Role of Mixed Anionic−Nonionic Systems of Surfactants in the Emulsion Polymerization of Styrene: Effect on Particle Nucleation

Damien Colombié, E. David Sudol, and Mohamed S. El-Aasser*

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, 111 Research Drive, Bethlehem, Pennsylvania 18015

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ABSTRACT: The batch emulsion polymerization kinetics of styrene using various ratios and amounts of anionic surfactant sodium lauryl sulfate (SLS) and nonionic surfactant Triton X-405 (octylphenoxypolyethoxyethanol with an average number of ethylene oxide units of 40) were studied at 70 °C using the Mettler RC1 reaction calorimeter. The presence of 1 mM SLS in the emulsion polymerization of styrene using 6.4 mM Triton X-405 greatly affected the kinetics of the reaction. The initial rate of polymerization was faster in the presence of the mixture of surfactants, as 17 times more particles were initially created (1.7×10^{16} versus 1.0×10^{15} particles/dm^3). This phenomenon was observed even though most of the nonionic surfactant was associated with the oil phase prior to the reaction. However, limited aggregation took place later in the reaction. No secondary nucleation was noted at the disappearance of the droplets when SLS and Triton X-405 were used in combination, as was reported when Triton was used as the sole surfactant. When increasing amounts of SLS (3 and 5 mM) were used in combination with 6.4 mM Triton X-405, the kinetics of the reaction became faster and the number of particles formed was high (1.1×10^{18} particles/dm^3 using 5 mM SLS). No secondary nucleation was noted at the disappearance of the droplets, and the resulting latexes were stable. The initial partitioning of the Triton X-405 into the styrene monomer was affected by the presence of SLS. When no SLS was used, 95% of the Triton X-405 was associated with the oil phase as opposed to 78% when 5 mM SLS was used. The longer PEO chains were mostly located in the aqueous phase. Increasing amounts of Triton X-405 in the water phase allowed the formation of mixed micelles in the aqueous phase at higher SLS concentrations (3 and 5 mM). The resulting kinetics were fast.

Introduction

Various types of surfactants have been used for the synthesis and stabilization of polymer latexes. Anionic surfactants provide electrostatic stability as described by the DLVO theory.[1,2] The efficiency of such surfactants is dependent on many parameters such as ionic strength and pH, and this can be a major drawback in terms of stability of the latex. Nonionic or polymeric surfactants provide steric stabilization. The repulsion between particles is provided by the thermodynamically favored steric repulsion of the adsorbed materials.[3,4] It is therefore practical to use mixtures of anionic and nonionic surfactants in emulsion polymerization to combine their different stabilization properties. Most industrial emulsion polymerization processes use mixtures of surfactants. Mixtures of anionic and nonionic surfactants have been extensively studied outside the context of emulsion polymerization (micelle formation and characterization,[5] adsorption at various interfaces,[6] practical applications[7]). There is, however, little work published on the use of mixtures of surfactants in reactive systems such as emulsion polymerization.

The use of mixtures of anionic and nonionic surfactants in emulsion polymerization has been reported by Woods et al.,[8] Chu and Piirma,[9−11] and Unzueta and Forcada.[12−14] Chen et al.[15] recently determined the cmc of a mixed anionic (SLS) and nonionic (Triton X-405, octylphenoxypolyethoxyethanol with an average number of ethylene oxide units of 40; Union Carbide) system of surfactants and its effect in the emulsion polymerization of styrene. The observed cmc of mixtures of surfactants has often been reported to be lower than expected on the basis of the individual cmc's of the two surfactants. This has been attributed to the interactions between different molecules in the formation of the mixed micelles as modeled by Rubingh[16] and Blankschtein et al.[17] The emulsion polymerization kinetics of the system were also studied for various ratios of the surfactants,[18] using gravimetry to follow the conversion as a function of time. They noted Smith−Ewart[19] kinetics when the nonionic surfactant content was below 50%. The rate of polymerization and the latex stability were optimized for 80% nonionic surfactant content. When the nonionic surfactant was used alone, the kinetics were slower and the number of particles decreased greatly. Their explanation was based on the fact that a large proportion of the nonionic micelles did not participate in nucleation and that not all the primary particles could survive the flocculation process. However, the work of Özdeğer[20] et al. on the same system, using calorimetry as a way of monitoring the rate of polymerization, provides another explanation. Most of the Triton X-405 partitions into the monomer droplets initially and is later released into the aqueous phase when the droplets disappear. Calorimetry also provided a better understanding of the kinetics of the classical emulsion polymerization of styrene using an anionic surfactant (SLS).[21] Above the cmc, no constant rate period was observed. The rate of polymerization and the number of particles were noted to increase even after the disappearance of the micelles which was attributed to homogeneous nucleation. Below the cmc, a short homogeneous nucleation was observed, followed by an extended constant rate period.[22]

In this article, the kinetics of the emulsion polymerization of styrene using mixtures of anionic (SLS) and nonionic (Triton X-405) surfactants are studied using the Mettler RC1 reaction calorimeter. The nonionic surfactant content is kept constant at 6.4 mM while the SLS concentration is varied. Control experiments are conducted where each of the surfactants are used as the

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Table 1. Recipe for the Emulsion Polymerization of Styrene at 70 °C Using Mixtures of SLS and Triton X-405

ingredient	amount (g)	concn (mM)
deionized water	464.0	
distilled styrene	134.0	1.3[a]
SLS	0.1344−0.6714	1.0−5.0
Triton X-405	0−5.9468	0−6.4
sodium bicarbonate	0.1043	2.6
potassium persulfate	0.6285	5.0

[a] In moles.

Table 2. SLS Concentrations Employed in the Emulsion Polymerization of Styrene at 70 °C Using Mixtures of SLS and 6.4 mM Triton X-405

experiment	SLS amount (g)	SLS concn (mM)
DCN-1	0.1344	1.0
DCN-2	0.6714	5.0
DCN-3	0.6714	5.0
DCN-4	0.4050	3.0
DCN-5[a]	0.1344	1.0
DCN-6	0.0000	0.0

[a] No Triton X-405 was added in this experiment

sole stabilizer in the polymerization. The kinetics results are correlated with the initial partitioning of the nonionic surfactant between the oil and aqueous phases, as a function of the anionic surfactant content in the system. The aqueous properties of the initial surfactant mixture are characterized. An alternate explanation for the results of Chen et al.[18] is proposed.

