EFFECT OF HEAT TREATMENT AND SURFACE CHARGE HETEROGENEITIES ON THE INITIAL RATE OF FLOCCULATION OF POLYSTYRENE PARTICLES

by

Connie Jo Leuderalbert

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ABSTRACT

EFFECT OF HEAT TREATMENT AND SURFACE CHARGE HETEROGENEITIES ON THE INITIAL RATE OF FLOCCULATION OF POLYSTYRENE PARTICLES

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DLVO theory, which governs particle-particle interactions, has been shown to predict a steeper stability ratio curve than is obtained experimentally during slow flocculation of colloidal particles. The objective of this work is to examine the effect of two of the more likely reasons for this classical discrepancy: surface roughness and surface charge heterogeneities.

Surfactant free polystyrene beads of D = 0.30 μm were obtained from Interfacial Dynamics corporation for the study. To reduce surface roughness, dispersions containing 0.05% solids were heated in a Parr bomb for 6, 12 or 24 hours at 120°C followed by slow cooling to examine the effect of length of heat treatment. Surface charge heterogeneities were mitigated by adding sodium dodecyl sulfate to obtain a final dispersion concentration of 1×10^{-5} M.

Results show that the effects of heat treatment are fully realized by 6 hours of heating at 120°C. It was also found that the addition of a surfactant lessens the disagreement between theory and experiment.

DEDICATION

TO

The loving memory of my father
who taught me that anything is possible

Mom
whose constant support encourages me to excel

Gary, Sandy, Jeff, Stephanie, Sharon, Jim, James, Scott, Ken, Jody, Rachel, Megan, Sean and Jessica
for your love and support, and for providing me with so much joy

Jody
for always being there for me, even in the bad times

Steve
for letting me lean on him when it all seemed hopeless
and for teaching me to believe in the future

and

Abhijit
for reminding me just how lucky I am; I wish life had given you more time

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NOMENCLATURE

Symbol	**Definition**	**units**
a	radius of polystyrene sphere	cm
A_{eff}	Hamaker constant	erg
c	electrolyte concentration	M
D	diameter of sphere	cm
D_{∞}	bulk diffusion coefficient	cm^2s^{-1}
$D(u)$	local diffusion coefficient	cm^2s^{-1}
e_o	protonic charge	dimensionless
I_o	initial scattering intensity	arbitrary units
k	Boltzmann constant	erg/K
N_A	Avogadro's number	$mole^{-1}$
n_o	initial number concentration of particles	mL^{-1}
r	center to center separation distance	cm
T	temperature	K
u	dimensionless separation distance	dimensionless
W	stability ratio	dimensionless
z	valence of charge	dimensionless

Greek Symbols

Symbol	**Definition**	**units**
$1/\kappa$	Debye length	cm
α	attachment efficiency	dimensionless
ε	dielectric constant	dimensionless
Φ_{ij}	total energy of interaction between non-identical particles	erg
Φ_R	repulsive energy	erg
Φ_T	total energy of interaction	erg
Φ_{vdW}	energy of vdW attraction	erg
η	viscosity	$kg\ m^{-1}s^{-1}$
κ	Debye-Hückel parameter	cm^{-1}
λ	wavelength	nm
σ	surface charge density	$C\ cm^{-2}$
Ψ	Stern potential	statvolt
ζ	Zeta potential	mV

1. INTRODUCTION

Colloidal behavior governs the performance of many industrial products, including surface coatings, adhesives, textiles, paints, and synthetic rubber. Colloids are defined as disperse systems of particles with one linear dimension between 10 nm and 1 μm. Over this size range, gravitational sedimentation is negligible, and Brownian motion is the major mechanism for diffusion. The stability of a colloidal dispersion is determined by the interplay between London and van der Waals attractive forces on one hand, and electrostatic and steric repulsive forces on the other. Therefore, the rate of flocculation, which is a measure of the stability of the system, is a sensitive method of determining the forces acting between particles.

