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Effect of Surfactant Concentration on Particle Nucleation in Emulsion Polymerization of *n*-Butyl Methacrylate

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ABSTRACT: The effect of surfactant concentration on particle nucleation in emulsion polymerization of *n*-butyl methacrylate has been studied using sodium dodecyl sulfate as the surfactant and potassium persulfate as the initiator. The rates of reaction as a function of time were determined for surfactant concentrations above and below critical micelle concentration of the surfactant. The order of dependence of the particle number on the surfactant concentration was found to be different in different ranges of surfactant concentration. This has been explained on the basis of the predominant phenomenon that affects particle nucleation in each range of surfactant concentration. In the range where the end of particle nucleation is determined by a critical surfactant coverage necessary for colloidal stability, the particle number is expected to increase in proportion to the third power of the surfactant concentration. It has been shown how a size-dependent volumetric growth-rate of particles can result in different exponents in the Smith−Ewart equation relating the particle number to surfactant concentration. A constant volumetric growth rate of particles is assumed in the Smith−Ewart theory of particle nucleation.

Introduction

n-Butyl methacrylate (BMA) is a common monomer for fundamental studies in emulsion polymerization. It has a low water solubility, e.g., ca. 3.2 mM at 70 °C,[1] which is comparable to that of styrene. This makes it a "conventional" monomer for emulsion polymerization. It has a high propagation rate constant (e.g., 1243 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 70 °C[2] compared to a value of 480 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ for styrene[3]). Sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) are probably the most extensively studied surfactant and initiator, respectively, in emulsion polymerization. SDS is a micelle-forming surfactant, and KPS is a thermal initiator that dissociates at high temperatures to form sulfate free radicals.

Surfactant plays a key role in particle nucleation in emulsion polymerization. It stabilizes the newly formed particles and the particles that continue to grow during the polymerization. The number of polymer particles formed during the emulsion polymerization is usually sensitive to the amount of surfactant in the recipe. The rate of polymerization and the molecular weight of the polymer are also affected by the surfactant concentration through their dependence on the particle size and number.

In this paper, the effects of surfactant concentration on the particle concentration and the rate of polymerization have been studied. The Mettler RC1 reaction calorimeter was used to obtain the rate of polymerization as a function of time. Dynamic light scattering and capillary hydrodynamic fractionation were used to determine the particle diameter and, hence, the particle concentrations in the final latexes. The expected dependencies of the particle number on the surfactant concentration, over different ranges of the surfactant concentration, are discussed.

Reaction calorimetry has been successfully used to determine the instantaneous rate of heat evolution, Q_r (J/s), during exothermic polymerization reactions.[4,5] The rate of heat evolution is proportional to the rate of polymerization R_p ($\mathrm{mol\ dm^{-3}\ s^{-1}}$) according to eq 1, where the molar heat of polymerization ΔH_p (J/mol) is obtained using eq 2.

$$R_p = \frac{Q_r}{\Delta H_p V_w} \qquad (1)$$

The rate of polymerization, R_p, is the moles of BMA polymerized per unit time per unit volume of water in the reactor, and V_w ($\mathrm{dm^3}$) is the volume of water in the recipe.

$$\Delta H_p = \frac{M_0 \int_0^t Q_r \, dt}{mx} \qquad (2)$$

where m (g) is the initial mass of monomer in the recipe, x is the fractional conversion of the monomer after time t (s) of reaction, M_0 (g) is the molecular weight of the monomer, and the integral can be evaluated from the experimental Q_r values. The heat of polymerization of BMA at 70 °C was determined to be 60.7 ± 1.2 kJ/mol at 70 °C.

Tauer et al. have reported some reaction calorimetric results for the emulsion polymerization of BMA using SDS surfactant.[6] They have compared the reaction rate profiles obtained using a nonionic initiator, poly(ethylene glycol)-azo-initiator, with those obtained using the ionic initiator, KPS. They found that the while the final particle size was affected by the KPS concentration, it was almost independent of the poly(ethylene glycol)-azo-initiator amount in the recipe. The shapes of the polymerization rate vs time curves reported in this paper differ from those observed by Tauer et al. but are consistent with the results of Varela de la Rosa et al.[5] for the emulsion polymerization of styrene.

