

Coagulative Stability of Miniemulsion Droplets

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ABSTRACT: Miniemulsion droplets were stabilized with a mixed emulsifier system consisting of an anionic surfactant such as sodium dodecyl sulfate and a costabilizer, which is typically a low-water-soluble, long-chain alkane or alcohol such as hexadecane or hexadecanol. The surfactant, anionic in nature, provided an electrostatic barrier against coagulation, and the costabilizer retarded molecular diffusion of the monomer or Ostwald ripening. The coagulation mechanism operative for the

stabilization of the miniemulsion droplets is theoretically considered here. The understanding provides insight into the role of the surfactant. The fate of the miniemulsion droplets during the course of polymerization is also discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1262–1270, 2008

Key words: barrier; calculations; stabilization; surfactants; theory

INTRODUCTION

Emulsion polymerization (macroemulsion, miniemulsion, or microemulsion) is essentially a process in which an aqueous dispersion of a monomer or a mixture of monomers is converted by free-radical polymerization superimposed over segregated polymerization loci into a stable dispersion of polymer particles. In a typical reactor environment, the monomer droplets, the monomer-swollen micelles, the monomer dissolved in the aqueous phase, and the monomer-swollen particles compete for the aqueous-phase free radicals. In conventional emulsion polymerization, the monomer droplets, because of their large size (1000–10,000 nm) and consequently small total surface area, do not compete favorably with other loci of particle nucleation and are not considered to contribute significantly to particle nucleation. They serve primarily as reservoirs that supply monomer to the growing particles that are formed predominantly through nucleation in monomer-swollen micelles and the aqueous phase. In miniemulsion polymerization, the monomer droplets, because of their small size (50–500 nm), become the predominant loci of particle nucleation and subsequent polymerization. In this size range, the total surface area of the droplets is such that the surfactant amount typically used is adsorbed predominantly on the droplets, which results in their unavailability to form micelles or to stabilize precipitated and growing oligomers in

the aqueous phase. This was experimentally demonstrated for the first time in 1972 at Lehigh University.¹ The stability to these systems is usually achieved by the use of an anionic surfactant, for example, sodium dodecyl sulfate (SDS), and a costabilizer (also known as a cosurfactant in earlier literature) that is only soluble in the oil phase. The only difference between miniemulsion polymerization recipes and a typical emulsion polymerization recipe is the presence of the costabilizer. Costabilizers should be water-insoluble and have a low molecular weight. The small size of the droplets is the result of the homogenization of the monomer–water mixture to high shear, which breaks the droplets into nanosizes, and these droplets are stabilized against coalescence and diffusional degradation for a long time by the appropriate surfactant/costabilizer combination. Coalescence may be precluded by the addition of an appropriate surfactant. Diffusional degradation or Ostwald ripening can be eliminated by the addition of a small amount of costabilizer. The term *miniemulsion* itself was created later by Chou et al.² Key factors contributing to the formation of miniemulsions or small, stabilized monomer droplets are the shear-induced creation of submicrometer or nanosize droplets and the addition of the costabilizer for their stability. The other ingredients, besides the costabilizer, required for the polymerization of miniemulsions are the same as in emulsion polymerization and include the surfactant, initiator, monomer, and water. It is agreed that the nucleation mainly starts in the monomer droplets. The characteristics of miniemulsions can be summarized as follows:

1. The creation of a miniemulsion requires high mechanical agitation or intense shear for the

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reaction to reach a steady state given by a rate equilibrium of droplet fission and fusion.

2. The osmotic stability of the miniemulsion droplets results from osmotic pressure in the droplets, which balances the Laplace pressure and, thus, prevents monomer diffusion. The osmotic pressure results from the addition of the costabilizer, which has an extremely low water solubility. It is expected that miniemulsions undergo structural changes to establish a situation of zero effective pressure.
3. The colloidal stability of miniemulsion droplets is achieved by the addition of a surfactant. The surface coverage of the miniemulsion droplets by surfactant molecules is not complete. The amount of surfactant required to form a polymerizable miniemulsion is small, usually between 0.5 and 25% with respect to the monomer phase.

