Evaluation of Alkylated Diphenyl Ether Disulfonate Surfactants in 60 : 40 Styrene–Butadiene Emulsion Copolymerization

J. W. VANDERHOFF, V. L. DIMONIE, and M. S. EL-AASSER, *Emulsion Polymers Institute, Lehigh University, Bethlehem, Pennsylvania 18015,* and L. A. SETTLEMEYER, *Applied Organics and Functional Polymers Research, The Dow Chemical Company, Midland, Michigan 48667*

Synopsis

Dowfax* 2A1 is a branched C_{12}-alkylated diphenyl ether disulfonate surfactant widely used in industrial emulsion polymerization because of its electrolyte tolerance, stability in concentrated acids and alkalis, oxidation resistance, temperature stability, efficiency in solubilization, and moderate foaming. This surfactant and other similar surfactants were evaluated as emulsifiers in 60 : 40 styrene-butadiene emulsion copolymerizations carried out at 70°C using persulfate ion initiator, and their solution properties were determined. The similar surfactants were Dowfax 3B2 (linear C_{10}-alkylated), XD-8390 (linear C_{16}), XD-8292 (linear C_6), XD-8174 (linear C_{12}), and various laboratory monoalkylated and dialkylated variations. Sodium lauryl sulfate, Aerosol MA, and Aerosol OT were used as standards for comparison. The emulsifier concentration required to give a 200-nm particle diameter varied strongly with the degree of alkylation of the emulsifier; the linear C_{16}-monoalkylated diphenyl ether disulfonate emulsifier gave the desired diameter with the lowest concentration. The adsorption isotherms of these emulsifiers on the 60 : 40 styrene–butadiene copolymer particles were determined and correlated with the emulsifier structure. The interfacial tensions between styrene and the aqueous emulsifier solutions were measured and used to calculate the free energies of micellization and adsorption.

INTRODUCTION

The objective of this research was to determine the surface properties of the different surfactants and to evaluate them as emulsifiers in model emulsion polymerizations. Therefore, the following five industrial alkylated diphenyl ether disulfonate surfactants with alkyl substituents of different chain length were evaluated in the preparation of 50% solids 60 : 40 styrene-butadiene copolymer latexes of the type used for coatings applications:

<div align="center">

Dowfax 2A1—C_{12}-branched

XD-8174—C_{12}-linear

Dowfax 3B2—C_{10}-linear

XD-8390—C_{16}-linear

XD-8292—C_6-linear

</div>

* Trademark of the Dow Chemical Company.

These industrial surfactants comprised an approximate 80 : 20 monoalkylated/ dialkylated ratio. To determine the effect of the monoalkylated or dialkylated substituents on performance in emulsion polymerization, laboratory samples of the following pure surfactants were also evaluated:

C_{12}-branched—monoalkylated

C_{12}-branched—dialkylated

C_{12}-linear—monoalkylated

C_{12}-linear—dialkylated

C_{10}-linear—monoalkylated

C_{10}-linear—dialkylated

C_{16}-linear—monoalkylated

C_{16}-linear—dialkylated

C_{6}-linear—monoalkylated

C_{6}-linear—dialkylated

EXPERIMENTAL DETAILS

The latexes were prepared by batch polymerization using a standard recipe (Table I) for a 50% solids 60 : 40 styrene–butadiene copolymer latex.[1] This recipe, which used a mixture of Dowfax 2A1 and Aerosol MA (sodium dihexylsulfosuccinate; American Cyanamid) as emulsifier, potassium persulfate initiator, and sodium bicarbonate buffer, gave stable 50% solids latexes of 180–190 nm particle diameter, a size range suitable for coatings applications. Dowfax 3B2, XD-8390, and XD-8292 emulsifiers were substituted for the Dowfax 2A1 in this recipe. For comparison, sodium lauryl sulfate (Texapon L100; Henkel) and Aerosol OT (sodium dioctylsulfosuccinate; American Cyanamid) were substituted for the Dowfax emulsifiers.

The polymerizations were carried out in 30 mL or 200 mL capped glass pressure bottles (respective charges 16 and 100 g) using the following procedure: the aqueous phase was prepared by dissolving the emulsifiers and buffer in the distilled-deionized water; the monomer mixture was prepared separately by adding the condensed liquid butadiene to the chilled styrene; the aqueous phase was charged to the bottles, sparged with nitrogen, and cooled in an ice bath;

TABLE I
Standard Polymerization Recipe[a]

Component	Parts
Inhibitor-free 60 : 40 styrene/butadiene monomer mixture	50.0
Distilled-deionized water	50.0
Dowfax 2A1 emulsifier (0.20% based on water)	0.10
Aerosol MA emulsifier (0.20% based on water)	0.10
Potassium persulfate initiator (1.20% based on water)	0.60
Sodium bicarbonate buffer (0.60% based on water)	0.30

[a] Batch polymerization; 70°C.

the monomer mixture was then weighed into the bottles, which were capped immediately with crown caps fitted with neoprene gaskets; the initiator solution was injected into the bottles, which were placed in a thermostated water bath and tumbled end-over-end at 36 rpm for 16 h at 70°C. The bottles were checked for internal pressure, and the polymerization was considered complete when it was found to be negative (vacuum). The bottles which showed a positive internal pressure were returned to the thermostated water bath for an additional time until they, too, showed a vacuum.

The latexes were filtered, and the coagulum was washed with water to remove occluded latex, dried at room temperature under vacuum, and weighed. The solids contents of the latexes were measured gravimetrically. The amounts of coagulum were generally higher than the values calculated assuming that it comprised only polymer; the coagulum was porous and probably contained occluded latex or water.

The latex particles were stained with osmium tetroxide and examined in the Philips 400 transmission electron microscope. The average particle sizes were determined from the electron micrographs using the Zeiss MOP-3 particle size analyzer. The average particle sizes were also determined by photon correlation spectroscopy using the Coulter N4M particle size analyzer.

The interfacial tensions between styrene and the emulsifier solutions were measured at room temperature using the drop volume method. In each measurement, the interface was created at a constant rate such that the detachment of the drop at the lowest interfacial tension took at least 3 min.

EXPERIMENTAL RESULTS AND DISCUSSION

Polymerizations Using the Standard Recipe

Table II gives the properties of the latexes prepared using the recipe of Table I. All polymerizations were complete after about 18 h at 70°C except that using XD-8292, the emulsifier of shortest alkyl chain length (C_6), for which an additional 4 h were required. This latex had the largest particle size of the series (424 nm) and the smallest number of particles; hence its polymerization rate was expected to be the slowest. The latexes prepared using Dowfax 2A1 and

TABLE II
Polymerizations Using Standard Recipe ([E] 0.60% 50 : 50 Mixture
with Aerosol MA; [I] 1.20%; 70°C; 36 rpm)[a]

Emulsifier	Reaction time (h)	Solids (%)	Coagulum (%)	Average particle size (nm)
Dowfax 2A1	18	49.7	1.6	248
Dowfax 3B2	18	47.3	6.4	229
XD-8390	18	41.3	18.5	248
XD-8292	22	49.2	0.4	424
Sodium lauryl sulfate	18	39.7	21.9	217

[a] [E] = emulsifier concentration. [I] = initiator concentration.