Experimental Section

Materials. The experiments were run using the recipe presented in Table 1. The styrene monomer (Aldrich) was washed with a 10 wt % NaOH solution to remove the inhibitor. The monomer was washed three times with water and dried overnight over magnesium sulfate (Fisher) and distilled no more than 2 weeks before the polymerization was run. It was stored at −15 °C until use. Deionized water was used for all the reactions. Ultrapure Bioreagent sodium lauryl sulfate (J.T. Baker) was used as the anionic emulsifier. Triton X-405 (70% solution in water, Aldrich) was dried in an oven for 24 h at 70 °C and used as the nonionic emulsifier. The various amounts of the surfactants used are listed in Table 2. The nonionic surfactant concentration was kept constant at 6.4 mM (based on the aqueous phase) in most experiments, while the anionic surfactant concentration was varied. Potassium persulfate (Aldrich) was recrystallized from deionized (DI) water before it was used as initiator. Sodium bicarbonate (J.T. Baker) was used as received.

Polymerizations. The polymerizations were run in the Mettler RC1 reaction calorimeter. The Mettler RC1 is a bench-scale calorimeter, which allows the determination of the heat of reaction every 2 s. The apparatus and its use for the monitoring of emulsion polymerization kinetics have been extensively described.[20,21] The rate of polymerization (R_p) can be calculated from the heat of polymerization (Q_r), according to the following equation:

$$R_p = \frac{Q_r}{V_{aq}\Delta H_p} \tag{1}$$

where V_{aq} is the volume of the aqueous phase and ΔH_p is the molar heat of polymerization. The fractional conversion (x) at time t is calculated according to the following equation:

$$x(t) = \frac{\int_0^t Q_r(t)\,dt}{\int_0^{t_f} Q_r(t)\,dt}\,x_{grav}(t_f) \tag{2}$$

where $Q_r(t)$ is the heat of polymerization, t_f is the time at which the reaction is stopped, and $x_{grav}(t_f)$ is an independent measurement of the conversion at the end of the reaction (performed by gravimetry).

The general procedure for running the experiments is as follows. The surfactants and the buffer are dissolved at 40 °C in the DI water and charged into the Mettler RC1 reaction calorimeter (MP10 reactor). Nitrogen (Zero Grade, JWS Technologies) is passed through the reactor for 10 min while stirring at 100 rpm. The styrene is then added, the reactor sealed, and a first calibration performed at 25 °C to determine the heat transfer coefficient through the wall of the reactor. The reactor temperature is then ramped to 70 °C in 15 min, and a second calibration is performed. The initiator is dissolved in 5 g of DI water and heated to the reaction temperature to minimize the heat perturbation upon addition and injected. During the reaction, samples (3 mL) are withdrawn regularly from the reactor. The samples are diluted to 0.5% using DI water, and the particle size and particle size distribution are determined by capillary hydrodynamic fractionation (CHDF, model 1100, Matec Applied Sciences). The number of particles (N_p) is calculated from the conversion and the particle size distribution (PSD) using the following equation:

$$N_p(t) = \frac{6M_0x(t)}{\pi\rho_p\sum_i n_iD_i^3} \tag{3}$$

where M_0 is the initial amount of monomer added with respect to the water phase, $x(t)$ is the fractional conversion, ρ_p is the polymer density, and n_i is the fraction of particles with particle diameter D_i. At the end of the reaction, 2 mL of a 1 wt % aqueous solution of hydroquinone is added to the reactor to short stop any further polymerization. A final calibration is then performed.

Determination of Triton X-405 Partitioning. To evaluate the initial surfactant partitioning between the aqueous phase and the monomer phase, the following experiments were performed. Emulsions of the water, monomer, buffer, and surfactants of experiments DCN-1 to DCN-6 were prepared and analyzed. The experimental procedure is as follows. The designated amount of surfactants and sodium bicarbonate are added to the DI water in a glass beaker. The mixture is stirred at 40 °C and 400 rpm using a magnetic stirrer, until the products are completely dissolved. Then, the styrene monomer is added. The emulsion is formed, and the temperature is raised to 70 °C in 15 min. The temperature is allowed to stabilize at 70 °C for 10 min at which point the agitation is stopped, and the beaker is transferred to a water bath at 70 °C. The emulsion is allowed to cream, and the aqueous phase is removed with a syringe and needle. A gravimetric analysis is then performed to measure the solids content in the aqueous phase and the extent of the surfactant partitioning through a mass balance. Two control experiments were performed in the Mettler RC1 reaction calorimeter to match the experimental procedure of the polymerizations and to make sure the results were similar to those obtained as described as above. The partition coefficient (p) is defined as follows:

$$p = \frac{m_{\text{Triton X−405 aqueous phase}}}{m_{\text{Triton X−405 total}}} \times 100 \tag{4}$$

where $m_{\text{Triton X−405 aqueous phase}}$ and $m_{\text{Triton X−405 total}}$ represent the masses of the surfactant in the aqueous phase and the total used in the experiment.

Determination of cmc. The surface tension measurements were made by the maximum bubble pressure technique using a Sensadyne ST 6000 instrument (Chemdyne). The measurements were performed at 25 and 70 °C, and the solutions (which included both surfactants at various concentrations keeping the sodium bicarbonate (buffer) concentration constant) were allowed to equilibrate until the surface tension stabilized.

Table 3. Number- and Weight-Average Particle Sizes and Polydispersity Indexes for the Emulsion Polymerization of Styrene at 70 °C; [SLS] = 1 mM, [Triton X-405] = 6.4 mM, [KPS] = 5 mM (Experiment DCN-1)

sample	1	2	3	4	5	6	7	final
conversion (%)	2.9	16.5	26.2	34.5	42.4	50.7	60.0	93.7
D_n (nm)	78.6	123.5	147.3	169.9	183.6	197.8	218.3	249.6
D_w (nm)	84.6	133.7	154.6	174.2	188.8	201.8	221.2	253.1
PDI	1.08	1.08	1.05	1.03	1.03	1.02	1.01	1.01
particle no. ($\times 10^{-16}$/dm^3)	3.2	4.6	4.3	3.7	3.6	3.4	3.0	3.1

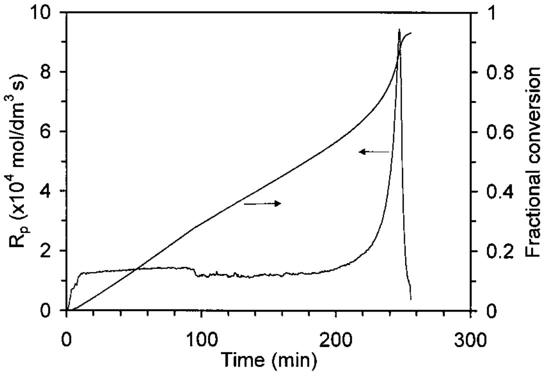

Figure 1. Rate of polymerization and fractional conversion as a function of time in the emulsion polymerization of styrene at 70 °C: [SLS] = 1 mM, [Triton X-405] = 6.4 mM, and [KPS] = 5 mM (experiment DCN-1).