Miniemulsions are also referred to as *nano-emulsions*, *ultrafine emulsions*, and *submicrometer emulsions*.³ The formation and stabilization of the droplets in the nanosize range involve pre-emulsification and emulsification steps.⁴ Pre-emulsification refers to the preparation of the homogeneous mixture of the monomer, surfactant, cosurfactant, and water, which is then, under high shear, broken into droplets during the emulsification step. Tang et al.⁵ conducted a comparative study of preparative variables in miniemulsion polymerization. These variables included (1) surfactant amount and type, (2) costabilizer amount and type, (3) monomer type(s), (4) temperature of preparation and polymerization, (5) means and conditions of homogenization, and (6) degree of aging of the emulsion. It was found that variations in the conditions used to prepare miniemulsions of monomers in water resulted in substantial differences in the polymerization kinetics and final particle sizes and distributions. The finest droplet size miniemulsions were obtained by (1) use of a costabilizer, (2) homogenization at an elevated temperature, (3) homogenization with a uniform high-shear device (microfluidizer), and (4) the limiting of the aging time before polymerization. Anderson et al.⁶ reported the preparation of small-diameter (~ 50 nm) polystyrene particles by miniemulsion polymerization. Bechthold et al.⁷ found that when the amount of the surfactant was varied, the particle size could be varied over a wide range. The surface coverage with SDS molecules of this state depended strongly on the particle size and could be determined by surfactant titrations and surface tension measurements. The smaller the droplets were and the more collisions they underwent, the more dense the coverage of the particles with surfactant had to be to keep the miniemulsion stable. In this way, it

was possible to determine the maximum surface area per SDS molecule in the dependence of particle size and latex concentration. Miller and coworkers^{8,9} reported the measurement of the average size of the miniemulsion droplet size distribution with the capillary hydrodynamic flow fractionation method. Landfester et al.¹⁰ used a combination of the small-angle neutron scattering method, conductivity, and surface tension measurements to measure the average size of the miniemulsion droplets and reported that a 1 : 1 copy between the initial droplet size distribution and the final particle size distribution was obtained due to miniemulsion polymerization. Do Amaral et al.¹¹ described the use of the scanning transmission electron microscopy technique for the direct measurement of droplet size and droplet size distribution in miniemulsion polymerization. Sood and Awasthi^{12,13} developed and validated a mathematical model for the miniemulsion polymerization of styrene, incorporating the full droplet size distribution and the particle size distribution. Reviews of miniemulsion polymerization can be found elsewhere.^{14–17}

Miniemulsions are not thermodynamically stable; they will eventually separate into their components. The initial droplet distribution can alter itself as a result of two phenomena: coalescence and molecular diffusion. Coalescence is the process of the formation of a droplet from two or more smaller droplets, with the significant step occurring when the two droplets get close enough to allow contact of the droplet phases. An insufficient barrier (e.g., electrostatic or viscoelastic) against contact may cause coalescence. SDS, an anionic surfactant, provides an electrostatic barrier against contact. In such cases, coalescence is normally called *coagulation*. In the molecular diffusion process, popularly known as Ostwald ripening, the two droplets can form a single droplet without coming into contact if the conditions are such that one droplet is allowed to grow while the other dissolves. The costabilizer, hexadecane (HD), or cetyl alcohol (CA; hexadecanol), relatively low-molecular-weight, less water-soluble compounds compared to the monomer retards molecular diffusion. It has been suggested that CA forms an interfacial film with the surfactant that resists rupture on contact and, hence, also provides a viscoelastic barrier against contact. Molecular diffusion (Ostwald ripening) is the more commonly used criterion for analyzing the stability of a miniemulsion system. In our earlier study,¹⁸ we analyzed the role played by the molecular diffusion phenomenon (Ostwald ripening) in providing stability to the miniemulsion systems. In this study, I considered the role of electrostatic stabilization provided by the surfactant in providing stability against coagulation.

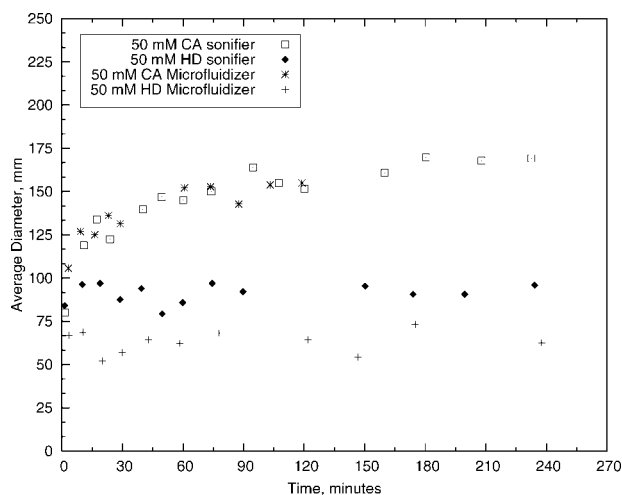


Figure 1 Variation of the droplet diameters with time for CA and HD for the sonifier and microfluidizer. (Reprinted, by permission of the publisher, from Miller et al.⁹ Copyright 1994 Elsevier Ltd.)

