

The stabilization effect of mixed-surfactants in the emulsion polymerization of styrene

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SUMMARY

The emulsion polymerization of styrene was performed at 50°C with a mixture of anionic and nonionic surfactants using different surfactant concentrations. In the single-surfactant systems, a proportional relationship was observed between the total particle surface area per cm³ of aqueous solution at 90% conversion (TS) and the amount of surfactant used for each polymerization. For mixed-surfactant systems an additivity was established between the TS value and surfactant composition. The study of the particle size data from low to high conversion showed that the particle number changed with conversion.

INTRODUCTION

The use of mixtures of anionic and nonionic surfactants in emulsion polymerization has been found to produce monodisperse latices when certain ratios of anionic to nonionic surfactants were used (1). This has focused attention on the effect of the surfactants present during emulsion polymerization (2,3).

Different approaches were utilized to study the effect mentioned above. These approaches included investigations of the rate of polymerization (3), micellar size (4), and stability (5) as a function of surfactant ratios. However, there was much room left for the study of particle size with different surfactant ratios throughout the polymerization, and for the development of empirical equations to describe the effect of surfactant present during emulsion polymerization. Attempts were made in this study to perform the above-mentioned aspects of particle stabilization in order to further understand these relationships.

EXPERIMENTAL

Materials

Styrene monomer was purified by prewashing and vacuum distillation. Nonionic surfactant (Emulphogene BC-840) was treated by heating at 70°C overnight under vacuum to remove peroxide. Water was doubly distilled. Others were used as received.

Polymerization Recipes

The general recipe is shown in Table 1, where K₂S₂O₈ is an initiator. In this work, the anionic surfactant was SDS

(sodium dodecyl sulfate), while the nonionic surfactant was Emulphogene BC-840 (tridecyl oxypoly(ethylenoxy) ethanol from GAF Corporation). In each run, a mixture of X grams of SDS and Y grams of BC-840 was used, where X ranged from 0 to 0.90 and Y ranged from 0 to 3.0.

Table 1

Polymerization recipe at 50°C	
Styrene	25.0 g
Water	55.0 g
K ₂ S ₂ O ₈	0.188 g
SDS	variable
BC-840	variable

Polymerization

Polymerizations were carried out in 4-ounce glass bottles with metal caps containing self-sealing butyl rubber gaskets. The capped bottles with their contents were rotated end-over-end at 45 rpm at 50°C, in a thermostated water-bath. Samples for monomer conversion and for particle size measurements were withdrawn using a hypodermic needle and a syringe. The conversion of monomer to polymer was determined gravimetrically.

Particle Size Analysis

The particle size was determined with a JEOL 120 transmission electron microscope (TEM). Pictures taken from TEM were enlarged and analyzed on a Carl-Zeiss TGZ-3 particle size analyzer. At least 1000 particles were counted for each sample. Data from the analyzer were treated to obtain the following quantities:

-Number average diameter of particles

$$D_n = \frac{\sum N_i D_i}{\sum N_i}$$

with N_i particles of diameter D_i

-Volume average diameter of particles

$$D_v = \left[\frac{\sum N_i D_i^3}{\sum N_i} \right]^{1/3}$$

-Weight average diameter of particles

$$D_w = \left[\frac{\sum N_i D_i^6}{\sum N_i D_i^3} \right]^{1/3}$$

-Number of particles per cm³ aqueous phase

$$N = \frac{(M/W) (\% \text{ conversion}) d_w}{100 d_p (\pi/6) (D_v \times 10^{-8})^3} \quad (1)$$

where (M/W) = weight ratio of monomer to water in the recipe

d_w = density of water = 1.00 g/cm³

d_p = density of polystyrene = 1.053 g/cm³

D_v = in Å

-Total particle surface area per cm³ aqueous phase

$$TS = \frac{6(M/W) (\% \text{ conversion}) d_w}{100 d_p D_v (10^{-24}) (\text{cm}/\text{Å})^3} \quad (2)$$

RESULTS AND DISCUSSION

Effect of the Amounts of the Surfactants on the Latex Particle Size

The volume average particle size data at 90% conversion are presented in Table 2. The particle sizes for the single-surfactant system of BC-840 are many times larger than those of the mixed-surfactant systems. The mixed-surfactant systems with higher amounts of anionic surfactant, SDS, have considerably smaller particle sizes. But at high weight ratios of SDS/BC-840, the effect of increasing the amount of SDS becomes undiscernible. The values of the particle size distribution, D_w/D_n , for these recipes containing only the single-surfactant BC-840 are broad (as high as 1.81), while values of D_w/D_n for recipes of the mixed-surfactant systems are quite narrow (below 1.20).

