*Dedicated to Prof. P.T. Frangopol on the occasion of his 75th anniversary*

# Role of Surfactants in Emulsion Polymerization

## Polymers by design

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*The determination of an emulsifier's adsorption properties under conditions similar to those occurring during emulsion polymerization can provide important information to aid in the selection of the most appropriate surfactant for a given system. Results show that the latex particle size is dependent on the strength of emulsifier adsorption ($\Delta E_{ads}$) at the particle/aqueous phase interface and is a function of the polymer polarity. Use of reactive surfactants can improve latex characteristics by reducing the desorption and migration of surfactant to film interfaces and minimize film water sensitivity. The fraction of bound surfactant can be maximized by using relatively low emulsifier concentrations and higher initiator concentrations.*

*Keywords: emulsion polymerization, latex, film water sensitivity*

Polymer production by emulsion polymerization represents one of the most widely used methods to manufacture in large capacity a number of commercially important polymeric materials with applications in synthetic rubber, adhesives and paints, paper coatings, carpet backing, and nonwoven fabrics.

Emulsion polymerization possesses some significant advantages over other polymerization processes, permitting the synthesis of high molecular weight polymers at fast polymerization rates with good heat transfer due to the thermal conductivity of water. In the meantime, since the polymer molecules are contained in discrete particles dispersed in water, the viscosity remains close to that of water and is not dependent on the polymer molecular weight as in solution or bulk processes.

In order to develop a successful emulsion polymerization process, the selection of the surfactant(s) is critical because it plays a major role in nucleating and stabilizing the latex particles and maintaining the colloidal stability against flocculation during the growth (propagation) stage and post-polymerization processing, as well as solubilizing insoluble monomers to assure their transport to the polymerization loci.

The emulsion polymerization reaction can be divided into particle nucleation and particle growth stages. The rate of polymerization, $R_{p,}$ as well as the number-average degree of polymerization, $X_n$, ( $X_n H \approx N_p/R_i$ ) is proportional to the number of particles, $N_p$. Thus, an increase in the value of $N_p$ gives a simultaneous increase in polymerization rate and polymer molecular weight, and therefore, the nucleation stage is most important. During this stage the monomer-swollen polymer particles are formed and stabilized by adsorption of emulsifier molecules on their surface. Independent of the mechanism of particle nucleation, whether by initiation in monomer-swollen micelles (micellar nucleation) or simple homogeneous nucleation in the continuous phase followed by coagulation of precipitated primary particles, the adsorption of the emulsifier molecules at the interface of newly created monomer-polymer particles, and their stabilization is the controlling phenomenon in the particle formation step.

In view of the large diversity of surfactants (anionic, cationic, nonionic, polymeric or zwiterionic), it is sometimes difficult to select the proper surfactant for latexes with various designations. Attempts have been made to determine which emulsifier properties should be used to judge the emulsifier suitability for use in specific systems. The hydrophilic-lipophilic balance (ratio) in a surfactant molecule, known as the HLB value, has been proposed, but only the type of emulsion formed can be determined (oil-in-water vs. water-in-oil) and not its effectiveness in emulsification or latex stabilization.

The energy state of the interface obviously determines the degree of adsorption of a surfactant, depending on the nature of the interface (more or less hydrophilic) and the chemical composition of the surfactant. For a given interface, surface-active substances with different structures adsorb with different energies. Therefore, determination of the surface properties of surfactants at the monomer-water interface would provide valuable information on their contribution to the process of particle formation and stabilization.

### *Emulsifier surface properties and performance in emulsion polymerization*

The emulsifier surface activity in emulsion polymerization can be evaluated from interfacial tension measurements between the monomer phase and aqueous surfactant solutions. Since, in general, the polymerization recipe includes a significant amount of salts (initiator + buffer), it is recommended to determine the surfactant surface activity under such conditions as those prevailing in the polymerization. From the interfacial tension measurements vs. surfactant concentration [1], some critical surface properties can be estimated such as: 1) critical micelle concentration, (cmc), that mostly depends on the type and structure of the hydrophobic part of the surfactant molecule; 2) surface "efficiency" ($pC_{20}$) representing the log of the surfactant concentration required to decrease the interfacial tension by 20 dynes/cm; 3) area occupied by a surfactant molecule ($a_s$). According to Smith-Ewart theory (case 2), the number of particles can be predicted as: $N_p = K(a_s[S])^{0.6}$. This equation was developed mainly for monomers with low water solubility and the exponent of the dependence of $N_p$ on [S] was found to vary in proportion to the water solubility of the corresponding monomers [2]. The value of $a_s$ will