XD-8292 contained little or no coagulum, that prepared using Dowfax 3B2 contained a significant amount, and those prepared using XD-8390 and sodium lauryl sulfate contained large amounts. Thus, most of these emulsifiers could not be substituted for Dowfax 2A1 in the standard recipe without the formation of significant amounts of coagulum. Figure 1 shows transmission electron micrographs of the osmium tetroxide-stained latex particles; the particle size distributions were all narrow, with few, if any, of the agglomerated or oversize particles which often result from the coagulation of primary latex particles.

The polymerization of these latexes showed the three classical stages of an emulsion polymerization: Stage 1, in which the polymer particles are nucleated by polymerization in the presence of monomer droplets; Stage 2, in which the polymer particles nucleated in Stage 1 grow by polymerization at a relatively constant monomer concentration, which is maintained by diffusion of monomer from the emulsion droplets through the aqueous phase into the particles; Stage 3, in which the emulsion droplets have disappeared and all of the monomer is in the particles. Stage 1 is the most important stage because it comprises the nucleation of the particles and their stabilization by adsorption of emulsifier. This adsorption of emulsifier molecules on the surface of the newly formed monomer-polymer particles and their stabilization against flocculation controls the particle nucleation, independent of whether the mechanism is nucleation in the monomer-swollen emulsifier micelles or homogeneous nucleation in the aqueous phase followed by coagulation of the primary particles.
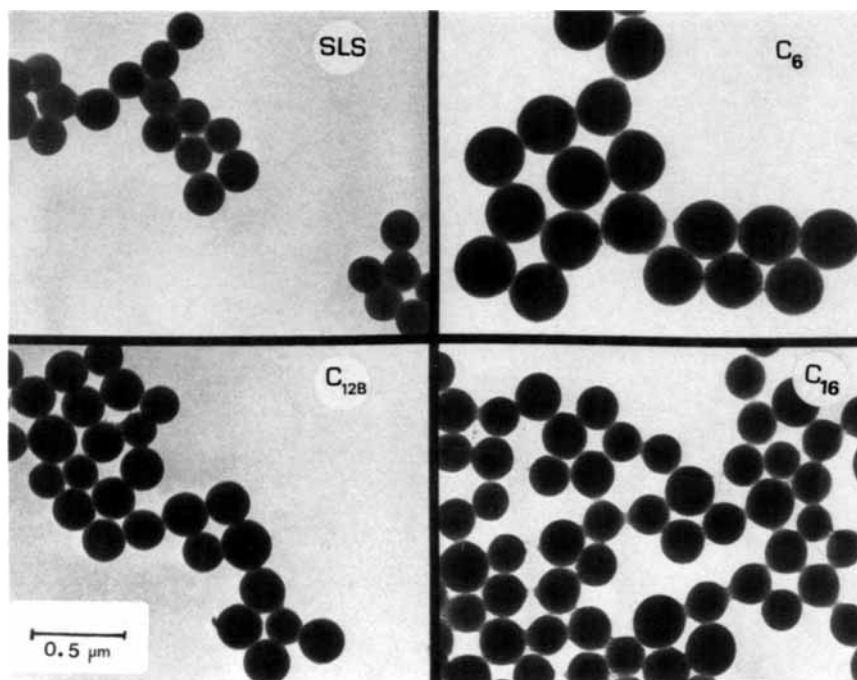

Fig. 1. Transmission electron micrographs of 60 : 40 styrene–butadiene copolymer latexes prepared using alkylated diphenyl ether disulfonate emulsifiers in the standard recipe; SLS sodium lauryl sulfate; C_6 XD-8292; C_{12B} Dowfax 2A1; C_{16} XD-8390.

Effect of Polymerization Parameters

Such polymerization process parameters as the emulsifier concentration, polymerization temperature, and tumbler rotation speed were investigated systematically, to determine their effect on the average latex particle size and the amount of coagulum formed.

Table III gives the variation of average particle size and percent coagulum with increasing emulsifier concentration at constant 50 : 50 weight ratio of Dowfax 2A1, Dowfax 3B2, XD-8390, XD-8292, or sodium lauryl sulfate to Aerosol MA. Increasing the emulsifier concentration affected the amount of coagulum formed only slightly; the amounts formed at 0.60% emulsifier were smaller than at 0.40%, and the amounts formed at 0.80% emulsifier were greater than at 0.60%. As expected, the particle size decreased with increasing emulsifier concentration. This decrease corresponded to a significant increase in the number of particles, which would result in an increased probability of inelastic collisions and hence the formation of a greater amount of coagulum.

Figure 2 shows that the variation of average particle size with emulsifier concentration was about the same for the latexes prepared using Dowfax 2A1, Dowfax 3B2, and XD-8390 emulsifiers, with the particle diameter decreasing slightly in the order C_{12}-branched > C_{10}-linear > C_{16}linear-alkylated.

The effect of polymerization temperature was also investigated. A lower temperature would give a slower rate of radical generation and hence a slower rate of particle nucleation, which would favor the adsorption of emulsifier on the particle surface reaching equilibrium before collision and coalescence of the primary particles. Table IV gives the results for polymerizations carried out at 60° and 70°C using 0.60% emulsifier, which was found earlier (Table III) to give the smallest amount of coagulum. These results showed that the

TABLE III
Effect of Emulsifier Concentration (50 : 50 Mixture with Aerosol MA; [I] 1.20%; 70°; 36 rpm)[a]

| Emulsifier	Emulsifier concn (%)	Coagulum (%)	Average particle size (nm)
Dowfax 2A1	0.40	6.9	222
Dowfax 2A1	0.60	3.7	186
Dowfax 2A1	0.80	5.2	170
Dowfax 3B2	0.40	5.7	196
Dowfax 3B2	0.60	3.4	163
Dowfax 3B2	0.80	4.4	156
XD-8390	0.40	3.7	178
XD-8390	0.60	3.2	170
XD-8390	0.80	2.7	145
XD-8292	0.40	8.1	400
XD-8292	0.60	1.4	328
XD-8292	0.80	4.3	310
Sodium lauryl sulfate	0.40	7.0	174
Sodium lauryl sulfate	0.60	3.5	164
Sodium lauryl sulfate	0.80	9.2	139