The relationship between the total particle surface area per cm^3 at 90% conversion (TS) and the amount of surfactant in each surfactant system was scrutinized first. The results are shown in Figure 1. A proportional relationship was found to fit each system. The values of the slope and intercept were determined. The relationship obtained was

$$TS = a w^b \quad (3)$$

where a is the intercept and b is the slope. The values of a were $3.372 \times 10^{21} \text{ \AA}^2/\text{g cm}^3$ water and $3.785 \times 10^{20} \text{ \AA}^2/\text{g cm}^3$ water for SDS and BC-840 respectively, while the values of b were 0.0792 and 1.001 for SDS and BC-840 respectively. Different characteristic relationships were found for both single-surfactant systems. SDS has a large intercept and small slope, whereas BC-840 has a small intercept and large slope. Thus, to stabilize the same total surface area, much more BC-840 is required than SDS.

An additivity was established between TS_m and $(TS_i + TS_n)$, where the subscripts i , n and m are denoted for SDS, BC-840 and the mixed-surfactant system respectively. The values of TS_m were plotted against $(TS_i + TS_n)$ in Figure 2. The relationship was expressed as

$$TS_m = c + d (TS_i + TS_n) \quad (4)$$

where c is the intercept and has the units of $\text{\AA}^2/\text{cm}^3$ water and d is the slope. In this treatment, X grams of BC-840 has a value of TS_n , Y grams of SDS has a value of TS_i and a mixture of X grams of BC-840 and Y gram of SDS has a value of TS_m .

Substituting Equations (2) and (3) into Equation (4) and filling those constants with values, we obtained the following equations:

$$[D_v]_m = (2.331 \times 10^{24})/(-9.9197 \times 10^{20} + 5.0091 \times 10^{20} x^{1.001} + 4.4625 \times 10^{21} y^{0.0792}) \quad (5)$$

and

$$1/[D_v]_m = (-4.2505 \times 10^{-4}) + (1.3231) [(1/[D_v]_n) + (1/[D_v]_i)] \quad (6)$$

The errors between the predicted values and the experimental values were calculated for Equations (5) and (6), as shown in Tables 3 and 4.

A series of limitations arise from the particle size determination by transmission electron microscopy (6). First, it is difficult to obtain a representative sample. There are as many as 10^{14} to 10^{17} particles per cm^3 of aqueous solution, but only a few thousand particles are counted. Second, the electron beam itself can introduce changes in the sample, for example, particles may swell or shrink. In general, an estimation of $\pm 10\%$ error was designated for the routine particle size analysis by Collins (6). If the system is not too polydisperse and the particles are carefully sized, an error of $\pm 5\%$ was estimated. Therefore, the precision of the final correlated relationships relies heavily on the precision of the particle size determination, and the improvement of precision in particle sizing is critically important.

Since the standard deviation values of particle sizes presented in Table 2 only represent the random error for the image analysis, they include only part of the whole set of sampling error analysis. A cautious analysis is essential for making the final judgement.

Table 2
Volume average particle diameters at approximately 90% conversion, (unit: Å).

Nonionic Surfactant, BC-840	Anionic Surfactant, SDS (g)						
	0	0.006	0.030	0.15	0.30	0.60	0.90
0	**	**	**	800 +11.6 *	755 +27.1 *	741	706 +49.0
1.00	-	-	-	765 +2.8 *	628 +23.5	545	536 +10.4
2.00	3089	-	-	606 +8.9	584 +2.2	494 +19.2	491 +20.4
3.00	2050	1320	724	620 +6.4	579 +23.4	486 +3.5	485 +19.6

** Highly unstable

* Slightly unstable

Variation of the Numbers of Particles During the Emulsion Polymerization

The particle number per cm^3 of the aqueous phase (N) did not remain constant during the polymerization as is shown in Figure 3. It was found that a rapid decrease in particle number after 72% conversion occurred in the recipe where the nonionic surfactant was the only emulsifier. This indicates that coagulation occurred under these circumstances.