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depend on type of surfactant and nature of the monomer phase [3]; 4) free energy of adsorption ($\Delta G_{ads}$). In the equilibrium process of adsorption/desorption of a surfactant molecule at the particle/aqueous phase interface, a more strongly adsorbed surfactant will provide for better stabilization against flocculation during polymerization. Therefore, for a surfactant with a higher $\Delta G_{ads}$ than another surfactant a larger particle surface area can be stabilized by the same amount of surfactant resulting in a higher number of particles of a smaller size.

In one of our previous works [4], a series of diphenylether disulfonate surfactants (DOWFAX™) with various alkyl chain length substituents were characterized and used in styrene/butadiene emulsion polymerizations. It was found that the longer the alkyl chain of the hydrophobic group, the stronger the surfactant adsorption at the interface. Independent of the structure of the alkyl substituent or the nature of the hydrophilic group, the average particle diameter was linearly dependent on the adsorption energy of the surfactant at the polymer/monomer particle interface. This means that the higher the adsorption energy, the larger the interfacial area that can be stabilized by the same amount of surfactant and therefore, a larger number of particles of a smaller size would result. This is illustrated in figure 1.

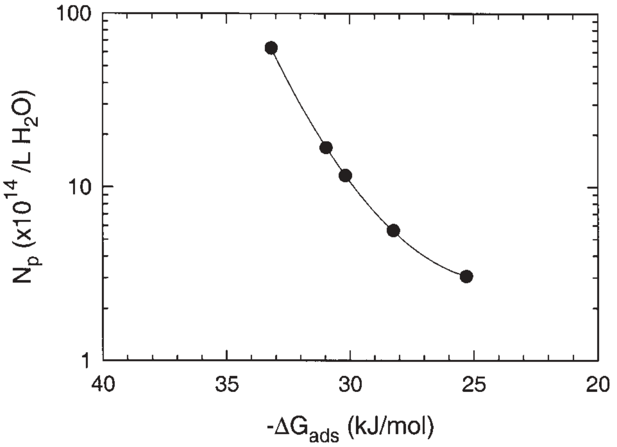

Fig. 1. Dependence of the number of particles on the surfactant adsorption energy in emulsion polymerization of 60/40 styrene/butadiene using various type of surfactants (data from Ref. 4)

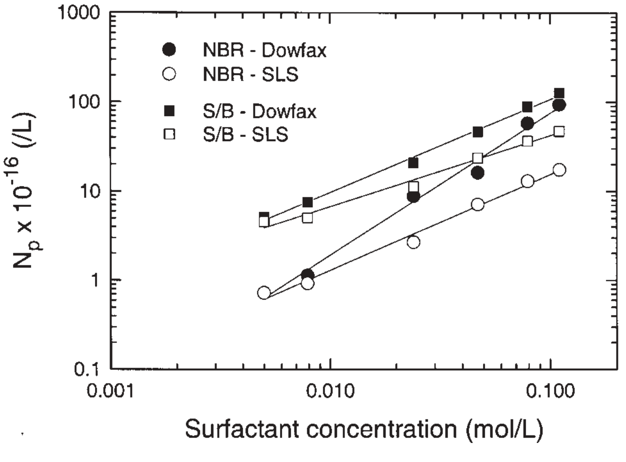

Fig. 2. Variation of particle number as a function of emulsifier concentration for two types of surfactants in emulsion polymerization of 60/40 styrene/butadiene (S/B) and 33/67 acrylonitrile/butadiene (NBR) latexes