The classical basis for colloid stability emerged in the 1940's when Derjaguin and Landau (Russian scientists) and Verwey and Overbeek (Dutch scientists), working independently, calculated the electrostatic repulsion between two particles on the basis of the interactions between the double layers (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). Their combined work, collectively known as DLVO theory, states that the stability of a colloidal dispersion depends on the sum of the electrostatic repulsive forces (due to the overlapping of ionic atmospheres around the particles) and the attractive forces (represented by London and van der Waals forces). The core of the theory is that attraction decays as the square of the inverse power of the separation distance and is nearly independent of electrolyte concentration, while the repulsive forces fall off exponentially over a range equal to the Debye length and are, therefore, strongly dependent on electrolyte concentration (Overbeek, 1982).

1.1 STABILITY RATIO

The stability of a colloidal dispersion is a function of the electrolyte concentration, and is usually presented as a plot of the log of the stability ratio (log W) against the log of electrolyte concentration (log c) (Figure 1-1). The plot yields two linear segments representing a slow flocculation (reaction-limited cluster aggregation) region and a rapid flocculation (diffusion-limited cluster aggregation) region. In the rapid flocculation regime, there is no energy barrier between the particles because the sum of attractive and repulsive forces is zero or negative. Therefore, every collision results in coagulation. In the slow flocculation regime, an energy barrier exists due to the dominance of repulsive forces over attractive ones and the rate of coagulation is retarded. As a result, only a fraction ($1/W$) of collisions leads to coagulation (Hidalgo-Alvarez *et al*, 1996). The intersection of the two linear segments of the stability ratio curve is known as the critical coagulation concentration (ccc).

1.2 PROBLEM DEFINITION

Polystyrene latexes are often used in the study of fundamental colloidal phenomena because they are spherical and nearly monodisperse, with well characterized surface functional groups. A large body of evidence suggests, however, that polystyrene latexes do not behave as the classical theories predict. For example, experimental flocculation stability ratio curves

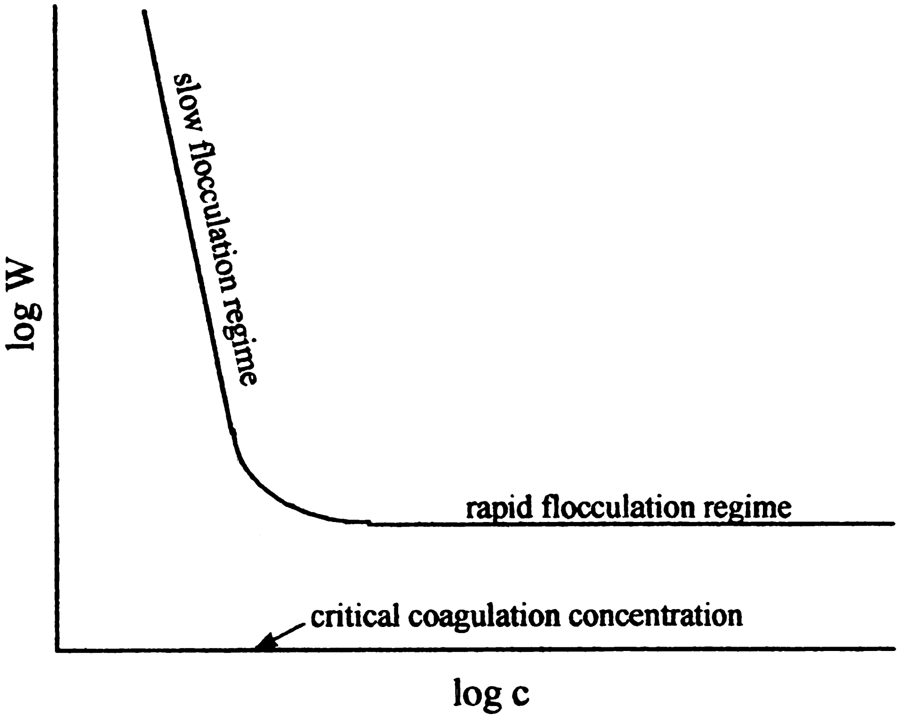


Figure 1-1: Typical stability ratio curve

are significantly different from those calculated on the basis of DLVO theory (Ottewill and Shaw, 1966); the ionic strength dependence of polystyrene latexes exhibits a maximum in zeta potential not predicted by theory (Rosen and Saville 1991, Hidalgo-Alvarez et al, 1992, Elimelech and O'Melia, 1990); and particle deposition rates in the presence of repulsive forces are grossly under-predicted by DLVO theory (Elimelech and O'Melia, 1990).