EXPERIMENTAL STUDY OF THE STABILITY OF THE MINIEMULSION DROPLETS

Miller and coworkers^{8,9} monitored the effects of changes in the pre-emulsification and emulsification steps on the resulting average size of the droplet size distribution with the capillary hydrodynamic flow fractionation method. The measured average size of the droplet did not change with time with HD as a costabilizer; whereas with hexadecanol as a costabilizer, the average droplet size increased with time up to 1.5 h and leveled off after that (Fig. 1).

The effects of several variables on the rearrangement behavior were studied. These variables included the amount of CA (10 to 140 mM), the ini-

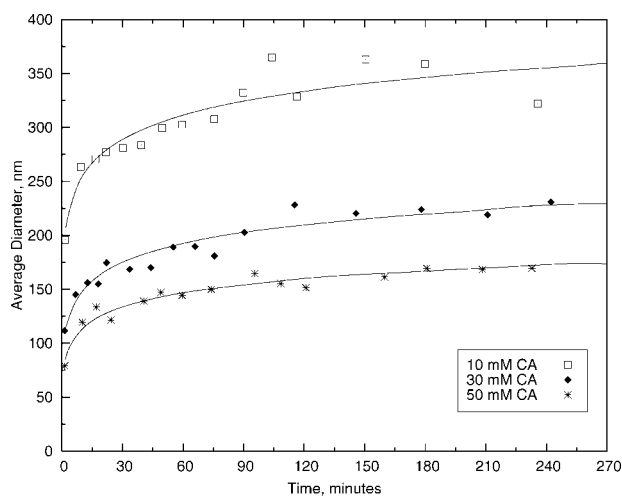


Figure 2 Variation of the diameters of CA containing droplets with time at low CA concentrations. (Reprinted, by permission of the publisher, from Miller et al.⁹ Copyright 1994 Elsevier Ltd.)

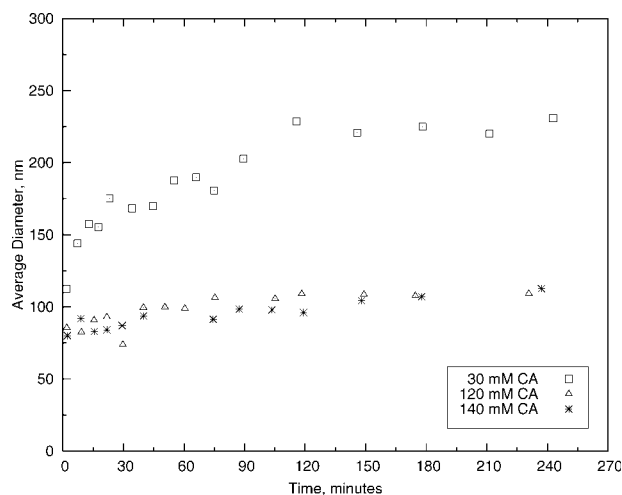


Figure 3 Variation of the diameters of CA containing droplets at high CA concentrations. (Reprinted, by permission of the publisher, from Miller et al.⁹ Copyright 1994 Elsevier Ltd.)

tial location of hexadecanol (in the gel phase or dissolved in the styrene monomer), the agitation rate (no agitation or agitation at 210 rpm), and the nature of the homogenization device (microfluidizer or sonifier), with the microfluidizer giving narrower distributions. This behavior was affected by the concentration of hexadecanol, and an increase in its concentration resulted in a decrease in the final average droplet size (Fig. 2). At much higher concentrations of hexadecanol (120 and 140 mM), the rearrangement in droplet size was negligible (Fig. 3). Also the rearrangement behavior was same for the cases when hexadecanol was dissolved in the toluene and when it was present in the gel phase (Fig. 4).

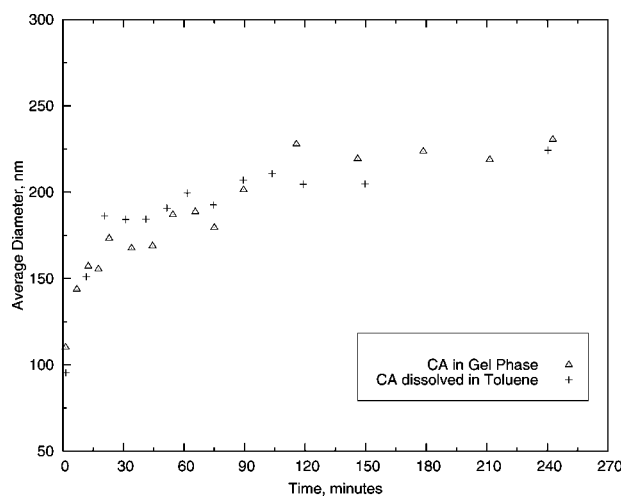


Figure 4 Variation in the droplet diameter with time for different initial locations of CA. (Reprinted, by permission of the publisher, from Miller et al.⁹ Copyright 1994 Elsevier Ltd.)