[a] [I] = initiator concentration.
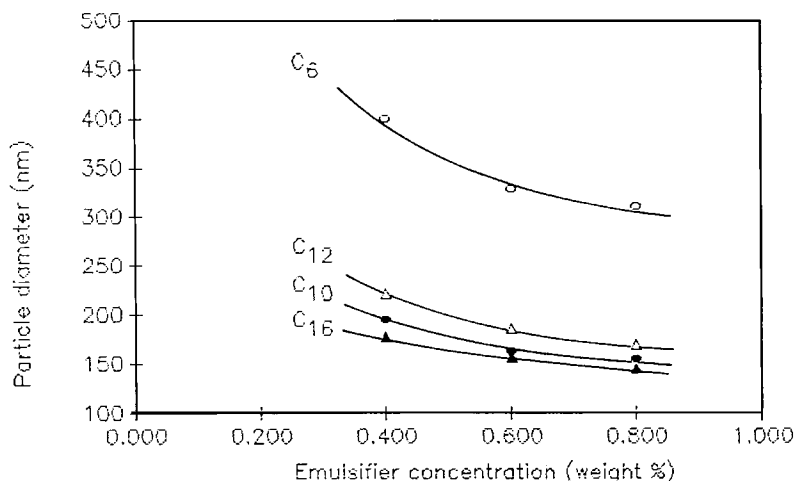
Fig. 2. Variation of average particle size with weight concentration of industrial alkylated diphenyl ether disulfonate emulsifiers in 50 : 50 mixture with Aerosol MA; C_6 XD-8292; C_{12} Dowfax 2A1; C_{10} Dowfax 3B2; C_{16} XD-8390.

decrease in polymerization temperature gave an increase in average particle size. At the higher temperature, the rate of radical generation would be faster, and more oligomeric radicals with sulfate endgroups would be generated in the initiation step; therefore, for the same emulsifier concentration, the greater number of surface sulfate endgroups would stabilize a greater number of primary particles and hence give a smaller average particle size.

The change in the polymerization temperature did not affect the amounts of coagulum significantly; the average amounts were 3.28% for 60°C and 3.04% for 70°C. These results suggest that electrostatic repulsion is not the only mechanism of stabilization operative in these latexes.

The amounts of coagulum formed during the polymerization showed significant experimental scatter. Therefore, the reproducibility of the properties of

TABLE IV
Effect of Polymerization Temperature ([E] 0.60% 50 : 50 Mixture
with Aerosol MA; [I] 1.20%; 36 rpm)[a]

	Reaction time (h)		Coagulum (%)		Average particle size (nm)	
Emulsifier	60°	70°	60°	70°	60°	70°
Dowfax 2A1	11	11	0.7	3.7	193	186
Dowfax 3B2	11	11	3.0	3.4	185	163
XD-8390	11	11	3.3	3.2	190	170
XD-8292	26	18	7.0	1.4	358	324
Sodium lauryl sulfate	11	11	2.4	3.5	181	164

[a] [E] = emulsifier concentration. [I] = initiator concentration.

TABLE V
Reproducibility of Polymerizations ([E] 0.40% 50 : 50 Mixture with Aerosol MA;
[I] 1.20%; 18 h; 60°C; 36 rpm)[a]

Emulsifier	Solids (%)	Coagulum (%)	Average particle size (nm)
Dowfax 2A1-A	44.9	11.3	205
Dowfax 2A1-B	49.2	2.6	220
Sodium lauryl sulfate-A	48.8	3.4	196
Sodium lauryl sulfate-B	40.9	19.2	200

[a] [E] = emulsifier concentration. [I] = initiator concentration.

latexes prepared under identical conditions was tested by duplicate polymerizations carried out using Dowfax 2A1 or standard sodium lauryl sulfate emulsifiers. Table V shows that the reproducibility of the particle sizes was good, but there were significant differences in the solids contents and amounts of coagulum.

These results, along with the apparent lack of dependence of the amounts of coagulum on the polymerization parameters, suggested that instability of the latex to the mechanical shear forces inside the polymerization bottles tumbled end-over-end caused the formation of coagulum, and that a reduction in the rate of tumbler rotation would diminish the mechanical shear forces and hence decrease the amount of coagulum formed.

Table VI gives the polymerization times, amounts of coagulum, and average particle sizes of latexes prepared at two different tumbler rotation speeds: the usual 36 rpm and the slower 16.5 rpm. Decreasing the tumbler rotation speed

TABLE VI
Effect of Tumbler Rotation Speed ([E] 0.40% 50 : 50 Mixture
with Aerosol MA; [I] 1.20%; 70°C)[a]

Emulsifier	Rotation speed (rpm):	Reaction time (h)		Coagulum %		Average particle size (nm)	
		36	16.5	36	16.5	36	16.5
Dowfax 2A1		11	9	9.2	1.3	222	219
Dowfax 3B2		11	9	4.9	1.1	196	187
C_{10}-linear monoalkylated		11	9	3.6	1.0	203	175
C_{10}-linear dialkylated		11	9	3.0	1.6	211	218
XD-8390		7	9	3.7	1.1	178	178
C_{16}-linear monoalkylated		7	9	5.1	0.8	176	176
C_{16}-linear dialkylated		27	18	7.8	1.6	318	300
XD-8292		27	18	8.1	0.9	400	350
C_6-linear monoalkylated		27	18	5.5	1.0	350	356
C_6-linear dialkylated		9	18	4.3	3.1	219	205
Sodium lauryl sulfate		11	9	6.4	1.1	174	176

[a] [E] = emulsifier concentration. [I] = initiator concentration.

had no effect on the time required to complete the polymerization or the average particle sizes of the latexes produced; however, the amounts of coagulum were significantly decreased; the averages were 5.6% for 36 rpm and 1.3% for 16.5 rpm. Thus, the amount of coagulum was determined primarily by the instability of the latex particles to mechanical shear, not the lack of electrostatic repulsion. Therefore, the slower 16.5 rpm was used in all succeeding polymerizations, and the average latex particle size was taken as representative of the comparative performance of the different emulsifiers in the preparation of the latexes.

Polymerizations Using Pure Monoalkylated and Dialkylated Emulsifiers

Laboratory samples of pure monoalkylated and dialkylated diphenyl ether disulfonate surfactants were evaluated as polymerization emulsifiers. Table VII gives the average particle sizes of the latexes prepared using all eight alkylated diphenyl ether disulfonate emulsifiers and sodium lauryl sulfate. All particle size distributions were unimodal and narrow, with no evidence of a second peak.

The dialkylated emulsifiers gave latexes of larger average particle size than the monoalkylated emulsifiers, with the exception of the C_6-linear alkylated emulsifiers; the differences were more pronounced for the C_{16}-linear and C_{12}-branched dialkylated emulsifiers compared with the corresponding monoalkylated emulsifiers than for the C_{10}-linear dialkylated emulsifier compared with the corresponding monoalkylated emulsifier. Sodium lauryl sulfate gave a latex of average particle size almost identical to those of the foregoing three monoalkylated emulsifiers. The fact that the industrial emulsifiers comprised an 80 : 20 monoalkylated-dialkylated mixture was reflected in latex average particle sizes which were intermediate between those produced by the monoalkylated and dialkylated emulsifiers, and only slightly higher than those produced by the monoalkylated emulsifiers.