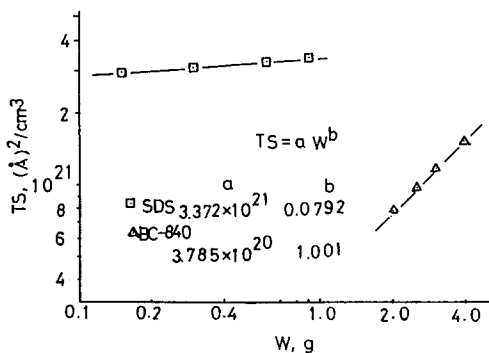


Figure 1. Correlation between the total particle surface area (per cm^3 aq. solution) at 90% conversion and the amount of surfactant (single-surfactant only)

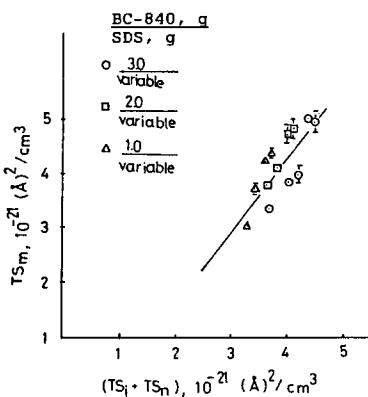


Figure 2. Total particle surface area stabilized by the mixed-surfactant (per cm^3 aq. solution)

Table 3

The error between the predicted values of Equation (5) and the experimental values

X(g)	Y(g)	$[D_V]_m$ Pred., Å	$[D_V]_m$ Expt., Å	%Error
3.00	0.15	536	620	-13.55
3.00	0.30	510	579	-11.92
3.00	0.60	486	486	0
3.00	0.90	472	485	-2.68
2.00	0.15	605	621	-2.58
2.00	0.30	573	584	-1.88
2.00	0.60	543	494	9.92
2.00	0.90	525	491	6.92
1.00	0.15	696	765	-9.02
1.00	0.30	654	628	4.14
1.00	0.60	614	545	12.66
1.00	0.90	592	536	10.45
Avg.				7.14

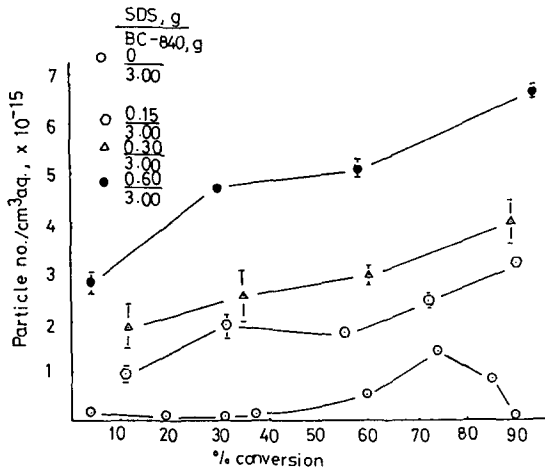


Figure 3. Effect of varying the amount of anionic surfactant with a fixed amount of non-ionic surfactant particle number (per cm^3 aq. solution) vs. percent conversion

Table 4

The error between the predicted values of Equation (6) and the experimental values

X(g)	Y(g)	$[D_V]_m$ Pred., Å	$[D_V]_m$ Expt., Å	%Error
3.00	0.15	533	620	14.03
3.00	0.30	507	579	12.44
3.00	0.60	499	486	2.67
3.00	0.90	478	485	1.44
2.00	0.15	603	621	2.90
2.00	0.30	570	584	2.40
2.00	0.60	559	494	13.16
2.00	0.90	533	491	8.55
Avg.				7.20

The error bars representing the random error from the TEM particle size analysis, shown in Figure 3, are mostly smaller than the fluctuations in the curves. No systematic error analysis was conducted here, so comparison with the fluctuations in the conversion-particle number curves cannot be made. However, the fluctuations in particle number could still be a valuable tool to compare the stability of emulsion systems as is illustrated by the following fact.

