 1.19E-3 g/ml (12). The densities (23°C) of mutually equilibrated mineral oil and water were determined to be 0.876 and 1.02 g/ml, respectively.

Surface and interfacial tensions were calculated from apparent surface and interfacial tension values using the relationship

$$\gamma = \gamma' F \tag{7}$$

where γ' is the apparent surface or interfacial tension (dial reading; dyne/cm) and F is a semiempirical correction factor dependent on the apparent surface or interfacial tension, densities of the upper and lower phases, and ring dimensions. For each surface or interfacial tension measured, the correction factor is given as (instrument manual)

$$F = 0.725 + \left[\frac{0.01452\gamma'}{C^2\,(\rho_l - \rho_u)} + 0.04534 - 1.679\,(r_w/R_r)\right]^{1/2} \tag{8}$$

where C is the ring circumference (cm), and ρ_l and ρ_u represent the density (g/ml) of the lower and upper phase, respectively. R_r and r_w represent the ring radius and the wire radius (cm), respectively. All surface and interfacial tension estimates discussed below were corrected using this equation.

Table I gives the values of the apparent surface tension and surface tension of water at various concentrations of Triton X405. This table also gives the computed correction factors (F) for each determination and the standard deviation

Table I. Effect of Triton X405 on Air–Water (Surface) Tension

C_e (g/ml)	γ' (dyne/cm)	F	γ (dyne/cm)	SD (dyne/cm)[a]
0	76.2	0.937	71.4	0.182
2.20E-4	44.7	0.904	40.4	0.200
4.41E-4	43.0	0.902	38.8	0.040
6.61E-4	42.4	0.902	38.2	0.080
8.82E-4	42.3	0.902	38.1	0.040

[a] Standard deviation; $n = 3$.

Table II. Effect of Triton X405 on Mineral Oil–Water (Interfacial) Tension

C_e (g/ml)	γ' (dyne/cm)	F	γ (dyne/cm)	SD (dyne/cm)[a]
0	32.1	1.04	33.3	0.040
2.20E-4	15.8	0.961	15.2	0.000
4.41E-4	14.7	0.954	14.0	0.040
6.61E-4	13.9	0.950	13.2	0.000
8.82E-4	13.1	0.945	12.4	0.000

[a] Standard deviation; $n = 3$.

associated with each determination. As the surfactant concentration increases, the surface tension decreases consistently over the concentration range studied.

Figure 1 depicts the linear relationship between $C_e/(\gamma^0 - \gamma)$ and C_e for the surface tension study. The slope of the line was estimated to be 3.04E-2 cm/dyne and the correlation coefficient was approximated as 0.999. Maximum surface tension lowering on monolayer completion is estimated from the slope of this relationship to be 32.9 dyne/cm. These data suggest (Table I) that the monolayer for the air–Triton X405–water surface was completed since the lowest observed surface tension was 38.1 dyne/cm and the predicted surface tension on monolayer completion would be 38.5 dyne/cm.

Table II gives the values of the apparent interfacial tension and the interfacial tension of mineral oil–water in the presence of various concentrations of Triton X405. This table also gives the computed correction factors (F) for each determination as well as the standard deviation associated with each determination. As the surfactant concentration increases, the interfacial tension decreases consistently for all systems studied.

Figure 2 depicts the linear relationship between $C_e/(\gamma^0 - \gamma)$ and C_e for the mineral oil–Triton X405–water system. The data exhibited a high linear correlation ($r = 0.999$), suggesting that the adsorption isotherm adequately describes this interfacial tension data.

The slope of the linear regression of the data in Fig. 2 is 4.58E-2 cm/dyne, which represents $1/\gamma_m$. From the reciprocal of the slope, γ_m is approximately 20.9 dyne/cm. This value is of the same order of magnitude as those reported for other mineral oil–surfactant–water systems (8). By definition, γ_m is the amount by which the mineral oil–water interfacial tension will be lowered when the Triton X405 monolayer is complete. This corresponds to an interfacial tension of 12.4 dyne/cm on monolayer completion. It would appear that completion of the adsorbed monolayer was realized for the mineral oil–water film since the lowest observed interfacial tension was 12.4 dyne/cm.