Materials

n-Butyl methacrylate (BMA, 99%, CAS # 97-88-1, MW = 142.20 g/mol, Sigma-Aldrich) inhibited by 10 ppm monomethyl

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ether of hydroquinone (MEHQ, CAS # 150-76-5) was used as the monomer. The monomer was freed from the inhibitor by passing it through an inhibitor-removal column (Sigma-Aldrich). Sodium dodecyl sulfate (SDS, CAS # 151-21-3, MW = 288.38 g/mol, Ultrapure Bioreagent, J.T. Baker) was used as the surfactant, potassium persulfate (KPS, CAS # 7727-21-1, 99+%, MW = 270.33 g/mol, ACS reagent, Sigma-Aldrich) as the initiator, and sodium bicarbonate (CAS # 144-55-8, MW = 84.01 g/mol, Mallinckrodt Baker, Inc.) as the buffer. The nitrogen gas (Zero Grade 0.5, minimum purity 99.998%, oxygen <0.5 ppm) was obtained from Airgas. All the chemicals except BMA were used as received.

Results and Discussion

Determination of cmc of SDS. A wide range of critical micelle concentration (cmc) values for SDS can be found in the emulsion polymerization literature. For example, Nomura et al. mention a cmc value of ca. 0.5 g/dm^3 (1.7 mM)[7] while Gilbert reports a value of 3.9 mM[8] and Varela de la Rosa states a value of 6.2 mM.[9] Schork and Ray have determined the surface tensions of solutions of SDS in pure water, and water saturated with methyl methacrylate, using the Wilhelmy plate method.[10] They found that the presence of methyl methacrylate (MMA) had little effect on the cmc or the surface tension at the cmc. However, at low surfactant concentrations, the surface tension in the presence of MMA was much lower than in its absence. Their data indicate a cmc of ca. 0.5 g/dm^3 (1.7 mM), the same as the value reported by Nomura et al. for styrene emulsion polymerization. Sutterlin has determined the cmc of SDS at 80 °C in the presence of 7.93 mM ammonium persulfate to be ca. 6 mM,[11] and Giannetti has reported the cmc to be 4.4 mM at 50 °C.[12]

The critical micelle concentration of SDS depends on its purity, the ionic strength of the solution, the water solubility of the monomer that may be surface active, the reaction temperature, etc. The cmc of SDS was determined at room temperature in pure water, in the presence of $NaHCO_3$, and monomer, by bubble tensiometry[13] using the Sensadyne (model 6000) bubble tensiometer. The cmc in pure water was ca. 9.1 mM, in good accord with the value of 9 mM reported by Dunn.[14] In water saturated with BMA, it was ca. 7.6 mM. The aqueous phase of our recipe contained 3 mM KPS and 9.65 mM $NaHCO_3$. The cmc in water containing ca. 9.65 mM $NaHCO_3$ was 6.2 mM and was almost the same when the water was saturated with BMA. However, in a 9.65 mM $NaHCO_3$ and 3 mM KPS solution in water, the cmc further decreased to ca. 5 mM. The surfactant used in our work was the Ultrapure Bioreagent obtained from J.T. Baker.

Effect of Surfactant Concentration. The use of reaction calorimetry in emulsion polymerization has been found to offer mechanistic insights that may not be possible with conventional methods like gravimetry, densitometry, etc.[5] The results of Varela de la Rosa et al. suggest continuous nucleation until, or even past, the disappearance of monomer droplets (ca. 40% conversion) during emulsion polymerization of styrene using SDS surfactant and KPS initiator.[15]

Table 1 gives the recipe to study the effect of surfactant concentration on the kinetics of emulsion polymerization of BMA. The reactions were performed in the Mettler RC1 reactor using a 4.5 cm diameter pitched blade turbine. The monomer and the DI water containing SDS were charged into the reactor. Nitrogen was passed through the reactor over the surface of the fluid for 45−60 min until the temperature stabilized at 25 °C. A calibration was performed to determine the heat transfer coefficient, U (W m^{-2} K^{-1}), between the emulsion and the fluid in the jacket surrounding the reactor, at the agitation speed employed. The temperature was ramped to 70 °C. A second calibration was done to determine U at the reaction temperature. The initiator and buffer were then injected as a 20 g solution in DI water. The total time between charging the emulsion in the reactor and adding the initiator solution was ca. 2.5 h. A sharp rise in the rate of heat evolution, from the baseline value, was observed as soon as the initiator solution was injected, and there was no induction period. About 3 cm^3 of 1 wt % aqueous hydroquinone solution was injected at the end of the reaction. A final calibration was performed to determine U for the latex. Heat transfer coefficients that are linear interpolations of the values determined at the beginning and end of the reaction were used to calculate the heat evolution rate, Q_r (J/s), during the reaction. Figure 1 shows the effect of surfactant concentration on the rate of polymerization, R_p, as a function of the reaction time. The rate of polymerization was calculated from Q_r using eq 1. The fractional conversion, x, of the monomer at time t during the polymerization was obtained from Q_r using eq 3:

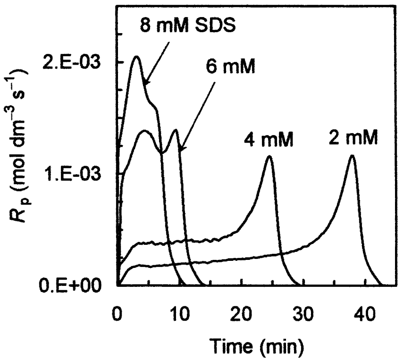

Figure 1. Effect of SDS concentration on the kinetics of emulsion polymerization of BMA using the recipes in Table 1 (T_r = 70 °C).