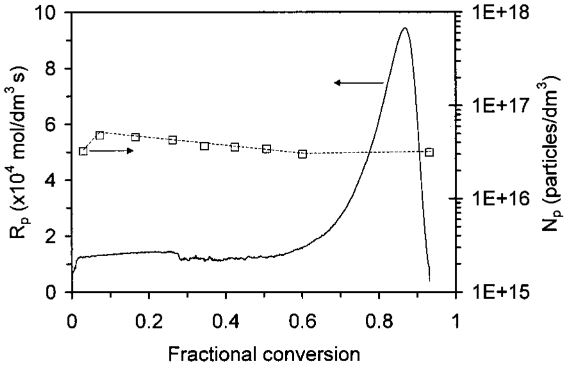

Figure 2. Rate of polymerization and number of particles as a function of fractional conversion in the emulsion polymerization of styrene at 70 °C: [SLS] = 1 mM, [Triton X-405] = 6.4 mM, and [KPS] = 5 mM (experiment DCN-1).

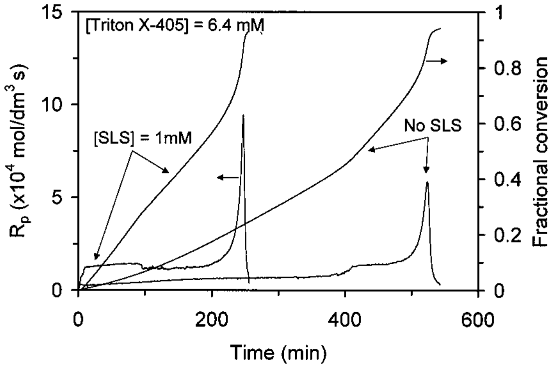

Figure 3. Effect of the presence and absence of 1 mM SLS on the rate of polymerization and fractional conversion as a function of time in the emulsion polymerization of styrene using 6.4 mM Triton X-405 and 5 mM KPS at 70 °C (experiments DCN-1 and DCN-6).

Results and Discussion

Kinetics Results. a. Effect of the Addition of 1 mM SLS on the Kinetics of the Emulsion Polymerization of Styrene Using 6.4 mM Triton X-405 Surfactant. Figure 1 shows the rate of polymerization and the fractional conversion as a function of time for experiment DCN-1 ([SLS] = 1 mM and [Triton X-405] = 6.4 mM). The kinetics of polymerization are slow. After a quick initial rise over 10 min, the rate of polymerization stabilizes and slowly increases until 90 min. The curve is relatively smooth until a small apparent drop in the rate of polymerization occurs. After this, the rate of polymerization is almost constant but somewhat noisier until about 190 min, at which time an intense gel effect begins. According to Özdeğer et al.,[20] when Triton X-405 is used as the sole surfactant, it is partitioned primarily into the styrene oil phase at the beginning of the experiment. Under these conditions, the aqueous concentration of Triton X-405 is below the cmc and the initial nucleation mechanism is homogeneous. In experiment DCN-1, the SLS concentration is lower than its cmc (6 mM)[22] as well. Slow kinetics resulting from homogeneous nucleation of a relatively small number of particles are expected until the disappearance of the monomer droplets.

Figure 2 depicts the evolution of the rate of polymerization and the number of particles as a function of the fractional conversion for the same experiment. In Table 3, the number- and weight-average particle sizes and the polydispersity indexes are reported. At first, the particle number increases and the polydispersity is around 1.08. After 16% conversion, the particle number appears to decrease with conversion (up to 60%). A slight discontinuity in the N_p data appears between 26% and 34% conversion, which corresponds to the discontinuity in the rate data and may indeed explain this phenomenon. This decreasing N_p is considered to be caused by some limited aggregation, as the polydispersity index decreases from 1.08 to 1.01 (even though the polydispersity should also decrease by particle growth alone).

As a control, a parallel reaction was performed without the addition of SLS (i.e., DCN-6 with 6.4 mM Triton X-405 as the sole surfactant). In Figure 3, the rate of polymerization and the fractional conversion as a function of time are compared for DCN-6 and DCN-1. Initially, the kinetics are relatively slow for both experiments, resulting from homogeneous nucleation. However, in the mixed surfactant experiment, the initial rate of polymerization is significantly faster (about 4 times). In experiment DCN-6, an increase in the rate of polymerization is observed after 380 min, before the occurrence of the gel effect. This effect was reported previously,[20] being further investigated by determining the evolution of the number of particles.

Figure 4 shows the rate of polymerization and the particle number as a function of the fractional conversion. As reported before,[20] the increase in the rate of polymerization in experiment DCN-6 corresponds to an increase in the particle number at approximately 45% conversion. Upon disappearance of the monomer droplets, the nonionic surfactant concentration in the aqueous phase increases sufficiently to result in a second nucleation. However, in experiment DCN-1 (mixed

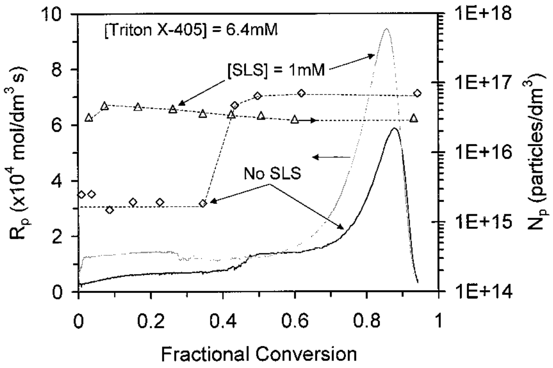

Figure 4. Effect of the presence and absence of 1 mM SLS on the rate of polymerization and number of particles as a function of fractional conversion in the emulsion polymerization of styrene using 6.4 mM Triton X-405 and 5 mM KPS at 70 °C (experiments DCN-1 and DCN-6).

surfactant system), the number of particles is initially higher (about 17 times) and decreases slightly during the experiment as described above. About 40% of the particles initially formed disappear during the course of the reaction. No secondary nucleation is observed in this case when the monomer droplets disappear. These results indicate that the partitioning of the nonionic surfactant is affected by the presence of the anionic surfactant.