For the C_6-linear mono-, and dialkylated emulsifiers compared with XD-8292, the order of the dependence of average particle size on the degree of alkylation was reversed; the C_6-linear monoalkylated emulsifier gave a latex of larger average particle size than the corresponding dialkylated emulsifier. The

TABLE VII
Effect of Alkyl Substituent ([E] 0.60% 50 : 50 Mixture with Aerosol MA;
[I] 1.20%; 70°; 16.5 rpm)[a]

Alkyl substituent	Average particle size (nm)		
	Industrial	Monoalkylated	Dialkylated
C_{12}-branched	186 (Dowfax 2A1)	160	400*
C_{10}-linear	163 (Dowfax 3B2)	159	201
C_{16}-linear	170 (XD-8390)	162	322
C_6-linear	328 (XD-8292)	347	195
Sodium lauryl sulfate	164	—	—

[a] Conversion 40%. [E] = emulsifier concentration. [I] = initiator concentration.

XD-8292 gave a latex of intermediate average particle size, which was slightly smaller than that produced by the monoalkylated emulsifier.

Thus, for 60 : 40 styrene-butadiene emulsion copolymerization, the determination of the experimental conditions required to show differences between the various industrial and laboratory alkylated diphenyl ether disulfonate emulsifiers and the standard sodium lauryl sulfate gave several conclusions.

1. Using a standard polymerization recipe based on a mixture of Dowfax 2A1 and Aerosol MA, stable 50% solids 60 : 40 styrene–butadiene copolymer latexes of average particle sizes suitable for coatings were prepared using the various industrial and laboratory emulsifiers.

2. The formation of coagulum during polymerization was attributed primarily to the instability of the latexes to mechanical shear; the amounts of coagulum formed were reduced or eliminated by decreasing the rate of tumbler rotation and hence the mechanical shear forces inside the polymerization bottles.

3. The average particle sizes of the latexes were determined by the type and concentration of emulsifier; the average particle sizes and their dependence on emulsifier concentration were similar for all alkylated diphenyl ether disulfonate emulsifiers (and sodium lauryl sulfate) except for XD-8292, which had the shortest alkyl substituent (C_6-linear) and produced latexes of larger average particle size, with a pronounced dependence on emulsifier concentration.

4. The degree of alkylation had a strong effect on the average latex particle size. For the monoalkylated emulsifiers, the average particle size was the same, independent of chain length and presence or absence of branching for the C_{10}-linear, C_{12}-branched, and C_{16}-linear alkylated diphenyl ether disulfonate emulsifiers; the size for the C_6-linear alkylated emulsifier was twice as great, indicating that it was a less effective emulsifier. For the dialkylated emulsifiers, the average particle sizes for the C_6- and C_{10}-linear alkylated emulsifiers were only slightly greater than those for the C_{10}–C_{16}-linear alkylated monoalkylated emulsifiers, but were much greater for the C_{12}-branched and C_{16}-linear alkylated emulsifiers, indicating that two C_6-linear substituents made the emulsifier more effective in controlling average particle size, whereas two C_{12}-linear or C_{16}-linear substituents made it less effective. For the industrial emulsifiers, the average particle sizes were consistent with the 80 : 20 monoalkylated/dialkylated ratio.

These results showed that, in mixture with Aerosol MA, there were no significant differences between sodium lauryl sulfate and the alkylated diphenyl ether disulfonate emulsifiers with C_{10}- or C_{16}-linear alkyl substituents. Therefore, 60 : 40 styrene–butadiene emulsion copolymerizations were carried out using the alkylated diphenyl ether disulfonate emulsifiers alone rather than in mixture with Aerosol MA.

Polymerizations Without Aerosol MA

Table VIII gives the polymerization times, amounts of coagulum, and average particle sizes of latexes prepared at 0.40% total emulsifier concentration with

TABLE VIII
Effect of Presence or Absence of Aerosol MA ([E] 0.40%; [I] 1.20%; 70°C; 16.5 rpm)[a]

Emulsifier	Aerosol MA (%)	Reaction time (h)	Coagulum (%)	Average particle size (nm)
Dowfax 2A1	—	9	0.9	167
Dowfax 2A1	0.20	9	1.3	219
Dowfax 3B2	—	9	0.6	180
Dowfax 3B2	0.20	9	1.1	187
C_{10}-linear monoalkylated	—	9	0.6	170
C_{10}-linear monoalkylated	0.20	9	1.0	175
C_{10}-linear dialkylated	—	9	0.8	220
C_{10}-linear dialkylated	0.20	9	1.6	218
XD-8390	—	9	0.7	179
XD-8390	0.20	9	1.1	178
C_{16}-linear monoalkylated	—	9	0.9	180
C_{16}-linear monoalkylated	0.20	9	0.8	176
C_{16}-linear dialkylated	—	12	6.2	500
C_{16}-linear dialkylated	0.20	18	1.6	300
XD-8292	—	10	1.2	220
XD-8292	0.20	18	0.9	350
C_6-linear monoalkylated	—	10	0.9	234
C_6-linear monoalkylated	0.20	18	1.0	356
C_6-linear dialkylated	—	10	1.2	187
C_6-linear dialkylated	0.20	18	3.1	205
Sodium lauryl sulfate	—	9	0.7	171
Sodium lauryl sulfate	0.20	9	1.1	175

[a] [E] = emulsifier concentration. [I] = initiator concentration.

and without Aerosol MA. All of the alkylated diphenyl ether disulfonate emulsifiers produced stable high-solids latexes of about the same particle size with low amounts of coagulum, with and without Aerosol MA. The times required to complete the polymerization were generally the same with and without Aerosol MA, except for the latexes prepared using the C_{16}-linear dialkylated analog of XD-8390, and XD-8292 and its monoalkylated and dialkylated analogs, for which longer polymerization times were required for the emulsifier mixture. For the latexes prepared using XD-8292 and its monoalkylated and dialkylated analogs, the presence of Aerosol MA gave a larger average particle size and a smaller number of particles, which would result in a slower polymerization rate. For Dowfax 2A1, the presence of Aerosol MA also gave a larger average particle size. Perhaps, the short C_6-linear and C_{12}-branched alkyl substituents of these emulsifiers enhanced the possibility of interactions with the Aerosol MA. For the C_{16}-linear dialkylated analog of XD-8390, the opposite was observed; the mixture with Aerosol MA gave a smaller average particle size (but a longer polymerization time). Further investigation of the surface activity of these emulsifier mixtures is necessary to elucidate their different behavior in emulsion polymerization.

Since stable high-solids latexes were prepared without Aerosol MA, the pure mono- and dialkylated diphenyl ether disulfonate emulsifiers alone were compared on an equimolar basis with sodium lauryl sulfate, Aerosol MA, and Aerosol

OT. The emulsifier concentration was varied from 2.0 to 120 mM (60-fold range) to determine the limits of latex stability. All of the emulsifiers (with the exception of Aerosol OT) gave stable latexes with relatively small amounts of coagulum, even at emulsifier concentrations as low as 2.0 mM, presumably because of the large number of surface sulfate endgroups incorporated by the persulfate initiator.