The importance of the nature of the particle surface was shown in experiments conducted under the same conditions for two different monomer phases having differing polarities as: 60/40 styrene/butadiene (SB) and 33/67 acrylonitrile/butadiene (NBR) [5]. In the case of the more hydrophobic monomer mixture (S/B), the total particle surface area stabilized by the same amount of surfactant was almost double that of the NBR latexes and the particle number density was respectively much higher (Figure 2). As observed also for other polar monomers [3], the cross sectional area per molecule of surfactant increased with increasing monomer polarity while a substantial decrease in adsorption energy resulted (for the DOWFAX surfactant, $\Delta G_{ads}$ = -32 kJ/mole for S/B compared to -28.8 kJ/mole in case of S/AN, while for SLS the values are -28.2 kJ/mole and -25.8 kJ/mole, respectively). These prove that the flocculation process is important in controlling the final latex particle size and particle flocculation strongly depends on the adsorption energy of surfactant molecules at the interface.

The particle nucleation stage can be avoided by "seeding", (i.e., by polymerization in the presence of a previously prepared latex) so that $N_p$ "seed" particles grow in size, without the formation of a new generation of particles. Seeded emulsion polymerization can be used in batch, semicontinuous, or continuous processes. Seeding ensures batch-to-batch reproducibility of the final particle size. To achieve this goal, the total surface area of the seed particles should exceed a minimum critical value [6]. In copolymerizations, besides having a controlled number of particles, it is also often desired to maintain a constant copolymer composition. Theoretical calculations based on a simplified model proved very helpful in the selection of monomer and surfactant feed rates in a semicontinuous emulsion copolymerization process [7] that ensured a constant particle number throughout the polymerization and resulted in a homogeneous copolymer composition.

### *Reactive surfactants vs. conventional surfactants*

Beside their crucial role in the preparation and stabilization of latexes, surfactants can have some adverse effects on the properties of latex products. These negative effects are caused by the desorption of the surfactant from the surface of the latex particles. This can cause foaming and reduce the latex stability, especially under high shear conditions [8]. When the latex application is in coatings, the free surfactant can migrate through the film during drying, forming aggregates that increase the water sensitivity and cause plasticization by water. The surfactants can migrate to the air-film interface creating islands and affect the gloss, or to the film-substrate interface, reducing adhesion. Also, in the polymer recovery via coagulation, the surfactant can create problems and increased cost in waste-water treatment [8,9].

A theoretically advantageous approach to reduce the negative effects of "conventional" surfactants is to use "reactive" surfactants, where the surfactant is chemically bound into the latex particles during the course of the polymerization so that desorption of the surfactant molecules or migration during film formation is limited. Important classes of reactive surfactants are those that participate in free radical polymerization as a combination of a surfactant and either an initiator (inisurf), a chain transfer agent (transurf), or a monomer (surfmer) containing a polymerizable functional group.

Many kinds of reactive surfactants of widely different surface active characteristics and copolymerization reactivity ratios have been used in emulsion polymerizations. According to Asua and Schoonbrood [10], an optimal reactive surfactant should fulfill the following characteristics: (1) it should not homopolymerize, (2) it should behave like a conventional surfactant, (3) most of the surfactant should not react in the early stages of the polymerization where the particle size can still increase significantly but instead it should be incorporated into the particle surface at the very end of the reaction process, and (4) it should improve the latex stability and resulting film properties.

Extensive investigations were dedicated to understand the behavior of the reactive surfactant TREM LF-40 (sodium dodecyl allyl sulfosuccinate) in emulsion polymerizations of styrene and vinyl acetate, two monomers with very different water solubilities. The measured surface-active properties of TREM LF-40 are similar to those of a conventional surfactant, its characteristics being the same as those of the hydrogenated version (H-TREM LF-40) without a double bond, therefore fulfilling the second condition. It was found that TREM LF-40 can also homopolymerize and its polymeric form also possesses surface-active properties.

Kinetic studies of the emulsion polymerization of vinyl acetate (VAc) in the presence of TREM LF-40 [11-12] showed that the rate of polymerization was slower than in the presence of H-TREM LF-40 and decreased with increasing surfactant concentration despite the fact that the number of particles increased. This is the opposite of the usual behavior found in conventional emulsion polymerization and suggested that TREM LF-40 does not act only as a surfactant. Solution copolymerization of VAc with TREM LF-40 indicated that the copolymerization rate was slower than the homopolymerization of VAc, this being one of the possible reasons for the “unconventional” behaviour. FTIR analysis of the aqueous phase showed the presence of PVAc in the serum of latexes prepared with the reactive surfactant while there was no PVAc detected with the nonpolymerizable derivative, H-TREM LF-40, confirming the formation of water soluble copolymers. Copolymerization experiments of TREM LF-40 with various comonomers showed very favorable reactivity ratios with VAc, ($r_1 = 0.48$ and $r_2 = 0.36$).