By combining the R_p and N_p data, the evolution of the radical concentration in the particles can be determined. The average number of free radicals per particle ($\bar{n}$) can be calculated during the experiment according eq 5:

$$\bar{n} = \frac{N_A R_p}{k_p [M]_p N_p} \tag{5}$$

where N_A is Avogadro's number, R_p is the rate of polymerization determined from the calorimetric data, k_p is the propagation rate coefficient (425.6 dm^3/(mol s)),[23] $[M]_p$ is the monomer concentration in the particles, and N_p is the number of particles per dm^3 of aqueous phase. Below 45% conversion (before the disappearance of the droplets[20]), the monomer concentration is assumed to be constant in the particles (5.6 M).[24] Above 45% conversion, all the styrene is considered to be located in the polystyrene particles and the monomer concentration in the particles can be calculated according to the following equation:

$$[M]_p = \frac{\dfrac{1-x}{M_0}}{\dfrac{1-x}{\rho_m} + \dfrac{x}{\rho_p}} \tag{6}$$

where x is the fractional conversion, M_0 is the molar mass of styrene, ρ_m is the density of styrene, and ρ_p is the density of polystyrene.

In Figure 5, the average number of free radicals per particle is plotted as a function of fractional conversion for both experiments DCN-1 and DCN-6. Both systems have a relatively high number of free radicals per particle ($\bar{n} > {}^1/_2$) due to the large particle size obtained by homogeneous nucleation. The $\bar{n}$ values are almost constant until 40% conversion at 0.8 and 8 for experiments DCN-1 and DCN-6, respectively. The particles formed at the beginning of experiment DCN-6 are larger than those of experiment DCN-1, which accounts for the large difference in $\bar{n}$ values. However, when a crop of smaller particles is formed in experiment DCN-6, the average number of free-radicals per particle drops to approximately 0.5. This value is typical for the emulsion polymerization of styrene under case 2 conditions ($\bar{n} = {}^1/_2$; small particle size, high radical flux).

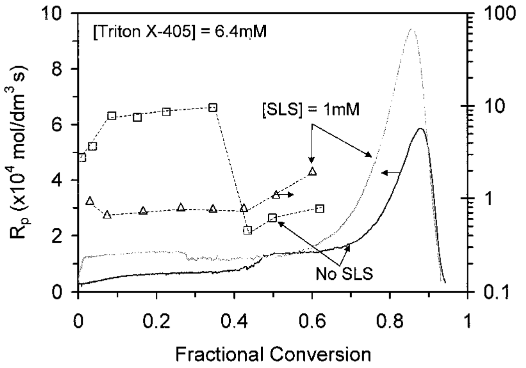

Figure 5. Effect of the presence and absence of 1 mM SLS on the rate of polymerization and average number of free radicals per particle as a function of fractional conversion in the emulsion polymerization of styrene using 6.4 mM Triton X-405 and 5 mM KPS at 70 °C (experiments DCN-1 and DCN-6).

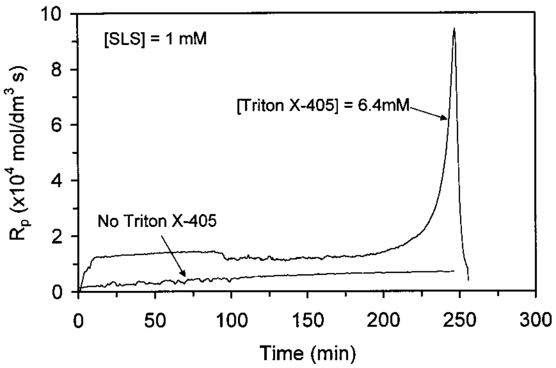

Figure 6. Effect of the presence and absence of 6.4 mM Triton X-405 on the rate of polymerization as a function of time in the emulsion polymerization of styrene using 1 mM SLS and 5 mM KPS at 70 °C (experiments DCN-1 and DCN-5).

b. Effect of the Presence of 6.4 mM Triton X-405 on the Initial Nucleation in the Emulsion Polymerization of Styrene Using 1 mM SLS Emulsifier. Despite the limited aggregation observed in experiment DCN-1, Triton X-405 allows more surface area to be stabilized during the nucleation step. This stabilization effect can be illustrated by comparing experiment DCN-1 ([SLS] = 1 mM and [Triton X-405] = 6.4 mM) to DCN-5 ([SLS] = 1 mM; no Triton X-405). Figure 6 shows the evolution of the rate of polymerization as a function of time for experiments DCN-1 and DCN-5. Experiment DCN-5 was stopped at a low conversion for stability reasons. The kinetics of this experiment were very slow due to the low amount of surfactant initially present in the system which did not lead to the stabilization of many particles. This effect is illustrated in Figure 7 where the rate of polymerization and the number of particles for experiments DCN-1 and DCN-5 are plotted as a function of fractional conversion. There is almost an order of magnitude difference in the number of particles generated in these two experiments. Although only a small fraction of the Triton X-405 is initially present in the aqueous phase in experiment DCN-1, it still helps to provide for the stabilization of a

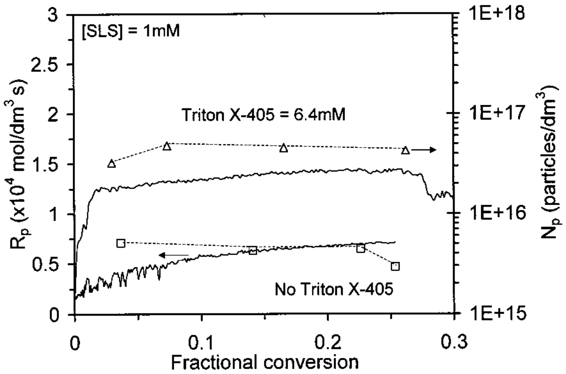

Figure 7. Effect of the presence and absence of 6.4 mM Triton X-405 on the rate of polymerization and the number of particles as a function of fractional conversion in the emulsion polymerization of styrene using 1 mM SLS and 5 mM KPS at 70 °C (experiments DCN-1 and DCN-5).

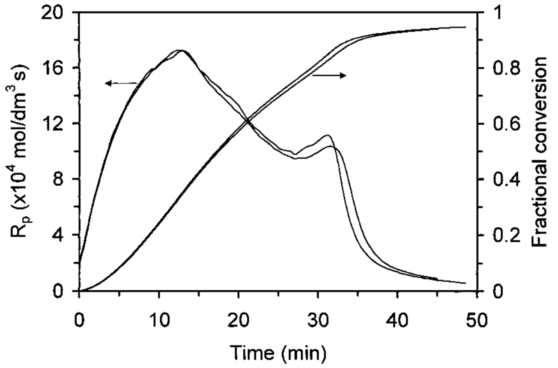

Figure 8. Rate of polymerization and fractional conversion as a function of time in the emulsion polymerization of styrene at 70 °C: [SLS] = 5 mM, [Triton X-405] = 6.4 mM, and [KPS] = 5 mM (experiments DCN-2 and DCN-3).