Table IX shows the polymerization times, amounts of coagulum, and average particle sizes for different emulsifier concentrations. Generally, the relatively small amounts of coagulum were greater at the lower emulsifier concentrations, the largest amounts being observed for the C_6-linear and C_{10}-linear dialkylated

TABLE IX
Effect of Emulsifier Type and Concentration ([I] 1.20%; 70°C; 16.5 rpm)[a]

Emulsifier	Emulsifier concentration (mM)					
	2.0	5.0	10	20	40	120
Reaction time (hr)						
C_{12}-branched monoalkylated	32	17	11	10	7	6
C_{10}-linear monoalkylated	—	39	24	17	7	6
C_{10}-linear dialkylated	15	14	15	10	—	—
C_{16}-linear monoalkylated	15	14	11	10	7	6
C_{16}-linear dialkylated	—	39	18	18	—	—
C_6-linear monoalkylated	—	39	39	38	18	11
C_6-linear dialkylated	—	14	15	14	—	—
Sodium lauryl sulfate	—	21	11	10	7	6
Aerosol MA	—	39	24	35	35	—
Aerosol OT	—	—	—	59	59	—
Coagulum (%)						
C_{12}-branched monoalkylated	1.9	0.8	0.8	3.7	0.6	0.7
C_{10}-linear monoalkylated	—	2.6	1.0	1.5	0.6	0.5
C_{10}-linear dialkylated	2.3	4.4	2.6	2.2	—	—
C_{16}-linear monoalkylated	1.7	1.8	1.8	0.9	0.6	1.1
C_{16}-linear dialkylated	—	—	2.4	1.5	—	—
C_6-linear monoalkylated	—	4.4	4.0	—	3.2	2.1
C_6-linear dialkylated	—	1.1	4.5	2.9	—	—
Sodium lauryl sulfate	1.9	1.6	0.8	2.7	0.8	0.7
Aerosol MA	—	6.3	1.2	1.9	3.2	—
Aerosol OT	—	—	—	43.4	17.3	—
Average particle size (nm)						
C_{12}-branched monoalkylated	522	320	248	184	185	138
C_{10}-linear monoalkylated	—	461	418	327	200	141
C_{10}-linear dialkylated	325	247	235	229	—	—
C_{16}-linear monoalkylated	215	182	185	192	187	140
C_{16}-linear dialkylated	—	402	361	339	—	—
C_6-linear monoalkylated	—	500	450	514	321	219
C_6-linear dialkylated	—	283	242	206	—	—
Sodium lauryl sulfate	443	408	259	188	201	171
Aerosol MA	—	394	404	400	—	—
Aerosol OT	—	—	—	—	—	—

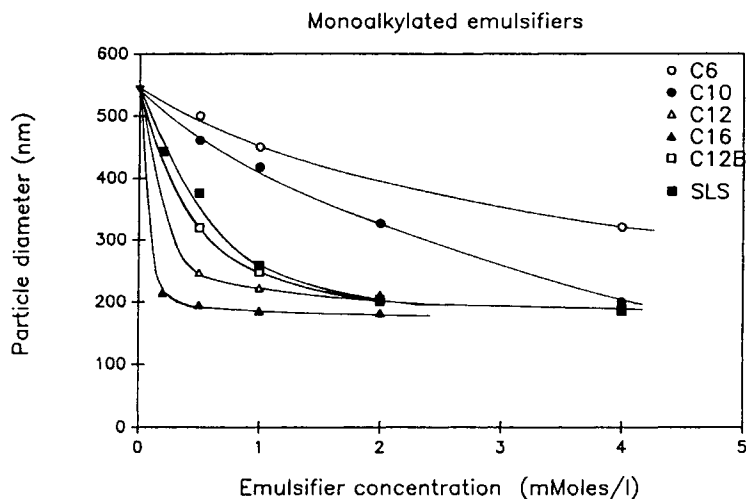[a] [I] = initiator concentration.

Monoalkylated emulsifiers

Fig. 3. Variation of average particle size with concentration of monoalkylated diphenyl ether disulfonate emulsifiers.

diphenyl ether disulfonates, and Aerosol MA. Aerosol OT was unsuitable for these emulsion copolymerizations because it gave very long polymerization times and unacceptably large amounts of coagulum. Aerosol MA gave a large particle size (ca. 400 nm) and no significant variation in particle size over the emulsifier concentration range studied.

The longer polymerization times observed at the lower emulsifier concentrations were attributed to the larger average particle sizes and the correspondingly smaller numbers of particles. Figures 3 and 4 show the variation of average particle size with emulsifier concentration for the monoalkylated and dialkylated
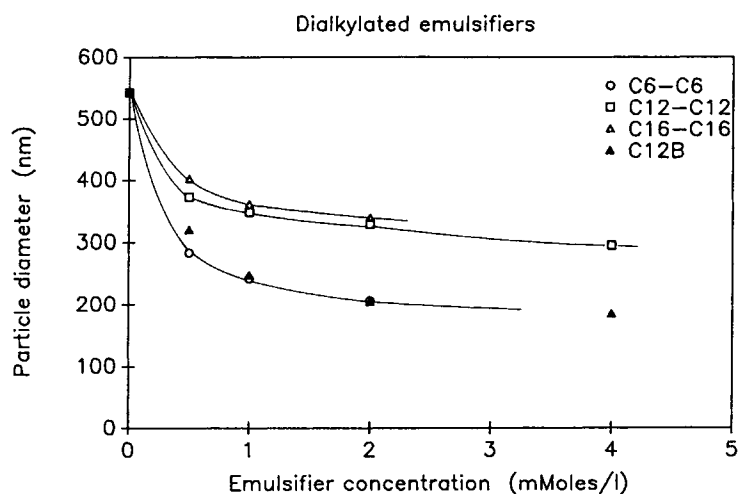
Dialkylated emulsifiers

Fig. 4. Variation of average particle size with concentration of dialkylated diphenyl ether disulfonate emulsifiers.

diphenyl ether disulfonate emulsifiers, respectively. The average particle sizes and their dependence on the emulsifier concentration were affected profoundly by the chain length of the alkyl substituent. For the monoalkylated emulsifiers, that of longest chain length (C_{16}-linear) had the strongest effect—only 2.0 mM gave an average particle size of ca. 200 nm—and that of shortest chain length (C_6-linear) had a much weaker effect—120 mM was required to give an average particle size approaching 200 nm. It is interesting that the emulsifier with the C_{12}-branched monoalkylated substituent (analogous to Dowfax 2A1) showed an almost identical variation of average particle size with emulsifier concentration as its homolog in chain length, sodium lauryl sulfate. These results suggest that the hydrophobic part of the emulsifier molecule, specifically the number of carbon atoms in the alkyl chain, plays an important role in determining the average particle size of the latex. This was confirmed in Figure 4 by the near-identical dependence of average particle size on emulsifier concentration for the C_6-linear dialkylated and C_{12}-branched monoalkylated diphenyl ether disulfonate. The contribution of these emulsifiers to particle nucleation and stabilization could be defined by measurement of their adsorption isotherms and adsorption free energies on latex particle surfaces as a function of alkyl chain length and degree of branching.

