

Notes

A Simple Model for the Structure of Spherical Microemulsions

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Introduction

Ultrafine microlatex particles ($20 < d < 100$ nm) can be prepared by using an oil-in-water microemulsion.¹⁻³ It has been found that the size of such formed microlatex particles depends on the amounts of initiator and stabilizer (surfactant).^{3,4} A well-established relationship between the amount of stabilizer and the microlatex particle size will enable us to engineer ultrafine microlatex particles with a desired diameter for various applications, such as drug carriers. Antonietti et al. proposed the simple model in Figure 1a to describe the relationship between the monomer core and stabilizer with a number of assumptions.⁴ On the basis of this model, they related the particle radius (R) to the stoichiometry as

$$R \cong b[1 - (1 + W_s/W_m)^{-1/3}]^{-1} \quad (1)$$

where W_s and W_m are the macroscopic weights of the stabilizer and the monomer. Recently, they again used this model to fit their microemulsion data and obtained a value of b (~ 3.5 nm), while the fully stretched stabilizer length is only 2.7 nm.⁵ They related this ~ 1 -nm difference to the hydrodynamically active hydration shell of the polar end. We found that there are two fundamental problems associated with their model. First, before polymerization, the hydrophobic tail of the stabilizer should partially immerse into the monomer core to form a surfactant interlayer, which is schematically shown in Figure 1b, because it is a thermodynamically more favorable state, or, in other words, the micelle formed by the stabilizers is swollen by the monomers.⁶ Thus, there exist three phases in this type of microemulsion system: the "oil" phase, the water phase, and the surfactant interlayer phase. After polymerization, the tails of the stabilizers will be trapped inside the final microlatex particles, only with the hydrophilic heads on the surface. Therefore, b , if it is observable, should be smaller than the length of the stabilizer and certainly smaller than the value listed in ref 5. Second, the average occupied surface area per stabilizer (s) should be considered as a fundamental parameter for governing the sizes of microemulsions and final microlatex particles. Due to the finite size of the stabilizer, there should exist a low limit for s . When this limit is reached, the microemulsions are completely covered. Further increase of the stabilizer will have the following possible consequences: (1) if the dispersion energy is not sufficient to break the existing microemulsions (the monomer droplets), the extra stabilizers will form additional micelles without the monomer core; (2) if the dispersion energy is high enough to produce microemulsions with smaller size, the extra stabilizers will be adsorbed on the microemulsions

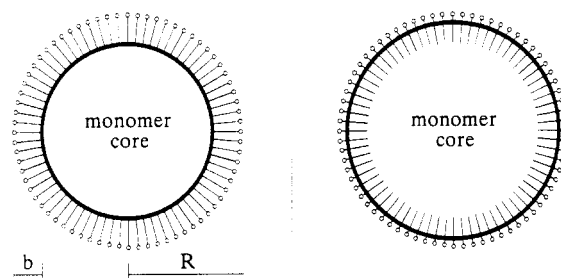


Figure 1. (a, Left) Antonietti's model of the structure of a microemulsion,⁵ where R is the diameter of the monomer core and b is the thickness of the stabilizer layer. (b, Right) A simple model of the structure of the microemulsion used in the present work, wherein the long hydrophobic tails of the stabilizer are immersed inside the monomer (oil) core instead of on the surface.

since, for a given amount of monomer, the smaller the monomer droplets, the larger the total particle surface area will be. The present work was designed to verify the two models with a set of carefully prepared microemulsions.

Experimental Section

Polymer Synthesis. We have adopted the identical procedure listed in ref 5 to prepare the microemulsions and synthesize the latex particles. The only difference is the initial composition. In this work, 100 g of aqueous solution contained 2 g, instead of 10 g used in ref 5, of freshly distilled styrene (monomer). The amount of stabilizer (cetyltrimethylammonium bromide (CTAB)) was changed from 0.4 to 6 g for different microemulsion samples. In all cases, the cross-linking density is 1/10, i.e., one cross-linking per 10 monomer units on average. By using a high-speed stirrer, we ensured that a sufficient dispersion energy was supplied. The details of synthesis can be found in ref 5.

Dynamic Light Scattering. The microlatexes were characterized at 25 °C with a commercial laser light scattering spectrometer (ALV-5000, Langen in Hessen, Germany) with an argon ion laser (Coherent INNOVA 90, operated at 488 nm and 100 mW) as the light source. The primary beam is vertically polarized. By placing a polarizer in front of the detector, we measured only the vertically polarized scattered light. All measured time correlation functions were analyzed by the Laplace inversion program (CONTIN)⁷ equipped with the correlator. The details of the laser light scattering instrumentation and its operation can be found elsewhere.^{8,9}

Results and Discussion

All results are summarized in Table 1. $\bar{D} = \int_0^\infty G(D)D dD$, where $G(D)$, the translational diffusion coefficient distribution, was the Laplace inversion result of the measured time correlation function. \bar{D} values obtained at finite concentrations (C) and scattering angles (θ) were extrapolated to $C = 0$ and $\theta = 0$. \bar{D} in Table 1 is the extrapolated result. R_h was calculated from \bar{D} by replacing the average \bar{D} with D in the well-known Stokes-Einstein equation, $R_h = k_B T / (6\pi\eta D)$, where k_B and η are the Boltzmann constant and the viscosity, respectively. $\mu_2/\bar{D}^2 = \int_0^\infty G(D)(D - \bar{D})^2 dD/\bar{D}^2$, which characterizes the distribution width of $G(D)$.¹⁰ Our results are similar to that in ref 5. However, the distributions of our samples, especially the samples prepared with the higher W_s/W_m ratio, are narrower than that in ref 5.