The main locus of TREM LF-40 copolymerization was considered to be at the particle/water interface and was demonstrated by measuring the amount of TREM LF-40 incorporated at the particle surface. To better differentiate between the copolymerization in the aqueous phase and at the particle/water interface, seeded competitive growth experiments with both TREM LF-40 and its nonpolymerizable version were carried out using two monodisperse polystyrene seed particles of differing size [12]. The particle size analysis of these latexes revealed that the reactions at the interface control much of the kinetics and the chain transfer reaction to the allyl double bond contributed to the reduced reaction rate. A mathematical model was developed [13] that was able to predict the decrease in the polymerization rate with increasing TREM LF-40 concentration, as well as to confirm that the chain transfer to TREM was the predominant factor explaining the kinetic results.

In contrast to the VAc results, the emulsion polymerization of styrene using TREM LF-40 as surfactant showed an increase in polymerization rate with higher surfactant concentrations, as expected. The results indicated that with varying TREM LF-40, there was no one-to-one correspondence between the rate of polymerization and the number of particles as is normally found in conventional emulsion polymerization ($R_p$ H≈$N_p^{0.7}$) [14]. This unusual proportionality between $R_p$ and $N_p$ could result from a combination of various factors: (1) copolymerization between TREM LF-40 and styrene (12-14% TREM LF-40 partitioned into the styrene phase), (2) chain-transfer to TREM during the polymerization ($C_s = 111 \times 10^{-4}$ determined by solution polymerization at ≤ 10% conversion) [15], and (3) reduced radical entry and exit because of the existence of a “hairy” layer of the polymeric surfactant, since TREM LF-40 can homopolymerize. Kinetics of seeded dispersion polymerization and the resulting polymer molecular weights [16] brought supporting evidence for the existence of the chemical reactions, primarily chain transfer to TREM LF-40 at the surface of the particles, that lowered the dependency of the rate of polymerization on emulsifier concentration.

Characterization of the latexes prepared using TREM LF-40 showed that maximum incorporation of the reactive surfactant (40 – 60%) can be achieved when using lower emulsifier concentrations but higher initiator concentrations. The particle surface area was considered to be the main parameter controlling the final amount of chemically bound surfactant [15, 17].

To avoid the disadvantages found for TREM LF-40, namely its homopolymerization and formation of water soluble polymers that can act as a conventional surfactant, another class of reactive surfactants was investigated in styrene emulsion polymerizations. The polyoxyethylene alkylphenyl ethers (Noigen RN series, DKS International) and their anionic sulfate salts (Hitenol BC series, DKS International), were fully investigated in emulsion polymerizations of styrene [18, 19].

The kinetics of emulsion polymerization of styrene using Hitenol BC20 (ethoxylated with 20 EO units) show a behavior similar to a conventional surfactant during most of the process. Hitenol BC20 behaved as a good conventional surfactant in terms of monomer emulsification and particle nucleation and stabilization. Bulk and solution polymerizations indicated that it can not homopolymerize. The latex characterization results showed that the total amount of bound surfactant remained low (10 – 20% of the surfactant) during most of the reaction and started to increase steeply after about 60% styrene conversion. Finally, about 90% of the BC20 was incorporated into the polymer particles at high conversion, of which 52% was located on the particle surface (Figure 3). Similar to TREM LF-40, the fraction of chemically bound BC20 decreased with increasing surfactant concentration and increased with increasing initiator concentration. When using the hydrogenated version, H-BC20, the latex characterization results showed that at the end of the polymerization only about 24% of the surfactant was incorporated into the polystyrene chains through chain transfer, of which most of the H-BC20 was incorporated during the nucleation stage. So the mechanism for incorporation of BC-20 in the early stages (20 - 24% conversion) should be mostly by chain transfer to the ethylene oxide group while about 65 - 70% of the BC-20 was incorporated in the later stages through copolymerization with styrene at the polymer particle/water interface.