The intercept of the linear regression of the data in Fig. 2 is 8.79E-7 (g cm cm^{-3} dyne^{-1}). Since the intercept is equal to $1/(\gamma_m B)$ and γ_m is 20.9 dyne/cm, B is estimated as

$$B = 1/(\gamma_m \times \text{intercept}) \tag{9}$$

From Eq. (9), B is approximately 5.44E4 cm^3/g. Recall that B is the ratio of the rate constant for surfactant adsorption to the interface to the rate constant for surfactant desorption from the interface into the bulk solution. B is much greater than unity, therefore, the data suggest that the adsorptive process is *kinetically* favored for this system.

Comparing the γ_m values for the surface and interfacial tension data reveals that Triton X405 is a more effective adsorber at the air–water surface than the mineral oil–water interface.

Table III shows the mass mean radius (r; nm), number mean radius (r_N; nm), and polydispersity ($P = r/r_N$) for the emulsions studied. The mean oil droplet radius was well under 1 μm for all of these emulsion systems. Therefore, these emulsions may all be classified as fine emulsions. In all cases, an increase in the surfactant concentration led to the expected decrease in the mean oil droplet radius.

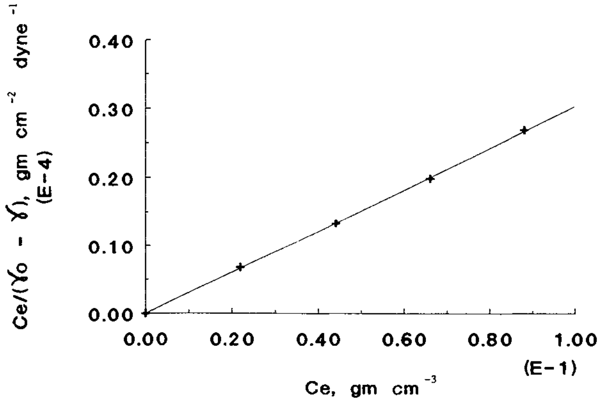

Fig. 1. Plot of $C_e/(\gamma^0 - \gamma)$ versus C_e for air–water surface in the presence of Triton X405. The solid line represents a linear regression of the data.

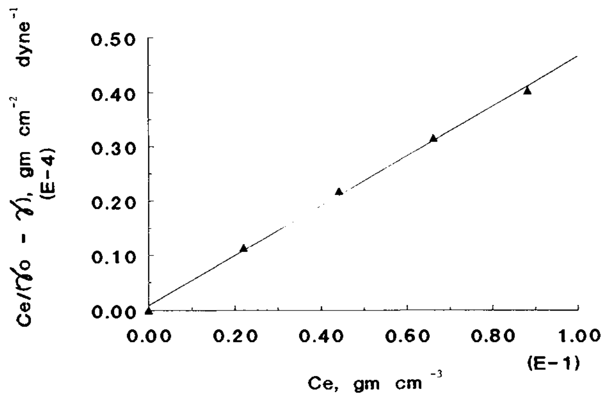

Fig. 2. Plot of $C_e/(\gamma^0 - \gamma)$ versus C_e for mineral oil–water interface in the presence of Triton X405. The solid line represents a linear regression of the data.

Table III. Photon Correlation Spectroscopy Studies for Mineral Oil-in-Water Emulsions Containing Various Concentrations of Triton X405

C_e (g/ml)[a]	r (nm)	r_w (nm)	P
0 (fresh)	400.6	53.1	7.54
0 (1 hr)	377.6	51.9	7.28
0.61E-2	21.1	15.9	1.33
1.22E-2	18.1	11.5	1.57
1.84E-2	10.8	6.5	1.66
2.45E-2	8.1	4.8	1.67
3.06E-2	6.0	4.2	1.43

[a] Grams per cubic centimeter of aqueous phase.