Table 1. Recipe for Studying the Effect of Surfactant Concentration in the Emulsion Polymerization of BMA Using the Mettler RC1 Reaction Calorimeter (T_r = 70 °C)

ingredient	weight (g)
DI water	540.00
BMA	60.00
SDS	0.312, 0.623, 0.934, 1.246 (2, 4, 6, 8 mM)[a]
KPS	0.438 (3 mM)[a]
$NaHCO_3$	0.438 (9.65 mM)[a]

[a] Based on water.

$$x = \frac{x_f \int_0^t Q_r \, dt}{\int_0^{t_f} Q_r \, dt} \tag{3}$$

where t_f is the total time of reaction and x_f is the monomer conversion in the final latex determined by gravimetry. Figure 2 shows the conversion (x) vs time (t) profiles for the different concentrations of SDS.

The particle diameters were determined by dynamic light scattering (Nicomp 370 Submicron Particle Sizer) and confirmed by capillary hydrodynamic fractionation (CHDF 1100, Matec Applied Sciences). The concentra-

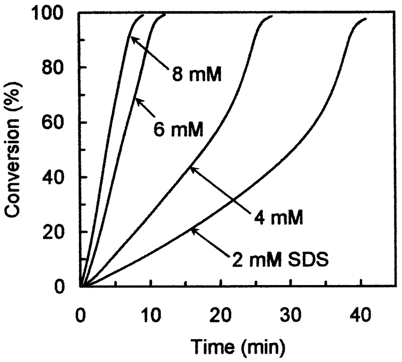

Figure 2. BMA conversion vs time profiles for emulsion polymerization of BMA using different SDS concentrations as shown in the recipes in Table 1 (T_r = 70 °C).

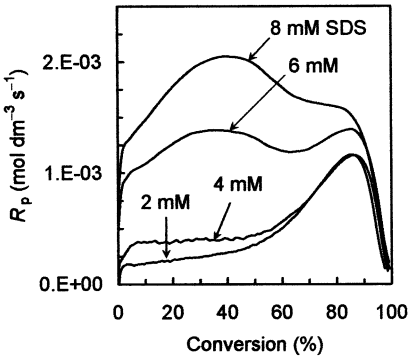

Figure 3. Effect of SDS concentration on R_p vs BMA conversion profiles. Recipes in Table 1 and T_r = 70 °C.

Table 2. Effect of Surfactant Concentration on Particle Diameter and Concentration in the Final Latex (Recipe in Table 1; T_r = 70 °C)

[SDS] (mM)	D_v (nm)	$N_p/10^{17}$ (dm^{-3} H$_2$O)
2	204	0.23
4	135	0.81
6	89	2.85
8	77	4.39

tion of particles in the final latex, N_p (no. per dm^3 water), was calculated using eq 4:

$$N_p = \left(\frac{m x_f}{w}\right)\left(\frac{\rho_w}{\rho_p}\right)\left(\frac{6 \times 10^{24}}{\pi D_v^{\,3}}\right) \tag{4}$$

where m (g) is the mass of monomer in the recipe, w (g) is the mass of water, ρ_w (g/cm^3) is the density of water, ρ_p (g/cm^3) is the density of polymer, and D_v (nm) is the volume-average diameter of the particles in the final latex. The monomer conversions in the final latexes were close to 100%. Table 2 gives the particle diameters and particle concentrations in the final latexes. In Figure 3, R_p is plotted against conversion.

For polymerization occurring predominantly in the polymer particles, the rate of polymerization is given by eq 5

$$R_p = k_p[\mathrm{M}]_p\left(\frac{\bar{n}N_p}{N_A}\right) \tag{5}$$

where k_p (dm^3 mol^{-1} s^{-1}) is the propagation rate constant, $[\mathrm{M}]_p$ (mol/dm^3) the concentration of monomer in the polymer particles, $\bar{n}$ the average number of free radicals per particle, N_p (dm^{-3}) the number of particles per unit volume of water, and N_A Avogadro's number.