It was found in this study that the stability data observed by the naked eye was consistent with the result obtained from the particle number data. Results in Figure 3 can be taken as an illustration. Recipes with good stability observed by the naked eye were found to have a steady increase in the particle number versus conversion. On the other hand, recipes with poor stability were found to have tremendous up-and-down oscillations in the particle number versus conversion. However, recipes with the stability somewhat in between where no obvious coagulation occurred, were hard to identify with the naked eye, but they were found to have few up-and-down fluctuations, as are shown in Figure 4.

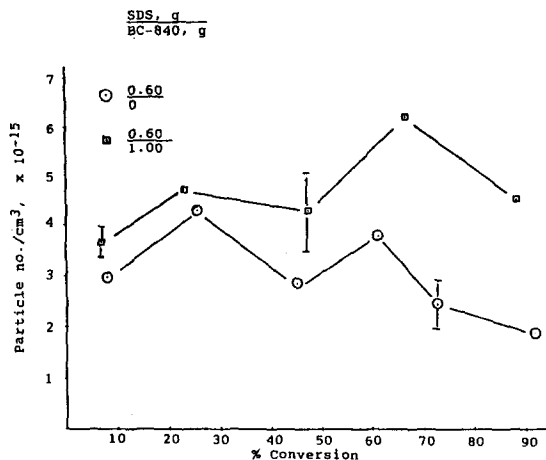


Figure 4. The up-and-down fluctuations in particle number (per cm^3 aq. solution) reveal some coagulations during the polymerization

Observations of particle number fluctuations have also been reported by Fitch and Tsai (7) and Bataille et al. (8), where the emulsifier-free polymerization or the emulsion polymerizations with a single anionic surfactant were conducted. The same finding has also been reported by Sheinker and Medvedev (9,10) and Medvedev (11). Therefore, it is proposed that a dynamic equilibrium between particle nucleation and coagulation occurs during the polymerization, and it depends on the surfactant concentration.

New particles may nucleate as long as free surfactant is available, and new particles may even nucleate in the aqueous phase in the absence of micelles. Coagulation occurs when the surfactant cannot fully stabilize the particles. A similar idea proposed by Roe (2) is that a particle nucleus or aggregate might become a polymer particle if it could gain enough protection from the adsorbed stabilizer. Otherwise the particle nucleus or aggregate might be swept up by the pre-existing polymer particles.

Particle Size Distribution

In order to obtain uniform latices, Ewart and Carr (12) and Roe and Brass (13) tried to control the surfactant concentration at much lower level than usual, where there was a short nucleation period and a long growth stage without nucleation. As a result, uniform sized latices were obtained, but the resultant latices were unstable toward storage or agitation. Woods et al. (1) obtained uniform particle size latices with good stability at higher emulsifier concentrations than usual.

Fluctuations in the particle size distribution or polydispersity, D_w/D_n , during the polymerization are shown in Figure 5. These fluctuations correspond to the fluctuations in particle number during the polymerization as shown in Figure 3.

The nucleation of new particles will increase the polydispersity, while the subsequent coagulation or growth may reduce the polydispersity. The new crop particle nucleation occurring right before 90% conversion will lead to a high polydispersity at final conversion, as was the case with a mixture of BC-840 and 0.03 gram of SDS.

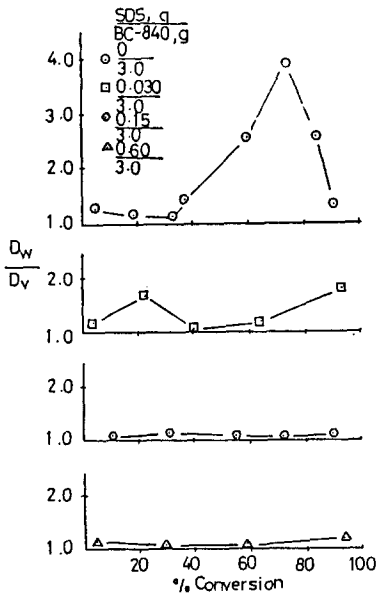


Figure 5. The variation of the polydispersity of the particle diameter during the polymerization

In this study, results similar to that of Woods et al.¹ were observed. Systems containing higher amounts of surfactant in the mixed-surfactant system showed less tendency to have fluctuations in the polydispersity during the polymerization. This is not due to the absence of new particle nucleation, but because there is sufficient surfactant present to stabilize every newly formed particle at an early growth stage, thus keeping the size small with a short growth rate.

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