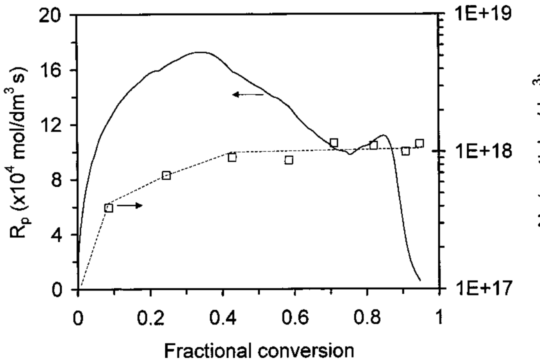

Figure 9. Rate of polymerization and number of particles as a function of fractional conversion in the emulsion polymerization of styrene at 70 °C: [SLS] = 5 mM, [Triton X-405] = 6.4 mM, and [KPS] = 5 mM (experiment DCN-2).

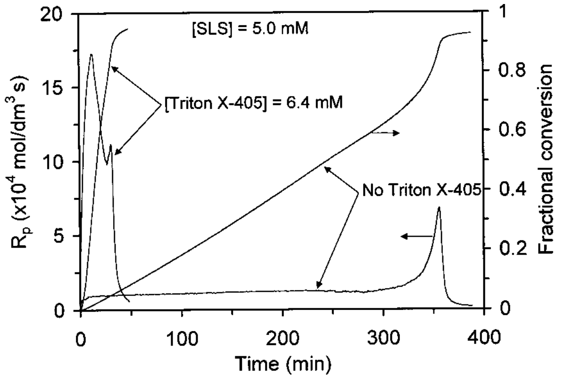

Figure 10. Effect of the presence and absence of 6.4 mM Triton X-405 on the rate of polymerization and fractional conversion as a function of time in the emulsion polymerization of styrene at 70 °C using 5 mM SLS and 5 mM KPS (experiment DCN-2 and data from Varela de la Rosa et al.[22]).

significantly larger number of particles than could be achieved without it and hence produce a faster rate of polymerization. However, with the formation of these particles, additional surfactant is required to stabilize the increasing surface area. This could explain the partial lack of stability observed in experiment DCN-1.

c. Effect of the Addition of Increasing Amounts of SLS on the Kinetics of the Emulsion Polymerization of Styrene Using 6.4 mM Triton X-405. In experiment DCN-2, the SLS concentration was increased to 5 mM. This amount was chosen to be just below the cmc of SLS. In Figure 8, the rate of polymerization and the fractional conversion are presented as a function of time for this reaction. Experiment DCN-2 was reproduced, and both the rate of polymerization and the fractional conversion curves are in close agreement as can be seen in Figure 8. The kinetics of the reaction are relatively fast; the reaction is complete in 50 min. No constant rate period is noted. In Figure 9, the rate of polymerization and the particle number are plotted as a function of fractional conversion. After 40% conversion (corresponding to 15 min in the reaction), the number of particles reaches a constant value of 1.2×10^{18}/dm^3. This behavior shows some similarities to the kinetics of the emulsion polymerization of styrene using SLS as the sole surfactant above its cmc.[21,22] At 50 °C, Varela de la Rosa et al.[21] suggested that the nucleation is micellar until 10−15% conversion after which homogeneous nucleation takes place up to 45% conversion. This suggests that the nucleation mechanism observed in experiment DCN-2 might be a combination of micellar and homogeneous nucleation as well. Initially, the SLS was added in an amount below its cmc. If the Triton X-405 is associated with the oil phase as reported in the literature,[20] its aqueous concentration should also be initially below its cmc. However, it is well-known that associations between the SLS and PEO type surfactants can exist.[25] Mixed micelle associations can be formed even below the cmc of each individual surfactant, and models have been developed to account for these phenomena.[16,17]

Figure 10 compares the evolution of the rate of polymerization and the fractional conversion of the emulsion polymerization of styrene using 5 mM SLS as the anionic surfactant in the presence and absence of 6.4 mM of Triton X-405 in the system. The data for the experiment in the absence of Triton X-405 were obtained from Varela de la Rosa et al.[22] using a similar recipe. According to Özdeğer et al.,[20] most of the Triton X-405 (>90%) is associated with the oil phase prior to the polymerization. As a consequence, the actual concentration of Triton X-405 in the water phase should be 0.6 mM. However, the kinetics of the reactions with and without Triton X-405 are extremely different. The reaction in the presence of the mixture of surfactants was much faster than when Triton X-405 was not used (50 min as opposed to 380 min for completion). The rate of polymerization and the number of particles as a function of fractional conversion are plotted in Figure 11. The number of particles formed in the presence of both surfactants is more than 90 times greater than when SLS was the sole surfactant. These results suggest

Table 4. Final Number- and Weight-Average Particle Sizes and Polydispersity Indexes of the Latexes Resulting from Experiments DCN-1 through DCN-6

experiment	DCN-1	DCN-2	DCN-3	DCN-4	DCN-5	DCN-6
[SLS] (mM)	1	5	5	3	1	
Triton X-405 (mM)	6.4	6.4	6.4	6.4		6.4
D_n (nm)	250	76	75	86	356	182
D_w (nm)	253		84	95	357	255
PDI	1.01		1.12	1.10	1.00	1.41
final particle no. ($\times 10^{-16}$/dm^3)	3.1		114.0	75.8	0.3	6.9

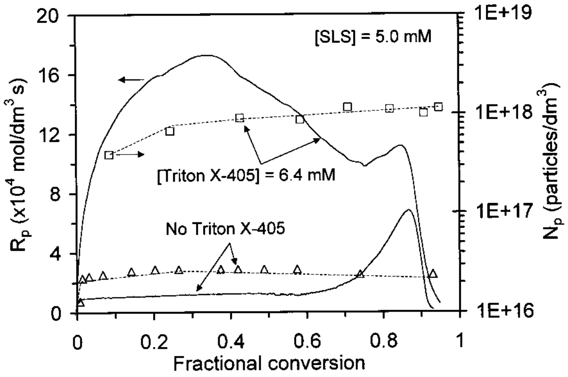

Figure 11. Effect of the presence and absence of 6.4 mM Triton X-405 on the rate of polymerization and number of particles as a function of fractional conversion in the emulsion polymerization of styrene at 70 °C using 5 mM SLS and 5 mM KPS (experiment DCN-2 and data from Varela de la Rosa et al.[22]).