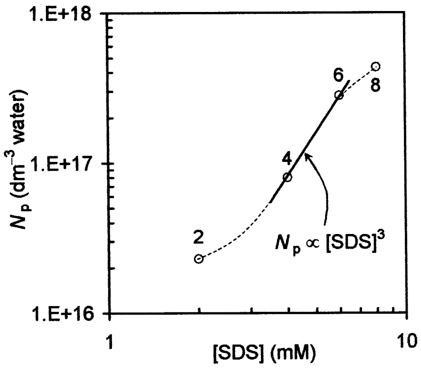

Figure 4. Dependence of N_p on [SDS]. Numbers near data points are SDS concentrations in mM. Recipes in Table 1, with [SDS] near the cmc, and T_r = 70 °C.

The saturation concentration of the BMA monomer in poly(BMA) polymer particles having an 80 nm diameter has been reported to be ca. 3.8 mol/dm^3 (at 50 °C).[16]

Figure 1 shows a clear difference in the shapes of the R_p vs time curves between the lower surfactant concentrations (2 and 4 mM) and the higher surfactant concentrations (6 and 8 mM). The curves in the former case show an almost constant rate period and are characteristic of polymerizations carried out below the cmc of the surfactant, while the curves for the higher surfactant concentrations do not show any constant rate period and are typical of reactions performed above the cmc.[5,15] Thus, from the shapes of the Q_r curves, it can be inferred that the cmc, under the reaction conditions, lies between 4 and 6 mM.

Using reaction calorimetry to determine monomer conversion and capillary hydrodynamic fractionation to determine the evolution of particle diameter and particle number with reaction time, Varela de la Rosa et al.[5] concluded that during the emulsion polymerization of styrene, with [SDS] (molar concentration of SDS based on water) greater than the cmc, the peak in R_p at ca. 40% conversion corresponded to the disappearance of the monomer droplets and that particle nucleation continued until the disappearance of the monomer droplets. R_p has another peak at ca. 85% conversion, especially at the lower surfactant concentrations. This acceleration in rate is a consequence of the gel effect. The gel effect occurs because of an increase in $\bar{n}$ due to a decrease in k_t (dm^3 mol^{-1} s^{-1}), the termination rate constant, with increasing conversion.[17] Since the polymerization temperature is greater than the glass transition temperature of the polymer (T_g), termination is dominated by the reaction between a long, entangled polymer chain and a short, mobile chain (unlike termination between two long entangled chains meeting each other by reaction−diffusion, below the T_g). As the conversion increases, the movement of the short chains becomes slower; they grow longer and become more entangled before they terminate. The net effect is a decrease in the average k_t and an increase in $\bar{n}$. R_p increases until the effect of decreasing $[\mathrm{M}]_p$ exceeds the effect of increasing $\bar{n}$. The more pronounced gel effect at lower concentration of SDS is due to the larger particles that can accommodate multiple radicals without mutual termination between them.

The sharp increase in the reaction rate from the recipe with 4 mM SDS to the recipe with 6 mM SDS corresponds to an increase in the particle number as shown in Figures 3 and 4. The order of dependence of N_p on

Table 3. Recipes To Study the Effect of SDS Concentration on Particle Number for [SDS] Greater Than the cmc (Bottle Polymerizer and $T_r = 50$ °C)

	amount (g)					
	1	2	3	4	5	6
BMA[a]	30.00	30.00	30.00	30.00	30.00	30.00
DI water	70.00	70.00	70.00	70.00	70.00	70.00
SDS[b]	0.4037	0.6056	0.8075	0.4037	0.6056	0.8075
KPS[c]	0.0378	0.0378	0.0378	0.0568	0.0568	0.0568
$NaHCO_3$[c]	0.0118	0.0118	0.0118	0.0176	0.0176	0.0176
D_v[d] (nm)	143	132	130	136	128	122
D_i[e] (nm)	149	138	135	139	133	126

[a] 30% solids. [b] Concentrations of 20, 30, and 40 mM based on water. [c] Concentrations of 2 and 3 mM based on water. [d] A value of ca. 120 nm is obtained with a 109 nm polystyrene standard. [e] Intensity-average particle diameter, determined by dynamic light scattering.