Any or both of the two phenomena, molecular diffusion (Ostwald ripening) and coalescence, could be responsible for the aforementioned instability seen in the miniemulsion droplets. These phenomena are discussed in detail later.

OSTWALD RIPENING

When an oil-in-water emulsion is created by the application of shear force to a heterogeneous fluid containing surfactants, a distribution of droplet sizes results. Interdroplet mass transfer (Ostwald ripening) determines the fate of this distribution because of their higher Laplace pressure. If the small droplets are not stabilized against diffusional degradation, they will disappear, which increases the average droplet size. It was shown by Mishchuk et al.¹⁹ that this disappearance can be very fast for small droplets.

The quantitative aspects of the rate of growth of large particles and the rate of dissolution of small particles in emulsions were theoretically examined by Higuchi and Misra²⁰ in 1962 for the case in which the process was diffusion-controlled in the continuous phase. It was shown that emulsion stability was proportional to particle volume. It was proposed in 1962 that unstable emulsions may be stabilized with respect to the Ostwald ripening process by the addition of small amounts of a third component, which must distribute preferentially in the dispersed phase.

Kabalnov et al.²¹ demonstrated by statistically analyzing experimental data that the changes in the particle size distribution function were in accordance with the predictions of Lifshitz–Slyozov theory (Ostwald ripening).²² An extension with respect to fluorocarbon emulsions was achieved later.²³ Because of the low solubility in water, fluorocarbon emulsions exhibit a higher stability and can, therefore, also be used for medical applications, for example, artificial blood.

This stabilization effect was theoretically described by Webster and Cates.²⁴ They considered an emulsion whose droplets contained a trapped species (insoluble in the continuous phase) and studied the emulsion's stability via Lifshitz–Slyozov dynamics (Ostwald ripening). They extended the work of Kabalnov et al.²¹ and derived general conditions regarding the mean initial droplet volume, which ensures stability in both the size and composition of the initial droplets even when arbitrary polydispersity is present. They distinguished nucleated coarsening, which requires either fluctuations in the mean-field equations or a tail in the initial droplet size distributions, from spinodal coarsening, in which a typical droplet is locally unstable. A weaker condition for stability, previously suggested by Kabalnov et al.,²¹ is sufficient only to prevent spinodal coarsening and is best viewed as a condition for metastability. The coarsening of unstable emulsions

after long times was considered and was shown to resemble that of ordinary emulsions with no trapped species but with a reduced volume fraction of the dispersed phase. The evolution of the emulsion is driven by the competition between the osmotic pressure of the trapped species and the Laplace pressure of the droplets. This is of high importance for the production of stable emulsions. Increased stability is desired for anesthetic/analgesic emulsions, the stability of which is provided by white mineral or other ripening inhibitors.²⁵

The rate of Ostwald ripening depends on the size, polydispersity, and solubility of the dispersed phase in the continuous phase. This means an already ultrahydrophobic oil dispersed in small droplets of low polydispersity shows low diffusion. However, by the addition a costabilizer, the stability can be increased by an additional increase in osmotic pressure. This was shown for fluorocarbon emulsions based on perfluorodecaline droplets and stabilized with lecithin. Through the addition of a hydrophobic component, for example, perfluorodimorphinopropane, the droplets' stability was increased, and they could be introduced as stable blood substitutes, as shown by Postel et al.²⁶ and Lowe.²⁷

Davis et al.²⁸ described that the added material reduced the total vapor pressure, as defined by Raoult's law. Hexane and HD demonstrated a slight negative deviation from ideality, and HD/fluorochemicals demonstrated a slight positive deviation from ideality. As in the case of a pure oil system, smaller droplets had a slightly higher vapor pressure (or solubility) than larger ones. To reach the equilibrium state, hexane left the small droplets and passed to larger ones. This loss of hexane caused an increase in the molar fraction of the third component in the small droplets and a decrease in the large droplets. Thus, the small droplets had a more reduced vapor pressure compared to the larger ones than was originally the case.