The latexes having a reactive surfactant incorporated on the particle surface presented improved stabilities against electrolyte and freeze-thaw destabilization. The resulting films cast from latexes prepared using BC-20 had a much higher contact angle than a similar one prepared with SLS, indicating that there was little surfactant migration during film formation.

*Control of composite particle morphology*

Composite latex particles are usually prepared by seeded emulsion polymerization where a second stage monomer is polymerized on a different seed polymer particle. Control of composite latex particle morphology is

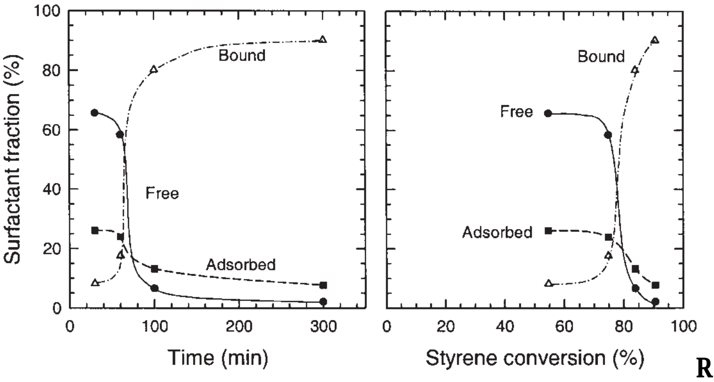

Fig. 3. Distribution of reactive surfactant BC20 versus reaction time and conversion in styrene emulsion polymerization

important since latex systems with well-designed morphology are necessary for advanced engineering plastics with high impact strength and improved toughening, or adhesives with optimum peel strength, and in other application areas such as membrane separations and biotechnology [21, 22]. The development of composite particle morphology is determined by the interaction of thermodynamic and kinetic factors, and the ultimate equilibrium morphology is dictated by the minimum surface free energy change principle [22], expressed as:

$$\Delta G = \Sigma\, \gamma_{ij} A_{ij} - \gamma_o A_o$$

where $\gamma_{ij}$ is the interfacial tension at various interfaces having an $A_{ij}$ interfacial area while $\gamma_o$ and $A_o$ correspond to the original polymer phase.

The interfacial tensions of the polymer-water and polymer-polymer interfaces have proved to be the key parameters in deciding the thermodynamically preferred morphology [23-25]. Therefore, factors affecting the interfacial tensions of the polymer phases are thought to be able to change the composite latex particle morphology. It was shown [26] that for polystyrene (PS) – poly(methyl methacrylate) (PMMA) composite particles, changing only the type of the nonionic surfactant used in the synthesis reversed the composite particle morphology, from PS particles being partially engulfed by PMMA domains when the surfactant was Igepal CO-990 (nonylphenol polyethoxylated) to a morphology showing PMMA domains being partially covered by the PS when Pluronic F-108 (polyoxyethylene-polyoxypropylene block-copolymer) was used as surfactant. The interfacial tensions of polymer phases swollen by MMA monomer against water containing the surfactant (measured by drop-volume method) were in good agreement with the observed particle morphologies. In the case of Igepal CO-990, the interfacial tension of PS-water was higher than that for PMMA-water ($\gamma_{PS\text{-}water} > \gamma_{PMMA\text{-}water,}$) and so the phase with the higher polymer-water interfacial tension will prefer to minimize its contact with the aqueous phase and resulting in being engulfed by the more polar phase (lower interfacial tension with water). By changing only the type of surfactant to Pluronic F-108, the order in values of interfacial tensions was reversed, $\gamma_{PS\text{-}water} < \gamma_{PMMA\text{-}water,}$ and so the equilibrium particle morphology was also reversed, with PMMA domains being covered by PS.

In conclusion, one can say that the determination of the surface-active properties of surfactants for a particular system and under conditions similar to those prevailing during polymerization can provide valuable information that is helpful in selecting the appropriate surfactant or stabilizer for a specific system and product.

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