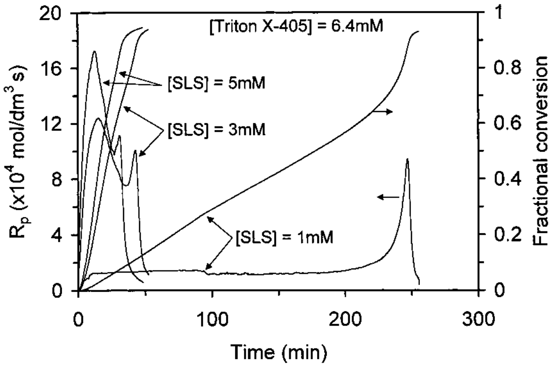

Figure 12. Effect of increasing SLS concentration on the rate of polymerization and the fractional conversion as a function of time in the emulsion polymerization of styrene using 6.4 mM Triton X-405 and 5 mM KPS at 70 °C (experiments DCN-1 ([SLS] = 1 mM), DCN-2 ([SLS] = 5 mM), and DCN-4 ([SLS] = 3 mM)).

that more Triton X-405 could be initially available in the water phase. The effect of the SLS concentration on the partitioning of the Triton X-405 is presented in the next section.

A third SLS concentration, 3 mM, was used in this polymerization series, and the combined results are shown in Figure 12, which compares the rate of polymerization and the fractional conversions as a function of time for increasing SLS concentrations (1, 3, and 5 mM), the Triton X-405 concentration being kept constant (6.4 mM). Two types of kinetics are observed, depending on the SLS concentration, and these correspond to two types of particle nucleation behavior. The corresponding number of particles as a function of conversion is plotted in Figure 13. The final latex particle size data are reported in Table 4. Large particles resulting from a short and limited nucleation period are reflected in the relatively low numbers of particles observed in the experiment with 1 mM SLS.

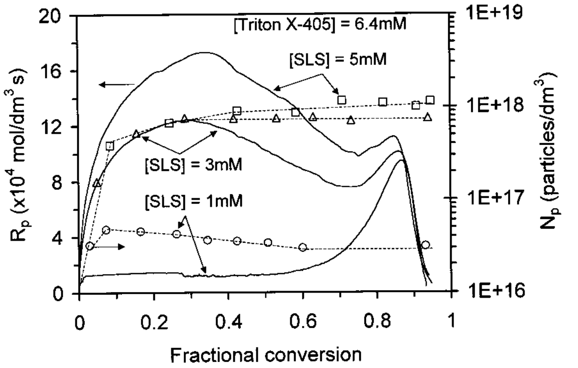

Figure 13. Effect of increasing SLS concentration on the rate of polymerization and the number of particles as a function of fractional conversion in the emulsion polymerization of styrene using 6.4 mM Triton X-405 and 5 mM KPS at 70 °C (experiments DCN-1 ([SLS] = 1 mM), DCN-2 ([SLS] = 5 mM), and DCN-4 ([SLS] = 3 mM)).

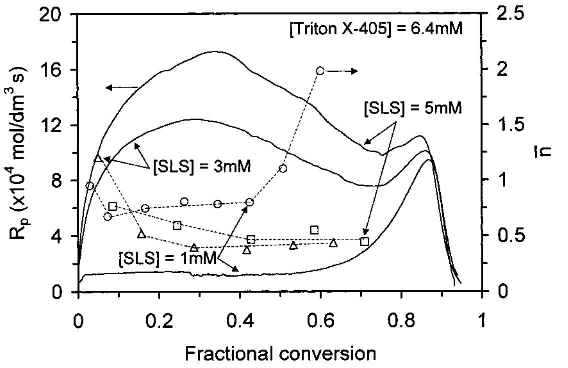

Figure 14. Effect of increasing SLS concentration on the rate of polymerization and the average number of free radicals per particle as a function of fractional conversion in the emulsion polymerization of styrene using 6.4 mM Triton X-405 and 5 mM KPS at 70 °C (experiments DCN-1 ([SLS] = 1 mM), DCN-2 ([SLS] = 5 mM), and DCN-4 ([SLS] = 3 mM)).

The nucleation period is much longer (with respect to conversion) in the experiments employing 3 and 5 mM. Correspondingly, the particles are smaller and more numerous. Just as in the previous section, the average number of free radicals per particle can be obtained from the rate of polymerization versus time curve, combined with the particle number data. In Figure 14, the average number of free radicals per particle is plotted as a function of conversion. As expected, experiments DCN-2 and DCN-4 are in the region of Smith–Ewart[19] case 2 kinetics ($\bar{n} \approx 1/2$). Experiment DCN-1 has a much higher average number of free radicals per particle ($\bar{n}$ around 0.75), due to the large size of the latex particles. The final polydispersity index for experiment DCN-1 (1.01) is much lower than for experiments DCN-3 (1.12) and DCN-4 (1.10). This difference is expected on the basis of the difference in the kinetics and nucleation mechanisms. No secondary nucleation is observed in any of these experiments. All these results suggest that the

Table 5. Surfactant Partitioning between the Aqueous and Oil Phases Prior to the Emulsion Polymerization of Styrene Using Mixtures of SLS and Triton X-405 at 70 °C (Experiments DCN-1 to DCN-6)

experiment	DCN-1	DCN-2	DCN-3	DCN-4	DCN-5	DCN-6
[SLS] (mM)	1.0	5.0	5.0	3.0	1.0	
[Triton X-405] (mM)	6.4	6.4	6.4	6.4		6.4
[Triton X-405]$_{aq}$ (mM)	0.6 (0.6)[a]	1.5	1.3[a]	1.0		0.5
% Triton X-405 in aqueous phase	9 (9)[a]	23	21[a]	16		7

[a] Determination in the RC1 reactor.

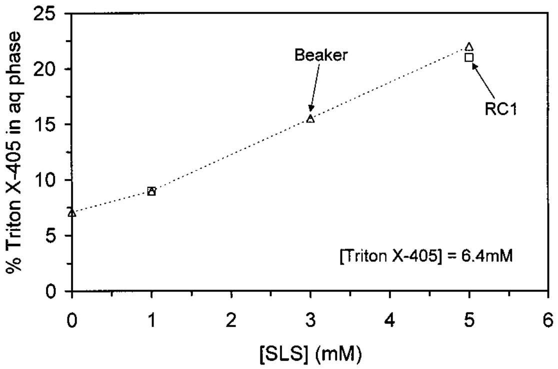

Figure 15. Amount of Triton X-405 recovered in the aqueous phase of monomer emulsions prior to polymerization as a function of the SLS concentration at 70 °C and 400 rpm (experiments DCN-1 to DCN-6); all emulsions contained 6.4 mM Triton X-405.

partitioning of the nonionic surfactant between the aqueous phase and the oil droplets is dependent on the amount of anionic surfactant present in the system. This is investigated in the next section.