Sood and Awasthi^{18,29} showed that it is the molecular diffusion phenomenon or Ostwald ripening that causes the reported^{8,9} instability for the hexadecanol system. As shown in their articles, there exists a minimum stable droplet size: the droplets below this size undergo molecular diffusion or Ostwald ripening and lose their monomer. Sood and Awasthi^{18,29} stated that in the presence of a costabilizer, compensation of the swelling effect by the mixing effect takes place. In the absence of costabilizer, the chemical potential of a small droplet is always larger than the chemical potential of the large droplet. In the presence of a costabilizer, the equality of chemical potential will require that the chemical potential of the small droplet should decrease and the chemical potential of the large droplet should increase as their sizes change due to molecular diffusion. Mathematically, this criterion requires that the chemical poten-

tial should be an increasing function of size. The minimum stable diameter was arrived at with this criterion, which was provided by Kabalnov et al.²¹ The minimum stable droplet diameter is related to the contribution to the chemical potential due to the free energy of the mixing term; the lower this contribution to the chemical potential is, the higher the critical droplet size and the greater the extent of rearrangement will be. Higher costabilizer volume fraction and temperatures, a lower interfacial tension, and a monomer–costabilizer system with lower values of the molar volume of monomer, ratio of equivalent number of molecular segments, and interaction parameter should be used to create stable miniemulsion droplets. The experimental observations,^{8,9} namely, the rearrangement of droplet size distribution only for the hexadecanol system and not for the HD system, and the retardation of the rearrangement with increasing hexadecanol amount was reconciled in terms of the aforementioned theoretical analysis. This unstable behavior would require that the initial droplet size distribution contains a significant proportion of small-diameter droplets, which is true for a broad distribution. Furthermore, this unstable behavior will lead to bimodal distributions. Durbin et al.³⁰ were the first to report that broad and sometimes bimodal particle size distributions were obtained in some commercial processes where the reactants were pre-emulsified before they were charged into a reaction vessel. Fitch³¹ discussed the phenomenon of diffusion degradation and how it leads to bimodal size distributions in the presence of water-insoluble components in the organic droplets. Since then, a number of workers^{32–38} have reported bimodal particle size distributions formed as a result of miniemulsion polymerization. I²⁹ showed theoretically that these bimodal particle size distributions can give latexes of high solid content and low viscosity, which has also been experimentally demonstrated.³⁹

COLLISION AND COALESCENCE

In addition to the molecular diffusion of the dispersed phase, the destabilization of an emulsion can also occur by collision and coalescence processes. Mishchuk et al.¹⁹ found that in the case of rapid Brownian coagulation in dilute oil-in-water emulsions, the deformation influence on droplet deformation and drainage was negligible. When the weak influence of droplet deformation on rapid coagulation was observed and the Borwanker–Ivanov theory,³¹ which states that the transition to charged droplets and lower electrolyte concentrations decreases droplet deformation, was taken into account, it was concluded that both slow and reversible coag-

ulation cannot be influenced by droplet deformation in miniemulsions. A droplet surface is homogeneous, in contrast to solid particles.

ELECTROSTATIC STABILIZATION OF MINIEMULSION DROPLETS

The framework for electrostatic stabilization is provided by Deryaguin–Landau–Verwey–Overbeek (DLVO) theory,⁴⁰ according to which the electrostatic stabilization of colloidal particles is explained by the combination of the attractive van der Waals dispersion forces with the repulsive electrostatic forces. In DLVO theory, it is customary to represent the interactions by the free energy or potential of interaction rather than by forces exerted on the particles. The approximations involved in the calculation of the electrostatic repulsive potential (V_R) renders this treatment more suitable for low potentials (or low surface charge densities). The problem of analyzing the electrostatic stabilization behavior of the droplets is posed in such a way so that these approximations are valid. The minimum surface charge density (q ; or surfactant surface coverage) necessary to fulfill the requirements of electrostatic stabilization is calculated. In the following paragraphs, the reduced but physically relevant and more amenable forms of the attractive and repulsive potentials are initially presented followed by brief discussions about the approximations involved in the derivation of the V_R 's and stability criteria. The outcome of this analysis is summarized in Table I. Then, the calculation of the actual surfactant coverage on the droplets is provided.

The van der Waals attractive potential (V_A) between two spheres of radius (a_1 and a_2) with Hamaker's theory is given by

$$V_A = -\frac{A}{6} \left[\frac{2a_1a_2}{H^2 + 2a_1H + 2a_2H} + \frac{2a_1a_2}{H^2 + 2a_1H + 2a_2H + 4a_1a_2} + \ln \left(\frac{H^2 + 2a_1H + 2a_2H}{H^2 + 2a_1H + 2a_2H + 4a_1a_2} \right) \right] \quad (1)$$

where A is Hamaker's constant and H is the interparticle separation. When $H \ll a_1$ and a_2 , the equation reduces to

$$V_A = -\frac{Aa_h}{12H} \quad (2)$$

$$a_h = \frac{2a_1a_2}{a_1 + a_2} \quad (3)$$

a_h is the hypergeometric radius.