Since it is well known that the surface sulfate endgroups introduced by the persulfate initiator contribute to the stability of the latex, the effect of initiator concentration on the latex properties was investigated. Table X gives the amounts of coagulum and average particle sizes for latexes prepared at constant ionic strength (adjusted using sodium sulfate) using three different initiator concentrations. The amounts of coagulum showed no distinguishable trend with decreasing initiator concentration, which also suggests that the formation of coagulum probably results from the instability of the latex to mechanical shear rather than to the lack of electrostatic repulsion.

TABLE X
Effect of Initiator Concentration ([E] 4.0 mM; 70°C; 16.5 rpm)[a]

Emulsifier	[I]: 1.20% Average particle size (nm)	Coag (%)	0.60% Average particle size (nm)	Coag (%)	0.30% Average particle size (nm)	Coag (%)
C_{12}-branched monoalkylated	185	0.6	167	3.7	180	1.2
C_{10}-linear monoalkylated	200	0.6	224	4.3	241	0.8
C_{10}-linear dialkylated	220	0.8	197	4.7	209	4.2
C_{16}-linear monoalkylated	187	0.6	172	2.5	182	3.9
C_{16}-linear dialkylated	—	—	—	—	229	20.0
C_6-linear monoalkylated	327	3.2	311	1.3	309	0.8
C_6-linear dialkylated	—	—	—	—	200	2.2
Sodium lauryl sulfate	201	0.8	182	3.6	196	4.6
None	540	8.3	540[b]	—	[c]	[c]

[a] 40% conversion. [E] = emulsifier concentration. [I] = initiator concentration.
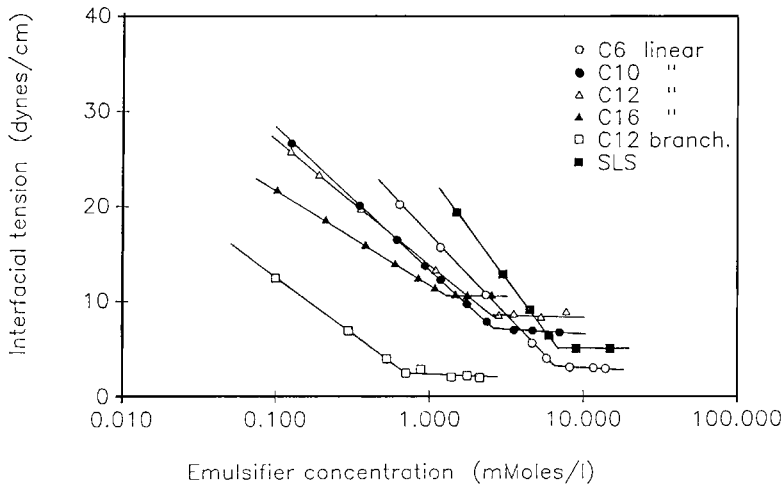[b] 40% conversion.
[c] No latex formed.

Fig. 5.   Variation with concentration of the interfacial tension between styrene and aqueous monoalkylated diphenyl ether disulfonate emulsifier solutions.

The variation of average particle size with initiator concentration was not significant; the particle size was determined principally by the type of emulsifier used. Without emulsifier, a stable high-solids latex was obtained only at the highest initiator concentration (1.20%); this latex was of large particle size (540 nm), the same as those of polystyrene latexes prepared by persulfate-initiated emulsifier-free polymerization; at lower initiator concentrations, the polymerization was not completed in the usual period of time.

These results demonstrate that the observed variations of average particle size with emulsifier concentration are a function of the emulsifier type and are not influenced by the concentration of sulfate endgroups on the surface of the particles.
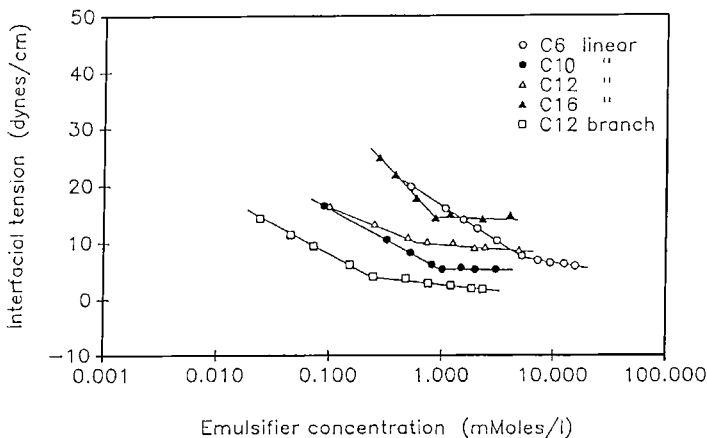

Fig. 6.   Variation with concentration of the interfacial tension between styrene and aqueous dialkylated diphenyl ether disulfonate emulsifier solutions.

TABLE XI

Adsorption of Monoalkylated Emulsifiers at the Styrene–Water Interface

Alkyl substituent	CMC (mM)	pC_{20}	A_s (A.^{2})	ΔG^0_{ads} (kJ/mol)	ΔG^0_{mic} (kJ/mol)
C_6-linear	6.5	2.9	55.9	−23.9	−22.4
C_{10}-linear	2.7	3.1	63.8	−25.3	−24.6
C_{12}-linear	2.5	3.1	71.9	−25.9	−24.7
C_{16}-linear	1.3	3.3	93.8	−29.5	−26.4
C_{12}-branched	0.7	4.2	80.6	−30.4	−27.9
Sodium lauryl sulfate	6.9	2.6	43.7	−21.1	−22.3

Interfacial Tension Between Styrene and Aqueous Emulsifier Solutions

Figures 5 and 6 show the variations with concentration of the interfacial tension between styrene and aqueous solutions of the monoalkylated and dialkylated diphenyl ether disulfonate emulsifiers, respectively; sodium lauryl sulfate was included for comparison. The inflection point of each curve defines the critical micelle concentration of the emulsifier. Tables XI and XII give the critical micelle concentrations of the monoalkylated and dialkylated emulsifiers, respectively.

As expected, the nature of the alkyl substituent was directly related to the critical micelle concentration and the interfacial tension corresponding to surface saturation (i.e., above the critical micelle concentration). For the monoalkylated emulsifiers, the critical micelle concentration decreased and the minimum interfacial tension increased with increasing number of carbon atoms in the linear alkyl substituents. The highest interfacial tension at surface saturation was measured for the C_{16}-linear substituted emulsifier, which suggests that the interaction between the hydrophobic groups of the emulsifier molecules in the micelles was stronger than that between the hydrophilic sulfonate groups and the water molecules, and that the packing of the hydrophobic groups in the micelle interior was tighter, which would result in the formation of smaller monomer-polymer particles.