Table 1. Summary of Dynamic Light Scattering Results of the Microlatex Particles in Dilute Suspensions at 25 °C^a

sample	W_s/m	$\bar{D}/(\text{cm}^2/\text{s})$	\bar{R}_h/nm	$1 + \mu_2/\bar{D}^2$
CTAB1	0.20	4.43×10^{-8}	55.1	1.07
CTAB2	0.25	5.40×10^{-8}	45.2	1.04
CTAB3	0.30	6.19×10^{-8}	39.4	1.05
CTAB4	0.35	7.22×10^{-8}	33.8	1.06
CTAB5	0.40	7.80×10^{-8}	31.3	1.04
CTAB6	0.45	8.45×10^{-8}	28.9	1.05
CTAB7	0.50	9.57×10^{-8}	25.5	1.05
CTAB8	0.60	1.06×10^{-7}	23.0	1.04
CTAB9	0.70	1.15×10^{-7}	21.2	1.06
CTAB10	0.80	1.26×10^{-7}	19.4	1.06
CTAB11	0.90	1.38×10^{-7}	17.7	1.04
CTAB12	1.00	1.49×10^{-7}	16.4	1.05
CTAB13	1.50	1.72×10^{-7}	14.2	1.07
CTAB14	2.00	1.86×10^{-7}	13.1	1.04
CTAB15	2.50	2.14×10^{-7}	11.4	1.04
CTAB16	3.00	2.37×10^{-7}	10.3	1.05

^a Relative errors: \bar{D} and \bar{R}_h , $\pm 2\%$; μ_2/\bar{D}^2 , $\pm 15\%$.

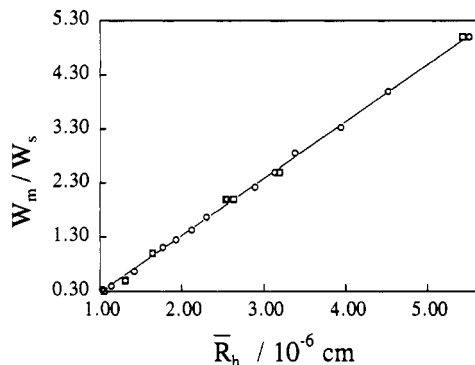


Figure 2. Plot of the macroscopic weight ratio of monomer to stabilizer (M_m/M_s) versus the hydrodynamic radius (\bar{R}_h).

On the basis of the model in Figure 1b, the average surface area (s) per stabilizer equals the ratio of the total surface area (A) to the total stabilizer number ($N_A W_s/M_s$), where M_s and N_A are the molar mass of the stabilizer and Avogadro's number, respectively, and A equals the one-particle surface area ($4\pi R^2$) multiplied by the total particle number $[(W_m + W_s)/(4/3\pi R^3 \rho)]$, i.e.

$$s = \left(4\pi R^2 \frac{W_m + W_s}{4/3\pi R^3 \rho} \right) / \left(\frac{W_s N_A}{M_s} \right) \rightarrow \frac{W_m}{W_s} = s \left(\frac{N_A \rho}{3M_s} \right) R + C \quad (2)$$

where ρ is the particle density (~ 1.05) and C is a constant. For a given W_s/W_m , in order to minimize the interface energy between monomers ("oil") and water, the particle surface should be fully covered by the stabilizer; i.e., s should approach its minimum constant value. Figure 2 shows a plot of W_m/W_s versus R_h , where "O" are the data from the present work and "□" are the data from ref 5. By assuming that the particles are uniform in density, we can replace R with R_h in eq 2 or, strictly speaking, with $R_h + \Delta R_h$, where ΔR is the contribution of the hydrophilic head

of the surfactants to R_h . It can be shown that if R is replaced with $R_h + \Delta R_h$, the term containing ΔR_h can be combined with C to form another new constant. Equation 2 has the essential feature. The data in Figure 2 convincingly show that s is a constant. Otherwise, the data would not follow a straight line so well. With the known values of ρ and M_s , we were able to obtain that $s = 0.182 \text{ nm}^2$ from the slope. In comparison with the value of 0.14 nm^2 listed in ref 5, the value of s obtained in the present work is more reasonable if we consider the cross section of the CTAB molecule. As we expected, the surfactant molecules on the latex surface in microemulsions have reached the densely packed state as surfactants in a monolayer, where $s \approx 0.18 \text{ nm}^2$.¹¹

Conclusion

We have shown that the structure of a spherical microemulsion can be better described with the simple model in Figure 1b, where the average occupied surface area per stabilizer is considered as a fundamental parameter for governing the size of microlatex particles and microemulsions. Our results suggest that, for a given experimental condition, the stabilizers have a tendency to reach a closely packed state on the particle surface to minimize the interface energy between oil and water. Therefore, if a sufficient dispersion energy is supplied, we are able to predict the sizes of microemulsions and final particles from the macroscopic weight ratio of monomer to stabilizer.

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