V_R between two dissimilar particles under conditions of constant charge⁴¹ is given by

$$V_R = \frac{\pi\epsilon_0\epsilon_1 a_h}{2} (\psi_{01}^2 + \psi_{02}^2) \left[\frac{2\psi_{01}x\psi_{02}}{\psi_{01}^2 + \psi_{02}^2} x \ln \frac{1 + e^{-kH}}{1 - e^{-kH}} - \ln(1 - e^{-2kH}) \right] \quad (4)$$

where ψ_{01} and ψ_{02} are the surface potentials of the two particles, κ is the inverse double-layer thickness, ϵ_0 is the permittivity of the vacuum, and ϵ_r is the dielectric constant of the dispersion medium. Under the conditions when the surface potentials on the two particles are the same ($\psi_{01} = \psi_{02} = \psi_0$, where ψ_0 is the electrostatic potential), the previous equation reduces to

$$V_R = -2\pi\epsilon_0\epsilon_r a_h \psi_0^2 \ln(1 - e^{-\kappa H}) \quad (5)$$

ψ_0 on the surface of a spherical particle of radius a with surface charge (Q) under the conditions when the Debye–Huckel approximation is valid ($\psi_0 \ll 25$ mV) is given by

$$\psi_0 = \frac{Q}{4\pi\epsilon_0\epsilon_r a(1 + \kappa a)} \quad (6)$$

When $\kappa a \gg 1$, the equation reduces to

$$\psi_0 = \frac{q}{4\pi\epsilon_0\epsilon_r \kappa} \quad (7)$$

where $q \equiv \frac{Q}{4\pi a^2}$ is the surface charge density.

The thickness of a double layer is normally characterized by the Debye length $1/\kappa$. The square of κ is given by

$$\kappa^2 = \frac{2\pi e_L N_A I_e}{\epsilon_0 \epsilon_r k_B T} \quad (8)$$

where e_L is the electronic charge and N_A is Avogadro's number. The double-layer thickness is a sensitive function of the concentrations and valencies of the ions of the medium, which is expressed in terms of ionic strength of the dispersion medium (I_e). I_e is given as

$$I_e = \frac{1}{2} \sum_{j=1}^n (C_{+j} Z_{+j}^2 + C_{-j} Z_{-j}^2) \quad (9)$$

where C is the concentration of ions and Z is the valency.

The subscripts $+j$ and $-j$ stand for the positive ion of component j and the negative ion of compo-

nent j , respectively, in the dispersion medium. For aqueous solutions at a temperature (T) of 300 K, the equation for κ^2 is given by

$$\kappa^2 = 10.822 I_e \left(\text{nm}^{-2}, I_e \text{ in M} \right) \quad (10)$$

Two approximations are made to calculate the magnitude of the electrostatic repulsive force between two charged particles. The first approximation is to use the linearized forms of the Poisson–Boltzmann equation, that is, the Debye–Huckel approximation, which is valid when the surface potentials on the two particle surfaces are less than 25 mV. The second approximation assumes that the interaction between double layers on spherical particles is made up of contributions from infinitesimally small parallel rings, each of which can be considered as a flat plate, that is, the Deryaguin approximation, which is valid provided that the thickness of the double layer is small compared to the particle size. Hogg et al.⁴¹ evaluated the effect of the aforementioned approximations on the magnitude of the repulsive potential calculated with the comprehensive equation for V_R as given before. According to them, the previous expression is a good approximation for surface potentials less than 50–60 mV and with $\kappa a > 5$.

The relative magnitude of the van der Waals attractive force and the electrostatic repulsive force determine the stability of the colloidal system. If the value of Hamaker's constant of polystyrene spheres is considered to be about 6.5×10^{-21} J,⁴² the attractive potentials between spheres with hypergeometric mean radii of 200 and 20 nm at a distance of closest approach of about 1 nm are of the order of $30k_B T$ and $3k_B T$, respectively, where k_B is Boltzmann's constant and T is the temperature (300 K). Both values will be sufficiently high in the absence of any repulsion to induce significant coagulation because their absolute magnitudes exceed the thermal energy available to the particle ($\sim k_B T$). In the presence of electrostatic repulsive forces, only a fraction of Brownian interactions would result in coagulation because only those particles with sufficient kinetic energy to overcome the electrostatic repulsive force would undergo coagulation. The ratio of the rates of Brownian interactions in the absence and presence of repulsive forces is given by the stability ratio (W), which can be calculated from the following relationship:

$$W = \frac{1}{\kappa a_h} e^{V_{T\max}/k_B T} \quad (11)$$

where $V_{T\max}$ is the height of the energy barrier to coagulation. Physically, this indicates that a Brownian encounter between particles having $V_{T\max}$ is

obtained as the maximum relative to H of the total potential (V_T), which is the sum of V_A and V_R . The stability criteria requires that the height of the primary maxima should be sufficiently large ($\geq 25k_B T$)