The "efficiency" of an emulsifier can be defined as that concentration required to produce a decrease in the interfacial tension of 20 dynes/cm.^{2} This value was selected because the surface concentration of the emulsifier was close to

TABLE XII

Adsorption of Dialkylated Surfactants at the Styrene–Water Interface

Alkyl substituent	CMC (mM)	pC_{20}	A_s (A.^{2})	ΔG^0_{ads} (kJ/mol)	ΔG^0_{mic} (kJ/mol)
C_6-linear	6.0	2.9	78.7	−24.7	−22.6
C_{10}-linear	1.0	3.9	87.9	−29.8	−27.1
C_{12}-linear	0.6	3.8	118.7	−29.2	−28.3
C_{16}-linear	0.85	3.1	44.1	−23.8	−27.5
C_{12}-branched	0.25	4.7	93.9	−32.9	−30.5

its maximum value when the interfacial tension was reduced by this amount. The $-\log C_{(\pi=20)}$ (written pC_{20}) was a more convenient and useful measure of the efficiency than $C_{(\pi=20)}$. The larger the value of pC_{20}, the greater was the efficiency of the interfacial tension reduction. An increase in the value of pC_{20} by one unit means that the emulsifier is 10 times more efficient.

The styrene-water interfacial tension was 35.2 dynes/cm. Therefore, the $C_{(\pi=20)}$ values corresponding to an interfacial tension of 15.2 dynes/cm were obtained from the curves of Figs. 5 and 6. The calculated pC_{20} values given in Tables XI and XII show that all of the alkylated diphenyl ether disulfonate emulsifiers were more efficient in reducing the interfacial tension than sodium lauryl sulfate. The replacement of the linear alkyl substituent in the emulsifier molecule with a branched substituent (e.g., as in Dowfax 2A1) gave a significant reduction in interfacial tension. Both the mono- and dialkylated C_{12}-branched substituted emulsifiers were more efficient than the other alkylated diphenyl ether disulfonate emulsifiers, the dialkylated C_{12}-branched substituted emulsifier being about 100 times more efficient than sodium lauryl sulfate.

For the emulsifiers with the linear alkyl substituents, the efficiency increased with increasing hydrophobic character of the substituent. Figure 7 shows that the efficiency factor pC_{20} increased linearly with increasing number of carbon atoms in the linear alkyl substituent.

To compare the efficiency of emulsifiers in reducing the interfacial tension by adsorption, the thermodynamic parameters associated with the formation of micelles and the adsorption of the emulsifiers were calculated. The free energies of micellization (ΔG^0_{mic}) and adsorption (ΔG^0_{ads}), as well as the molecular area of the emulsifier (A_s) corresponding to saturation adsorption, were used to compare the different emulsifiers.

The standard free energy of micellization has been calculated using the expression[3]:

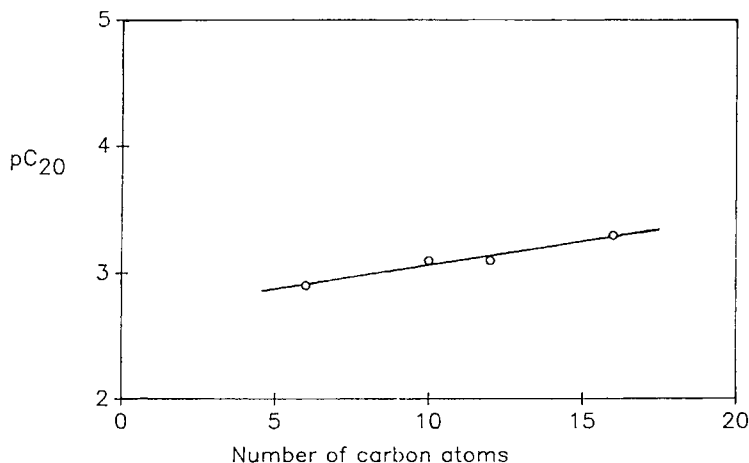$$\Delta G^0_{mic} = 2.303 RT \log C^* \qquad (1)$$

Fig. 7.   Variation of efficiency of adsorption (pC_{20}) at the styrene-water interface with alkyl substituent chain length of monoalkylated diphenyl ether disulfonate emulsifiers.

where C^* is the mole fraction of emulsifier at the critical micelle concentration.

The surface excess concentration (Γ_m), the emulsifier concentration at surface saturation of the interface, can be calculated from the interfacial tension data using the Gibbs eq. (4):

$$\Gamma_m = (1/2.303RT)(\Delta\gamma/\log C) \qquad (2)$$

where γ is the interfacial tension.

The surface concentration can be obtained from the slope of the γ–log C plot. The experimental data at concentrations below the critical micelle concentration were fitted with the equation:

$$\gamma = \gamma_0 - \log C \qquad (3)$$

The linear regression analyses for all of the emulsifiers gave values of the correlation coefficient (r) varying from 0.980 to 0.998.

The area per emulsifier molecule (A_s) was calculated from the measured surface excess concentration using the equation:

$$A_s = 10^{16}/N\Gamma_m \qquad (4)$$

where N is Avogadro's number and Γ_m is in mol/cm^2.

The adsorption energies of the emulsifiers were determined from the initial slopes of the interfacial tension–emulsifier concentration curves using the Langmuir adsorption isotherm equation:

$$\Delta G^0_{ads}/RT = \ln(\partial\gamma/\partial C)/\delta RT \qquad (5)$$

where δ is the thickness of the adsorbed layer, which was estimated to be 1.2 nm.[5]

Tables XI and XII give the values of A_s, ΔG^0_{ads}, and ΔG^0_{mic} for the mono- and dialkylated diphenyl ether disulfonate emulsifiers, respectively.

The "effectiveness" of adsorption is defined as the maximum concentration the emulsifier can attain at the interface; hence, it is inversely proportional to the interfacial area occupied by one emulsifier molecule; the smaller its cross-sectional area (A_s) at the interface, the greater is its effectiveness of adsorption. Table XI shows that the size of the hydrophilic group has a major effect on the cross-sectional area of the emulsifiers and hence on their effectiveness of adsorption. Sodium lauryl sulfate, which has a much smaller hydrophilic group than the alkylated diphenyl ether disulfonate emulsifiers, has the smallest molecular area, only 43.7 A.^{2} The only alkylated diphenyl ether disulfonate emulsifier with a comparable molecular area was the C$_{16}$-linear dialkylated diphenyl ether sulfonate, with a value of 44.1 A.^{2} This greater effectiveness of adsorption was probably the result of the combined effects of mutual attraction of the long hydrophobic alkyl chains and their perpendicular orientation to the interface.