[SDS] is ca. 3 near the cmc of SDS, as shown in Figure 4. This third-order dependence of N_p on [SDS] has been reported for emulsion polymerizations of BMA at 30 °C by Brodnyan et al.[18] when the SDS concentration was in the range 17.3 mM (5 g/dm^3 water) to 69.4 mM (20 g/dm^3 water). The resulting particle concentrations were greater than 2×10^{17} dm^{-3} water. They also found that the particle concentration was almost independent of the concentration of the ammonium persulfate initiator, when it was varied between 2.2 mM (0.5 g/dm^3) and 19.7 mM (4.5 g/dm^3), and also of the initial amount of monomer in the recipe (200 g/dm^3 water and 430 g/dm^3 water). These results greatly differ from the predictions of the Smith–Ewart theory for micellar nucleation.[19] It should be pointed out that at the reaction temperature of 30 °C the rate of generation of free radicals from ammonium persulfate is expected to be relatively low. Although no direct explanation can be found for the observed effects of [SDS] on the particle concentration in the paper by Brodnyan et al., they have proposed that at low [SDS] the rate of polymerization will be proportional to the particle volume and at high [SDS] the rate is proportional to the particle surface area.

The differences between Brodnyan's recipe and the recipe in Table 1 are the lower surfactant concentrations and a higher reaction temperature in the latter. To determine the dependence of N_p on [SDS], at concentrations significantly greater than the cmc, latexes were prepared using the recipes in Table 3 and a bottle polymerizer. The reaction temperature was 50 °C. The monomer conversion at the end of the reactions was greater than 99%. The table also shows the volume-average and intensity-average particle diameters, determined by dynamic light scattering. In Figure 5, N_p is plotted against the concentrations of SDS for the two different initiator concentrations. It is seen that the order of dependence of N_p on [SDS] is ca. 0.44, lower than the value of 3 found by Brodnyan et al., and also lower than the Smith–Ewart prediction of 0.6. Thus, for the recipe in Table 1, where the surfactant concentration was low, log(N_p) vs log([SDS]) has a slope of ca. 3, while at surfactant concentrations significantly greater than the cmc, the slope is ca. 0.44.

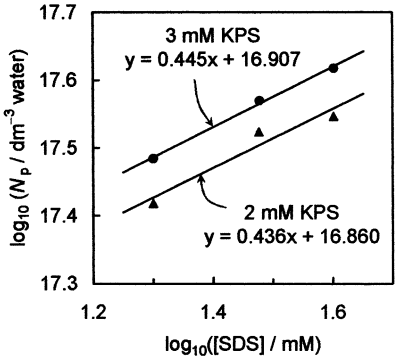

Figure 5. Dependence of N_p on [SDS]. Recipes in Table 3 with [SDS] greater than the cmc and two different initiator concentrations ($T_r = 50$ °C).

This is consistent with the data of Sutterlin, who has reported the particle concentrations for a series of polyacrylate and polymethacrylate latexes as a function of the SDS concentration in the recipe.[11] An S-shaped curve was obtained when N_p was plotted against [SDS]. When the slopes of log(N_p) vs log([SDS]) are evaluated in different ranges of surfactant concentration, it is observed that at low surfactant concentrations (less than ca. 0.1 mM) N_p shows only a weak dependence on [SDS] (slope of ca. 0.1). For [SDS] near the cmc, the order of dependence of N_p on [SDS] is ca. 3, and at higher [SDS] the dependence is again weak, near the value of 0.6 predicted by Smith and Ewart. The higher order of dependence is also evident in the data of Tauer et al.[6] A line of slope 3 can be drawn through the points corresponding to SDS concentrations of 6.1 and 8.7 mM. Poly(ethylene glycol)-azo initiator, with a molecular weight of 200 g/mol of the poly(ethylene glycol) chain, was used in their experiments. Florence et al.[20] have also reported a surfactant exponent of 0.49, lower than the Smith–Ewart value of 0.6, for the dependence of N_p on [SDS] during emulsion polymerization of BMA using SDS concentrations ranging from ca. 17 to ca. 73 mM.

Expected Dependence of N_p on [SDS]. There are two widely accepted mechanisms of particle nucleation in emulsion polymerization. According to the micellar nucleation theory,[19,21] a particle is nucleated when a free radical enters a monomer swollen surfactant micelle and reacts with the monomer. According to the homogeneous nucleation mechanism described by Priest,[22] the free radical reacts with the dissolved monomer in the aqueous phase until the oligomeric radical loses its water solubility and precipitates to form a "primary" particle. Priest also proposed the idea of coagulation between the primary particles to an extent depending on the quantity of surfactant used. In the absence of any surfactant, the final particle size would depend on the relative number of sulfate groups on the surface of the particles, in the case of a persulfate initiator. These sulfate end groups stabilize the particles against coagulation by electrostatic repulsion. Numerous refinements to both these theories have appeared in the literature. For example, see Ugelstad and Hansen,[23−26] Gilbert and Napper,[27] Giannetti,[28] Fitch and Tsai,[29] Fitch,[30] Goodwin et al.,[31] and the references therein.