The minimum surface potential (or q) necessary for the colloidal system to meet this stability criteria can be calculated by with the following two equations for the H distance, corresponding to V_{Tmax} and the surface potential ψ_0 , for a given value of a_h and κ (or I_e):

$$\frac{\partial V_A}{\partial H} + \frac{\partial V_R}{\partial H} = 0 \quad (12)$$

$$V_A + V_R = 25k_B T \quad (13)$$

The values of q can be obtained from the values of ψ_0 and κ with $q = \frac{Q}{4\pi r^2}$. The values of κa , surface potential ψ_0 , and surface charge density Q corresponding to various values of the hypergeometric mean radius are summarized in Table I. The value of the ionic strength used for these calculations is 10 mM (8 mM arising from 2.66 mM initiator potassium persulfate, whereas the surfactant dissolved in the aqueous phase contributes the remaining 2 mM). This value represents the maximum ionic strength in the reactor for a typical recipe considered for polymerization, with 2.66 mM as the highest initiator concentration used. Also given is the value of surfactant surface coverage on the droplets (θ_{sd}), which will provide the minimum q .

The basic principle behind the electrostatic stabilization of a latex system is the acquisition of charges on the surfaces of the particles. The minimum q (and surfactant coverage area) required for electrostatic stability is shown in Table I. The aim now is to calculate the q (and surfactant coverage area) on the droplets under the conditions existing in the reactor. The various ways through which a particle can acquire charge include adsorption of ionized emulsifier, surface grouping from the initiator radical, and adsorption of ions from the medium.

TABLE I
Minimum Values of the Parameters for Electrostatic Stability

a_h (nm)	κa	ψ_0 (mV)	Q	θ_{sd} (%)
5	1.7	57	0.0123	4.6
10	3.5	44	0.0095	3.6
15	5.2	38	0.0082	3.0
20	6.9	34	0.0074	2.8
25	8.6	32	0.0068	2.6
30	10.4	30	0.0064	2.4
40	13.8	27	0.0059	2.2
60	20.8	24	0.0053	2.0
80	27.7	22	0.0047	1.8
100	34.6	20	0.0044	1.6

The surface charge density arising from the surfactant coverage (q_s) is given by

$$q_s = \frac{Ze_L}{a_{sd}} \theta_{sd} \quad (14)$$

where Z is the valency of the surfactant coverage anion ($Z = 1$ for sulfate groups from SDS) and a_{sd} is the area occupied by a surfactant molecule on the droplet surface. θ_{sd} can be obtained by the assumption that the adsorption of the surfactant follows the Langmuir isotherm:

$$\theta_{sd} = \frac{b_{sd} C_{sw}}{1 + b_{sd} C_{sw}} \quad (15)$$

where b_{sd} is a constant and is the one used in the previous work.⁴² The surfactant concentration in the aqueous phase (C_{sw}) can be obtained from the mass balance for the surfactant:

$$C_{sw} V_w = C_{st} V_t - \frac{A_d \theta_{sd}}{a_{sd} N_A} \quad (16)$$

where C_{st} is the total concentration of the surfactant in the reactor, V_t is the total volume of the reaction mixture. A_d is the total surface area of the droplets, and V_w is the volume of the aqueous phase.

The value of θ_{sd} calculated through the solution of the previous two equations for a typical recipe involving 20 wt % monomer and 10 mM SDS and with the assumption that the initial surface area of the droplets corresponds to a surface average diameter of 100–150 nm varies between 18 and 22%. Landfester et al.,⁴³ through surfactant titrations and surface tension measurements, experimentally determined the surfactant coverage of SDS on miniemulsion droplets with an average size of 138 nm to be 28%. Paunaov et al.⁴⁴ theoretically estimated the surfactant coverage of SDS on miniemulsion droplets for the conditions used in the experiments of Landfester et al.⁴³ to be 25.8%. On the basis of these theoretical calculations and experimental measurements, one can conclude that the actual value of surfactant coverage is an order of magnitude greater than the minimum value required for stability; thus, the initial droplet size distribution is electrostatically stable. During polymerization, θ_{sd} would change due to the creation of the particle surface and would depend on the affinity of the surfactant molecule for the droplets and the particles. The droplets would only become electrostatically unstable during polymerization if their surface coverage fell from about an initial 20% to about 2%. A corollary of the previous result is that practitioners can formulate a miniemulsion recipe with lesser amounts of surfactant. As stated, a surfactant concentration of 10 mM (based on water) is used in a typical miniemulsion recipe, which results in a surfactant coverage of 18–20%,

whereas for coagulative stability, the required surfactant coverage is 1–5%. This would not only provide cost effectiveness, as surfactant is a costly recipe component, but it would also reduce the deleterious effects of surfactant on certain specific properties, such as optical clarity, adhesion to substrates, and weather durability, of bulk polymers produced by emulsion polymerization.