Determination of the Initial Aqueous Phase Properties. a. Surfactant Partitioning. At first, the individual partitioning behaviors of SLS and Triton X-405 in styrene emulsions were determined at 70 °C. For SLS alone, 91% of the SLS was recovered in the aqueous phase, the remaining quantity being associated with the oil phase (which formed an emulsion). In contrast, with Triton X-405 as the sole surfactant, only 7% was found in the aqueous phase. Emulsions DCN-1 to DCN-5 were subsequently prepared in a glass beaker; emulsions DCN-1 and DCN-2 were prepared in the Mettler RC1 calorimeter as well. The partition coefficients were determined and are listed in Table 5. Figure 15 depicts the evolution of the amount of Triton X-405 recovered in the aqueous phase as a function of the SLS concentration. The method of preparation of the monomer emulsion (RC1 or beaker) barely influences the measurement. Özdeğer et al. already proved that most of the nonionic surfactant is associated with the oil phase, when used as the sole surfactant.[20] This graph shows that even in the presence of SLS, the majority of the Triton X-405 is initially associated with the oil phase (78−92%). However, there is more nonionic surfactant in the aqueous phase with increasing anionic surfactant content. A possible explanation for this occurrence is the formation of mixed micelles, which influence the partitioning of the Triton X-405 between the oil and aqueous phases. Less Triton X-405 is present initially in the oil phase with higher SLS concentrations. This suggests that the association between the SLS and the ethylene oxide chains of the Triton X-405[25] in the aqueous phase competes partially with the preference of the Triton X-405 for the oil phase.

Table 6. Average Number of EO Units per Triton X-405 Chain in the Surfactant Associated with the Aqueous Phase of the Emulsions Formed Prior to Experiments DCN-1 and DCN-2 As Determined by ^{1}H NMR

experiment	DCN-1	DCN-2
[SLS] (mM)	1	5
[Triton X-405] (mM)	6.4	6.4
area $-C_4H_6-$	4866	1648
area $-O-CH_2-CH_2-$	275719	90514
average no. of EO units	53	55

As noted previously, Triton X-405 is a polydisperse surfactant with a number of EO units per molecule ranging from 20 to 60.[20] The shorter chains are more hydrophobic. Therefore, they should partition more into the oil phase. This was investigated using NMR. The Triton X-405 recovered in the aqueous phase was dried and redissolved in D_2O. The average number of EO units of the Triton X-405 in the aqueous phase was determined by ^{1}H NMR by calculating the ratio of the $-C_4H_6$ peaks of the hydrophobic end to the $-O-CH_2-CH_2$ peak (3.6 ppm). The results are given in Table 6. As expected, the more hydrophilic chains (longer PEO segments) are present in the aqueous phase.

b. Determination of the cmc of the Mixed Emulsifier System. The cmc's of the mixed surfactant systems were determined as follows. The molar ratio of the anionic surfactant to the nonionic surfactant in the aqueous phase prior to experiments DCN-1 ([SLS] = 1 mM; [Triton X-405] = 6.4 mM) and DCN-2 ([SLS] = 5 mM; [Triton X-405] = 6.4 mM) were calculated from the partition coefficients of the Triton X-405. This ratio was kept constant, and solutions of increasing total surfactant concentration were prepared. The buffer concentration (2.6 mM $NaHCO_3$) was kept constant in all measurements. Figure 16a,b shows the variations of the surface tension of aqueous solutions of mixtures of SLS and Triton X-405 as a function of the total concentration of surfactant, the ratio of the two surfactants being kept constant. The vertical arrows indicate the concentrations of surfactant in the aqueous phase of emulsions DCN-1 and DCN-2, respectively. A break in the slope of the curves is observed and attributed to the cmc. On the basis of these curves, the differing kinetics of experiments DCN-1 ([SLS] = 1 mM; [Triton X-405] = 6.4 mM) and DCN-2 ([SLS] = 5 mM; [Triton X-405] = 6.4 mM) can be better understood. In the case of DCN-2, the amount of surfactant in the water phase was large enough to allow the formation of mixed micelles, whereas in experiment DCN-1, there was too little surfactant in the aqueous phase to create micelles. In experiment DCN-4 ([SLS] = 3 mM; [Triton X-405] = 6.4 mM), although the rate of polymerization profile suggests micellar nucleation, the reaction is slower than in experiment DCN-2 due to the lower total amount of surfactant in the aqueous phase (i.e., fewer micelles).

c. Analysis of Particle Surface Coverage. When comparing the emulsion polymerization of styrene using

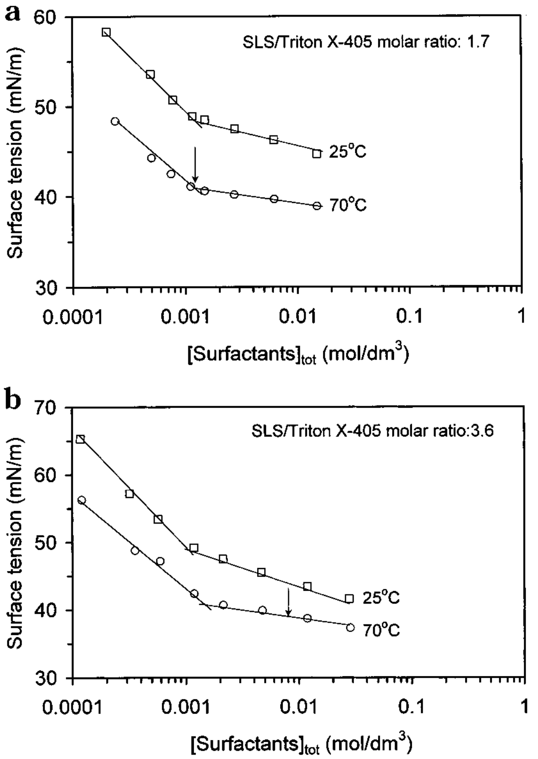

Figure 16. Surface tension versus total surfactant concentration at 25 and 70 °C in aqueous solutions of SLS and Triton X-405, the ratio of the two surfactants being kept constant: (a) SLS/Triton X-405 molar ratio is 1.7 (experiment DCN-1), and (b) SLS/Triton X-405 molar ratio is 3.6 (experiment DCN-2); the vertical arrows indicate the experimental conditions for the polymerizations.

6.4 mM Triton X-405 with and without 1 mM SLS (experiments DCN-1 and DCN-6), one of the main differences is the occurrence of secondary nucleation when no anionic emulsifier is used. As stated in the above section, the main reason for this difference is the number of particles initially nucleated. In the absence of anionic surfactant, very little nonionic surfactant is initially available for nucleation, and a relatively small number of particles is formed (on the order of 10^{15} particles/dm^3). As shown in the previous section, the presence of 1 mM of the anionic surfactant changes the initial partitioning of the nonionic surfactant. Both emulsifiers help stabilizing more primary particles (17 times more than in the absence of Triton X-405). Therefore, more surface area is available for surfactant adsorption. At the disappearance of the monomer droplets, fewer Triton X-405 molecules are available in the aqueous phase, and no secondary nucleation is observed.