The mathematical model for the homogeneous nucleation mechanism that incorporates the effects of the physical factors influencing the capture rate of oligomers and the limited flocculation of the primary particles is known as the HUFT (Hansen−Ugelstad−Fitch−Tsai) theory.[32] Lichti et al.[33] have pointed out the subtle differences between their coagulative nucleation mechanism and the homogeneous nucleation mechanism, in that the primary particles according to their theory do not polymerize rapidly and coagulate with other primary particles. Only after enough polymer is present in the coagulated entities does sufficient monomer absorption occur, and the resulting mature latex particle starts growing rapidly. Also, from the early-time particle size distributions in emulsion polymerization of styrene using SDS well above the cmc indicate that the particle nucleation rate should be an increasing function of time, which cannot be accounted for by the micellar and homogeneous nucleation theories. In the coagulative nucleation theory, the coagulation rates were obtained through the DLVO theory, and the variation of the particle concentration with initiator concentration and ionic strength agreed with the experimental data.

For detailed mathematical models based on the above mechanisms, the reader is referred to the chapter on particle formation in Gilbert's book.[34] In the following analysis, simple equations will be used to explain the observed dependencies of N_p on [SDS]. Only the order of dependence will be of interest, and a quantitative prediction of the particle concentration on the concentration of SDS is not attempted. Three ranges of surfactant concentration are considered: low, intermediate, and high. The actual concentration values in these ranges will be characteristic of the system (monomer, surfactant, initiator, ionic strength, and temperature). In our experiments, the "low" range includes surfactant concentrations ranging from zero to concentrations well below the cmc. The "intermediate" range is the range of concentrations around the cmc, and the "high" range includes concentrations significantly greater than the cmc.

Low Surfactant Concentrations. At low surfactant concentrations, the primary particles formed by precipitation of the oligomeric radicals formed in the aqueous phase will undergo rapid coagulation until the surface charge density of the resulting entity is sufficiently high to impart colloidal stability. The surface charge density of the colloidally stable mature particles is mainly derived from the initiator end groups. The surface area formed by coagulative growth of the particles provides a radical capture rate high enough to preclude formation of any new primary particles. The surfactant molecules adsorb on the surface of the particles and are expected to play only a minor role in determining the final particle number.

Ottewill has shown some calculations illustrating the dependence of colloidal stability on the size of the aggregated primary particles and the electrolyte concentration.[35] The main factors that will decide the particle number are the rate of generation of free radicals and the ionic strength of the solution. The order of dependence of N_p on the surfactant concentration will be low in this regime.

Intermediate Surfactant Concentrations. At low surfactant concentration, the surface charge density due to the initiator end groups determines the particle number in the latex. At intermediate surfactant concentrations, the surface charge density mainly due to the adsorbed surfactant molecules determines the particle number. The primary particles aggregate to a smaller extent because of the higher surfactant concentration.

The first step in the particle nucleation process is the formation of oligomers in the aqueous phase of a certain degree of polymerization at which they precipitate for form primary particles. Below the cmc, in the absence of micelles, the kinetics of this step will be identical for all surfactant concentrations. The primary particles will undergo aggregation to produce "precursor" particles that are still colloidally unstable and, finally, the colloidally stable "mature" particles. The number of mature particles, N_c, will depend on the surfactant concentration. The formation of the mature particles is accompanied by adsorption of surfactant on the surface of the polymer particles. Initially, the surface coverage of the precursor particles by the surfactant molecules is low because of the large number of precursor particles. Upon aggregation, the total surface area of the particles decreases, and the surfactant coverage increases. The aggregation of the precursor particles continues until the surfactant coverage increases to a critical value Γ_c. Let D_c be the diameter of these N_c mature particles. It is assumed that the surface area of these N_c mature particles is high enough so that any new radical that is generated in the aqueous phase is captured by the mature particles, and no more particles are nucleated. The diameter D_c and the surface coverage Γ_c are related according to

$$\Gamma_c = \frac{SD_c}{6V_c} \tag{6}$$

where S is the moles of surfactant in the system and V_c is the total volume of polymer particles at the end of the particle nucleation stage. In this simple analysis, it is assumed that the surfactant adsorbed on the surface of the droplets, or present in the aqueous phase, is negligible. Thus