Experimental studies on miniemulsion polymerization have revealed that the fraction of droplets nucleated is not 100%. Choi et al.⁴⁵ described that only 20% of their droplets were nucleated (with styrene as the monomer and CA as the costabilizer). Chern et al.⁴⁶ determined that 55% (with styrene as the monomer and blue dye as the costabilizer) to 60% (with styrene as the monomer and DMA as the costabilizer)⁴⁷ of their droplets were nucleated. Reimers and Schork⁴⁸ reported a droplet nucleation of 95% (with polymer as the costabilizer). These experimental results led to an important question regarding the fate of the remaining droplets. The models for miniemulsion polymerization that incorporated the thermodynamic partitioning of the monomer among the different phases predicted that the remaining miniemulsion droplets continue to transfer their monomer to the growing particles but do not disappear completely, as in conventional emulsion polymerization; but can exist until the end of the polymerization.^{12,13,49–52} The existence of monomer droplets until the end of polymerization was questioned in the work by Rodriguez,⁵² where droplets were considered to disappear as a result of collision and coalescence. In another study,⁴² it was found that the predictions of the model improved when coagulation of miniemulsion droplets with the particles was incorporated. The model of Sood and Awasthi^{12,13} revealed that participation of the miniemulsion droplets in particle nucleation during the later stages of polymerization, although small, contributed significantly to increasing the standard deviation of the particle size distribution; therefore, the existence of stable monomer droplets until the end of polymerization is necessary to predict the large standard deviations of the particle size distributions that were reported experimentally by Miller and coworkers.^{8,53} In this article, I have revealed that droplets would only become electrostatically unstable during polymerization if their surface coverage fell from about an initial 20% to about 2%. In the light of the aforementioned results, this seems highly unlikely.

CONCLUSIONS

In this article, I theoretically analyze the coagulative stability mechanism of miniemulsion droplets. I have shown that there is a sufficient electrostatic barrier

provided by the surfactant against contact, and hence, coagulation is not responsible for the previously experimentally reported instability of miniemulsion droplets. The minimum surfactant coverage required for stability is 1–5% on the basis of the framework provided by DLVO theory, whereas the actual value of surfactant coverage for a typical recipe found with the Langmuir isotherm varies between 18 and 22%. Thus, the actual surfactant coverage is an order of magnitude greater than the minimum required for electrostatic stabilization. Therefore, I concluded that the initial droplet size is stable against coagulation. It can be reasoned further that the amount and nature of the surfactant in the experimental study are same whether HD or CA is used as a costabilizer, and so if insufficient stabilization provided by the surfactant is the cause of instability, this would result in the rearrangement of the droplet size distribution for both these costabilizers, but only rearrangement with CA as the costabilizer was seen. A corollary of the previous result is that the practitioners can formulate a miniemulsion recipe with lesser amounts of surfactant. This would not only provide cost effectiveness, as surfactant is a costly recipe component, but it would also reduce the deleterious effects of surfactant on certain specific properties, such as optical clarity, adhesion to substrates, and weather durability, of bulk polymers produced by emulsion polymerization.

I further discussed that the existence of stable droplets until the end of polymerization and their participation in particle nucleation is necessary to explain the large standard deviations of the final particle size distributions in miniemulsion polymerization.

NOMENCLATURE

Symbols

a, a_1, a_2	radius of spheres
a_h	hypergeometric radius
a_{sd}	area occupied by a surfactant molecule on the droplet surface
A	Hamaker's constant
A_d	total surface area of the droplets
b_{sd}	constant used in Langmuir's isotherm
C	concentration of ions
C_{sw}	surfactant concentration in the aqueous phase
C_{st}	total surfactant concentration in the reactor
e_L	electronic charge
H	interparticle separation
I_e	ionic strength of the dispersion medium
k_B	Boltzmann's constant
N_A	Avogadro's number

q	surface charge density
Q	surface charge
T	absolute temperature
V_A	van der Waals attractive potential
V_R	electrostatic repulsive potential
V_{Tmax}	height of the energy barrier to coagulation
V_t	total volume of the reaction mixture
V_w	volume of the aqueous phase
Z	valency of the ions

Greek letters

ϵ_0	permittivity of the vacuum
ϵ_r	dielectric constant of the dispersion medium
θ_{sd}	surfactant surface coverage on the droplets
κ	inverse double-layer thickness
Ψ_{01}, Ψ_{02}	surface potentials of the particles

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