The mineral oil-in-water emulsions containing no surfactant were particle sized at time 0 and at 1 hr. For the initial particle size estimate, a mass mean radius of 400.6 nm and a polydispersity of 7.54 were obtained. After the emulsion had aged 1 hr, a mass mean radius of 377.6 nm and a polydispersity of 7.28 were obtained. The similarity of these data suggests that despite the wide droplet distribution profiles, no substantial aging effects occur over the first hour. As such, the initial mass mean radius (400.6 nm) was accepted as an estimate of r_0, the mass mean oil droplet radius in a 10% (v/v) mineral oil-in-water emulsion in the absence of surfactant.

For all surfactant-containing emulsions, the polydispersity was 1.67 or less, which suggests that the oil droplet radius distribution profiles were very narrow for these mineral oil emulsions.

The external phase concentration (C_e) may not be directly determined without disrupting the system equilibria. Therefore, it was necessary to approximate this value for further calculations. In the absence of significant surfactant partitioning into the oil phase, it may be assumed that the majority of surfactant would be free in the external emulsion phase since the surfactant load used was moderately high. Under these conditions, C_e may be approximated as the mass of surfactant per unit volume of aqueous phase.

Figure 3 is the plot of $C_e/(r_0 - r)$ versus C_e. Theoretically, this plot should be linear and the observed linear correlation coefficient was high ($r = 0.999$). Thus, the theoretical model presented herein as well as the assumptions and conditions applied to the data appear to depict adequately the dependence of mean oil droplet radius on external phase surfactant concentration for these mineral oil–Triton X405–water systems.

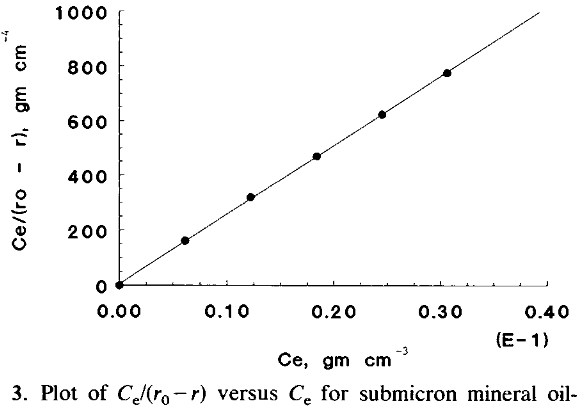

Fig. 3. Plot of $C_e/(r_0 - r)$ versus C_e for submicron mineral oil-in-water emulsions in the presence of Triton X405. The solid line represents a linear regression of the data.

The slope of the linear regression of the data in Fig. 3 is estimated as 2.53E4 cm^{-1} and the intercept as 5.07 g/cm^4. If it is assumed that γ_m is a true constant (20.9 dyne/cm obtained from mineral oil–Triton X405–water studies), then δP may be estimated from either the slope or the intercept of the linear regression of the data in Fig. 3. From Eq. (6), the slope is

$$\text{slope} = \delta P/(2\gamma_m) \tag{10}$$

or

$$\delta P = 2\gamma_m \text{ slope} \tag{11}$$

For this system, δP is approximated as 1.05E6 dyne/cm^2. This is consistent with previous estimates of δP (7).

The theory within has two advantages over previously described models. First, the model accounts for nonlinear surfactant adsorption to the interfacial region. Second, the model is not restricted to low surfactant loads provided that only a surfactant monolayer is adsorbed.

The utility of the model is that the necessary experimental data (system constants such as δP, B, and γ_m) may be readily estimated and may be used to predict accurately the mean oil droplet radius in an oil-in-water emulsion.

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