$$D_c = \frac{6\Gamma_c V_c}{S} \tag{7}$$

The number of mature particles N_c is given by

$$N_c = \frac{6V_c}{\pi D_c^{\,3}} \tag{8}$$

From eqs 7 and 8

$$N_c = \frac{S^3}{36\pi V_c^{\,2}\Gamma_c^{\,3}} \tag{9}$$

Thus, the order of dependence of the concentration of polymer particles on the surfactant concentration is 3. Clearly, all the mature particles will not be formed by aggregation of the same number of primary particles and, therefore, will not be of the same diameter D_c as assumed above. However, it can be shown that a distribution of diameters of the mature particles will merely introduce another factor in the expression for N_c in eq 9, but the order of dependence of N_c on the surfactant concentration will remain unaffected. For example, in the case of a log-normal size distribution (with parameters μ and σ) of the mature particles, where the volume-average diameter, D_v, is $\exp(\mu + 3\sigma^2/2)$ and the surface-average diameter, D_s, is $\exp(\mu + \sigma^2)$ (see Supporting Information), N_c will be given by

$$N_c = \frac{S^3 \exp(3\sigma^2)}{36\pi V_c^{\,2} \Gamma_c^{\,3}} \qquad (10)$$

A similar third-order relationship can be obtained assuming that the total surface area of the polymer particles in the final latex will be equal to the area that can be fully covered by the surfactant molecules.[37] The latter area is given by Sa_sN_A, where a_s (m^2) is the adsorption area occupied by one surfactant molecule and N_A (mol^{-1}) is Avogadro's number. In such a case the surfactant coverage of the polymer particles in the final latex will be 100%. However, this requires continuous aggregation between the polymer particles despite saturation surfactant coverage to compensate for the increase in the surface area due to particle growth, which may not be realistic in the case of an electrostatic stabilizer such as SDS. Moreover, the surfactant coverage values in our final latexes, calculated using the adsorption isotherm of SDS on PBMA particles, were ca. 12%, 18%, 21%, and 25%, with SDS concentrations of 2, 4, 6, and 8 mM, respectively.[36] The values of 18% and 21% corresponding to the intermediate surfactant concentrations are nearly the same, as expected from the analysis leading to eq 9.

High Surfactant Concentrations. We will next consider the case where the surfactant concentration is much greater than the critical micelle concentration. For a surfactant concentration of 30 mM, a cmc value of ca. 5 mM, and an average micellar aggregation number of ca. 162, the total number of micelles is of the order of 10^{20} per dm^3 water.[12] The final number of particles is usually of the order of 10^{17} per dm^3 water. This suggests that only a small fraction of the micelles are nucleated. The polymer particles grow in size by polymerization of the monomer diffusing from the monomer droplets into the particles. The surfactant molecules (supplied by the unnucleated micelles) continue to adsorb on the increasing surface area of the particles to give a 100% surface coverage, until no more micelles are present. Smith and Ewart proposed that the particle nucleation ends at this point.

By assuming a constant volumetric growth rate of particles and a micellar nucleation mechanism, Smith and Ewart have derived the 0.4 order of dependence of the particle number on the initiator concentration and the 0.6 order of dependence on the surfactant concentration.[19] As shown by Roe,[38] the same dependencies of particle number on the concentrations of the surfactant and the initiator can be obtained without assuming the micellar nucleation mechanism. Irrespective of the actual mechanism of particle nucleation, the Smith−Ewart approach would be valid when the criterion for the end of particle nucleation is that the total surface area of the particles during the nucleation stage exceeds the area that can be covered by the surfactant molecules. Thus, for a surfactant concentration much higher than the cmc, the order of dependence of the particle concentration on the surfactant amount is expected to be lower than the third-order dependence seen previously.

Although the mathematical elegance and simplicity of the Smith−Ewart derivation is appealing, it is fairly easy to derive exponent values different from the 0.4 and 0.6 values of Smith and Ewart by minor modifications of their assumptions. Nomura et al. have shown that radical desorption from the particles increases the order of dependence of N_p on the surfactant concentration from 0.6 to 1.0 and decreases the initiator dependence exponent from 0.4 to 0.[39] As discussed below, the effect of particle size on the volumetric growth rate of the particles, when taken into consideration, also gives different exponent values for [SDS] and [KPS] dependence of N_p.

Modification of Smith−Ewart Derivation of Particle Number To Account for Size-Dependent Volumetric Growth Rate of Particles. According to the Smith and Ewart theory, the polymer particles are formed by the entry of free radicals generated in the aqueous phase into monomer-swollen micelles. Assuming that the free radicals generated in the aqueous phase are captured only by the micelles, the rate of nucleation is equal to the rate of generation of free radicals in the aqueous phase. For the more realistic assumption that both the micelles and the polymer particles capture free radicals, Smith and Ewart found that the orders of dependence of the particle number on the surfactant and initiator concentrations were the same as those obtained using the former assumption. Smith and Ewart have also assumed a constant volumetric growth rate of the particles. However, the rate of propagational volume growth per particle can be a function of particle radius[12,40,41] because the monomer concentration inside the polymer particle depends on particle size as predicted by the Morton equation.[42] The average number of free radicals per particle also, in general, depends on the particle size due to the size dependence of the entry, exit, and termination rates.[33,43] Chern and Poehlein have shown that the free radicals tend to segregate near the surface of the polymer particles because of the hydrophilicity of their sulfate end groups.[44] In such a case, one could expect that the polymerization occurs near the particle−water interface as also suggested by Medvedev[45] and that the rate of polymerization and volumetric growth rate of a particle will depend on its surface area.