To quantify these differences, an estimation of the surfactant surface coverage at the disappearance of the droplets is performed in both cases. The following assumptions are made: 1) the monomer droplets disappear at 44% conversion; 2) the number of particles and the surface area are estimated before the occurrence of secondary nucleation (i.e., right after the release of the surfactant into the aqueous phase and right before new particles are formed); and 3) the mixed adsorption of SLS and Triton X-405 is cooperative. A recent work[26] showed that an excess adsorption of the two surfactants (200% as compared to their monolayer surface coverage) occurs when they are used together.

Table 7. Estimation of the Surfactant Surface Coverage at 44% Conversion in the Emulsion Polymerization of Styrene at 70 °C Using 6.4 mM Triton X-405, with and without 1.0 mM SLS as Emulsifiers

experiment	DCN-1	DCN-6
[SLS] (mM)	1	
[Triton X-405] (mM)	6.4	6.4
N_{total} (particles)	1.7×10^{16}	8.7×10^{14}
S_{sw} (m^2)	3290	1230
S_{surf} (m^2)	1880	3080
surface covered (%)	57	100

In a latex containing N particles of diameter d, the total volume (V) and surface area (S) of the particles is given by eqs 7 and 8, respectively.

$$V = \frac{4}{3}\pi N\left(\frac{d}{2}\right)^3 \tag{7}$$

$$S = 4\pi N\left(\frac{d}{2}\right)^2 \tag{8}$$

By substituting eq 7 into eq 8, the total surface area of the particles is given by eq 9.

$$S = (4\pi N)^{1/3}(3V)^{2/3} \tag{9}$$

At the disappearance of the droplets, the total volume of the swollen particles is given by assuming additive volumes:

$$V_{\text{sw}} = V_{\text{polymer}} + V_{\text{monomer}} = m_0\left(\frac{x}{\rho_{\text{p}}} + \frac{1-x}{\rho_{\text{m}}}\right) \tag{10}$$

where m_0 is the initial mass of monomer in the system (kg), x is the fractional conversion, and ρ_{m} and ρ_{p} are the densities of the monomer and polymer, respectively (kg/m^3). As a result, the total surface area of the swollen particles (S_{sw}) is given by eq 11.

$$S_{\text{sw}} = (4\pi N)^{1/3}\left[3m_0\left(\frac{x}{\rho_{\text{p}}} + \frac{1-x}{\rho_{\text{m}}}\right)\right]^{2/3} \tag{11}$$

The total surface area, which can be covered by each surfactant system (S_{surf}, m^2) is calculated as follows:

$$S_{\text{surf}} = \frac{1}{e}(n_{\text{SLS}}a_{0\ \text{SLS}} + n_{\text{Triton X-405}}a_{0\ \text{Triton X-405}}) \tag{12}$$

where e is the fractional excess surfactant coverage, n_j is the number of molecules of surfactant j, and $a_{0\,j}$ is the surface occupied by one molecule of surfactant j as a monolayer on the polystyrene particles (m^2/molecule). These values were determined from the adsorption isotherms of the surfactants on polystyrene particles.[26] In experiment DCN-1 (mixed emulsifier system), e is equal to 2.0. In experiment DCN-6, e is equal to 1.0. The results are given in Table 7.

As expected in experiment DCN-6, there is a large excess of surfactant available in the system when the monomer droplets disappear. Even if a part of this surfactant partitions into the aqueous phase before the disappearance of the droplets, a large proportion of the emulsifier is available for nucleating new particles. When 1 mM SLS is added to the system, the initial partitioning is affected (leading to the creation of a larger number of particles). Even if most of the nonionic surfactant remains dissolved in the droplets, there would be enough surface to adsorb the excess surfactant when the droplets disappear. Moreover, the cooperative adsorption of SLS and Triton X-405 is probably occurring as detailed elsewhere.[26]

Comparison with the Work of Chern et al.[15,18,27] The results presented above correlate with the experimental data of Chern et al.[15,18,27] Fast kinetics were observed for various ratios of their mixed surfactant systems, due to the high amount of initial anionic surfactant present in their experiment (5.5 mM). The anionic surfactant allowed more of the nonionic surfactant to be available in the aqueous phase, hence promoting the formation of mixed micelles. However, when the Triton X-405 was used as the sole surfactant, it was mostly partitioned into the oil phase, which is a more likely explanation for the slower initial kinetics. Moreover, the increase in the rate of polymerization observed at higher conversions can be attributed to secondary nucleation (due to the release of nonionic surfactant into the aqueous phase as the monomer droplets disappear) as shown by Özdeğer et al.[20] At high conversion, when the nonionic surfactant is used alone ([NP40] = 100%, $X = 90\%$), the TEM micrograph presented by Chern et al.[18] indeed suggested the presence of a second crop of particles.

Summary and Conclusions

Particle nucleation in the presence of mixtures of SLS and Triton X-405 in the batch emulsion polymerization of styrene was examined in this work. The partitioning of the nonionic surfactant in the oil phase greatly influenced the polymerization kinetics of the system (determined by the use of reaction calorimetry). The SLS concentration was varied, keeping the Triton X-405 concentration constant at 6.4 mM. At low concentrations of anionic surfactant (1 mM), most of the nonionic surfactant was associated with the oil phase, and no micelles were present in the system. The nucleation was homogeneous, and the nonionic surfactant repartitioned into the aqueous phase to adsorb onto the surface of the particles. The initial number of particles formed in the system was enhanced (as compared to the anionic surfactant used solely at the same concentration or the nonionic surfactant used alone), but the surfactant was not sufficient to prevent some limited aggregation from taking place as the reaction proceeded. When a mixed emulsifier system was used, the relatively high surface area available for adsorption on the particles, combined with cooperative adsorption of the two surfactants, prevented the occurrence of a secondary nucleation at the disappearance of the monomer droplets (as opposed to the case when the nonionic surfactant was used as the sole emulsifier). At higher SLS concentrations, the initial partitioning of the nonionic surfactant into the oil phase was lowered, and the amount present in the aqueous phase allowed the formation of mixed SLS/Triton X-405 micelles. The kinetics of the subsequent reactions were fast. No secondary nucleation was observed as well. Again, the high surface area of the particles prevented the occurrence of a secondary nucleation at the disappearance of the monomer droplets. In this case, the stability of the system was preserved during the whole course of the polymerization.

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