The increasing size of the hydrophobic groups promoted both adsorption and micellization: the values of ΔG_{ads}^0 and ΔG_{mic}^0 became increasingly more negative with increasing substituent chain length. Table XI shows that the greater the number of carbon atoms in the linear alkyl substituent, the greater was the emulsifier molecular area and the smaller were the values (the greater the negative values) of ΔG_{ads}^0 and ΔG_{mic}^0. The simultaneous decrease in the effectiveness of adsorption (larger A_s) and increase in the free energy of adsorption (more strongly adsorbed) resulted in the stabilization of a larger surface area of the monomer-polymer particles by the same amount of emulsifier and hence the nucleation of a larger number of particles of smaller particle size. This relationship was observed experimentally for the monoalkylated diphenyl ether disulfonate emulsifiers with C_6–C_{16} linear substituents.

The branched alkyl substituents of both the mono- and dialkylated diphenyl ether disulfonate emulsifiers showed a greater tendency for adsorption and micellization relative to the linear alkyl substituents, as was shown by the more negative values of the free energies. For the Dowfax 2A1 with its branched-C_{12} substituent, this tendency was the opposite to that reported earlier for three isomeric dodecylbenzene sulfonates.[6]

The percent coverage of the latex particle surface was calculated from the average particle size of the 60 : 40 styrene-butadiene copolymer latex and the molecular area of the emulsifier. Table XIII shows that the percents coverage of the latexes prepared using 4.0 mM emulsifier were low. With the exception of the C_{12}-branched and C_{12}-linear dialkylated diphenyl ether disulfonate emulsifiers, the percents coverage were a near constant 10–15%, independent of the type of emulsifier. The latex prepared using 4.0 mM sodium lauryl sulfate had a lower percent coverage (6.6%). Reducing the emulsifier concentration in the polymerization recipe gave an exponential decrease in the final percent coverage. Further investigations (e.g., determination of the number of particles at the end of Stage I) are needed to elucidate the contribution of these emulsifiers to particle nucleation in emulsion polymerization. Of particular interest is the mechanism of particle nucleation in these polymerizations with high persulfate initiator concentrations because

TABLE XIII
Surface Coverage of Latexes Prepared Using 4.0 mM Emulsifier ([I] 1.20%; 70°C; 16.5 rpm)

Alkyl substituent	Monoalkylated		Dialkylated	
	Average particle size (nm)	Surface coverage (%)	Average particle size (nm)	Surface coverage (%)
C_6-linear	330	14.8	200	12.6
C_{10}-linear	200	10.3	220	15.5
C_{12}-linear	200	11.5	300	28.6
C_{16}-linear	175	13.2	350	12.4
C_{12}-branched	185	12.3	600	45.2
Sodium lauryl sulfate	190	6.6	—	—

[I] = initiator concentration.

a high concentration of surface sulfate endgroups would decrease the adsorption of emulsifier at the particle surface and increase the stability of the particles.

SUMMARY

The industrial Dowfax 2A1, Dowfax 3B2, XD-8390, and XD-8292 emulsifiers with respective linear alkyl substituents of C_{12}, C_{10}, C_{16}, and C_6 chain lengths (80 : 20 monoalkylated/dialkylated ratio) and experimental pure monoalkylated and dialkylated diphenyl ether disulfonate emulsifiers were used in 60 : 40 styrene-butadiene emulsion copolymerizations. The standard recipe used 0.20% each of Dowfax 2A1 and Aerosol MA. Substitution of the alkylated diphenyl ether disulfonate emulsifiers for the Dowfax 2A1 gave stable high-solids latexes of the desired average particle size of ca. 200 nm with little or no coagulum (with the exception of XD-8292); however, these emulsifiers gave the same results without the Aerosol MA. The experimental monoalkylated and dialkylated diphenyl ether disulfonate emulsifiers gave stable high-solids latexes of 160–200 nm average particle size, except the monoalkylated C_6-linear, dialkylated C_{12}-branched, and dialkylated C_{16}-linear substituted emulsifiers, which gave much larger sizes. The average particle size was determined principally by the type of emulsifier; the monoalkylated C_{16}-linear substituted emulsifier was the most efficient emulsifier in that only 0.020% was required to give an average particle size of 200 nm, whereas 0.40% was required for Dowfax 2A1 and more than 1.20% for XD-8292. These differences in average particle size correlated well with the emulsifier surface properties and adsorption characteristics; when the chain length of the alkyl substituent of the emulsifier was increased, the average particle size decreased owing to the increase in the emulsifier effectiveness (greater cross sectional area) and the stronger adsorption at the interface (lower ΔG^0_{ads}).

Generally, the average particle size was not affected significantly by the initiator concentration; the 1.20% concentration of the standard recipe gave the best latex stability; lower concentrations gave poorer stability. The stability of the latex was determined more by its lack of stability to mechanical shear rather than inadequate electrostatic repulsion. The critical micelle concentrations of the emulsifiers decreased with increasing alkyl substituent chain length for both the mono- and dialkylated emulsifiers and were lower for the branched substituents than for the linear substituents; all showed critical micelle concentrations equal to, or less than, that for sodium lauryl sulfate. The emulsifier molecular areas increased with increasing chain length of the mono- and dialkylated substituents, except for the dialkylated C_{16}-linear substituted emulsifier, for which it was lower; that for the sodium lauryl sulfate was lower than all except the dialkylated C_{16}-linear substituted emulsifier, for which it was about the same. The free energies of adsorption and micellization became increasingly more negative with increasing chain length of the linear substituent of both the mono- and dialkylated emulsifiers, except for the dialkylated C_{16}-linear substituted emulsifier; the values for sodium lauryl sulfate were more negative than those for the alkylated diphenyl ether disulfonate emulsifiers.

Their surface coverages were a near constant 10–15%, independent of emulsifier type, except for the C_{12}-linear and C_{12}-branched emulsifiers, for which it was greater, and sodium lauryl sulfate, for which it was only 6.6%. Thus, these alkylated diphenyl ether disulfonate emulsifiers are suitable for practical high-solids 60 : 40 styrene-butadiene emulsion copolymerizations.

References

1. E. B. Bradford and J. W. Vanderhoff, *J. Macromol. Chem.*, **1**, 335 (1966).

2. M. J. Rosen, *J. Am. Oil Chem. Soc.*, **51**, 461 (1974).

3. J. M. Corkill, J. F. Goodman, and S. P. Harrold, *J. Chem. Soc. Faraday Trans.*, **60**, 202 (1964).

4. M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley-Interscience, New York, 1978, p. 59.

5. V. I. Yeliseyeva and A. V. Zuikov, *Emulsion Polymerization, ACS Symp. Ser.*, **24**, Am. Chem. Soc., Washington, DC, 1976, p. 62.

6. W. Greiss, *Solution Chemistry of Surfactants*, K. L. Mittal, ed., Plenum, New York, 1978, Vol. 1, p. 51.