Consider the empirical equation of Bradford et al. for the volumetric growth rate of a polymer particle[46]

$$\frac{dV}{dt} = \frac{d}{dt}\left(\frac{4}{3}\pi r^3\right) = Kr^a \qquad (11)$$

where V is the volume of the polymer particle, r is the radius of the particle, t is time, and K and a are constants. Using the equation for the radius of a particle as a function of time, obtained by solving eq 11, and following the procedure of Smith and Ewart, expressions for the particle number, N_p, shown in eq 12, can be derived (see Supporting Information).

$$N_p = \frac{[a_sN_A(5-a)]^{(3-a)/(5-a)}}{(3-a)(4\pi)^{(1-a)/(5-a)}}\left(\frac{\rho}{K}\right)^{2/(5-a)}[S]^{(3-a)/(5-a)} \qquad (a \neq 3)$$

$$= \frac{2\pi\rho}{K}\ln\left\{1 + \frac{a_sN_AK}{8\pi^2\rho r_0^{\,2}}[S]\right\} \qquad (a = 3) \qquad (12)$$

where r_0 (m) is the initial radius of the particle (micelle, precursor, or mature particle). r_0 is assumed to be equal to zero in the original Smith−Ewart derivation and also in the case of $a \neq 3$.

Thus, the order of dependence of N_p on the surfactant concentration is given by $(3 - a)/(5 - a)$ where a is the order of dependence of the volumetric growth rate of the particle on the particle radius. When $a = 0$, that is, the volumetric growth rate of a polymer particle is independent of the particle size, eq 12 reduces to the Smith−Ewart equation. If the volumetric growth rate of a particles is proportional to the particle radius ($a = 1$), eq 13 predicts the order of dependence on surfactant concentration to be 0.5, and if the growth rate is proportional to the surface area of the particle ($a = 2$), the exponent of surfactant concentration is 0.33.

Conclusions

The effect of SDS concentration on particle nucleation in emulsion polymerization of BMA has been studied. The order of dependence of the particle concentration in the final latex on [SDS] is found to differ greatly from the Smith−Ewart prediction of 0.6, especially near the cmc. Our data are consistent with the data reported by Sutterlin and Tauer et al. We have shown how different exponent values are expected in different ranges of surfactant concentrations. At low (near zero) SDS concentration, the initiator end groups provide most of the colloidal stabilization, and the order of dependence on the SDS concentration will be low. At intermediate concentrations of SDS, the order of dependence was shown to be 3 on the assumption that the particle nucleation ended when a critical degree of surfactant coverage was reached during the polymerization. At high surfactant concentrations, as pointed out by Roe, irrespective of the particle nucleation mechanism, if the end of particle nucleation corresponds to the disappearance of the micelles, an exponent of 0.6 is expected according to the derivations of Smith and Ewart. However, if a radius-dependent growth rate of particles is considered, exponent values lower than the Smith and Ewart value of 0.6 are expected. The dependence of the volumetric growth rate of the monomer-swollen polymer particles can be due to several reasons, including (1) thermodynamic dependence of $[M]_p$ on particle size, (2) dependence of $\bar{n}$ on particle size, and (3) dependence of the rate of polymerization on the particle surface, if the polymer−water interface is the main locus of polymerization. The effect of size dependence of $[M]_p$ on the volumetric growth rate of particles is well-known, and its influence on N_p is discussed in ref 36.

Comprehensive mathematical models exist in the literature that can be used to numerically predict the effect of surfactant concentration on the particle number. However, as pointed out by Gilbert,[47] many of these sophisticated quantitative theories require parameters that cannot be determined a priori for comparison of the predictions with experimental results. The purpose of the semiquantitative approach of this paper is to bring out the effects of some mechanistic features that are unique to each range of surfactant concentration on the concentration of polymer particles.

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Supporting Information Available: Mathematical derivation of the effect of polydispersity of the size of mature particles, on the order of dependence of particle number on surfactant concentration, at intermediate surfactant concentrations and modification of Smith−Ewart derivation of particle number to account for size-dependent volumetric growth rate of particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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