There have been many discussions in the literature as to the nature of the factors responsible for the deviations between theory and experiment. This study is designed to investigate two of the hypotheses proposed: 1) that a hairy layer on the surface of the particle induces surface roughness, causing the particle to not conform to the spherical shape on which the classical theories are based; and 2) surface charge heterogeneities produce a particle that cannot be characterized by a constant surface potential (Litton and Olson, 1994; Seeburgh and Berg, 1995). The two factors are discussed in more detail below.

1.2.1 MODIFICATION OF SURFACE MORPHOLOGY BY HEAT TREATMENT

The "hairy layer" hypothesis suggests that a layer of flexible polymer chains is present on the surface of the polystyrene particle (Rosen and Saville 1990; Midmore and Hunter, 1988; Chow and Takamura, 1988). Zimehl and Lagaly (1987) suggest that hairy particles are one of several types produced during emulsion polymerization. The hairs extend into the bulk solution because of electrostatic repulsion between the ionic groups which terminate the hairs and charges anchored to the surface. The hypothesis is that when the particle is heated above its glass transition temperature (98°C), it becomes amorphous, and the sticky, mobile polymer chains can rearrange and collapse on the particle surface, resulting in a smoother particle (Rosen and Saville 1990).

Based on evidence from light scattering and photon correlation spectroscopy, Seebergh and Berg (1995) concluded that the thickness of the hairy layer on PS particles was between 4-7 nm thick and that heat treatment collapses this layer. In addition, they report that heat treatment reduces the absolute electrophoretic mobility and attribute this to a loss in surface charge density by hydrolysis of the sulfate during heat treating (Seebergh and Berg, 1995). Lastly, they observed a change in the critical micelle concentration (ccc) upon heat treatment which they attributed to the collapse of the hairy layer (Seebergh and Berg, 1995).

Ofoli (1994) also investigated this factor by heat treating polystyrene particles for 6 hours prior to measuring the rate of flocculation. He found that results for heat treated particles were in better agreement with theoretical calculations than those for unheated dispersions. This raises the question as to what effect extended heat treatment would have on the agreement of experimental flocculation rates with DLVO theory. The current work addresses this issue.

1.2.2 REDUCTION OF SURFACE CHARGE HETEROGENEITY BY ADDITION OF A SURFACTANT

The deposition rates of particles onto granular quartz beds is often studied using latex particles. The attachment efficiency (α) of the particles onto the beds is inversely proportional to the stability ratio (W). Investigators have found that experimentally observed attachment rates are grossly underestimated by DLVO theory when calculations are done on the basis that charge is uniformly distributed on particle surfaces (Elimelech and O'Melia, 1990; Gregory and Wishart, 1980). On the other hand, theoretical models that incorporate surface charge heterogeneity yield results that are closer to experimentally observed attachment efficiencies (Kihara et al. 1992).

Litton and Olsen (1994) investigated this factor by assuming that the surface of the colloidal latex was characterized by uncharged regions as well as regions negatively charged with sulfate ions. It is known that anionic surfactants "shield" the uncharged regions by hydrophobic attachment of the surfactant alkyl chain to polystyrene oligomer exposed at the surface (Kayes, 1976; Kandori et al, 1989). To examine the effect of covering uncharged regions of the latex with anions, Litton and Olsen (1994) added sodium dodecyl sulfate (SDS) at slightly below the critical micelle concentration to their carboxyl latex dispersions. They found that this addition greatly improved the agreement between experiment and theory.

2. GENERAL BACKGROUND

2.1 DLVO THEORY

The quantitative theory which describes the interplay between electrostatic repulsion and van der Waals attraction was formulated by Derjaguin and Landau (1941) and Verway and Overbeek (1948), and is known collectively as DLVO theory. It states that the total energy of interaction between particles (Φ_T) is the sum of the electrostatic repulsion (Φ_R) and van der Waals attraction (Φ_{vdW}). The repulsive forces are given by (Russel et al., 1989):

$$\Phi_R = 32\pi\varepsilon a\left(\frac{\gamma k T}{ze}\right)^2 e^{-\kappa h} \tag{1}$$

where

$$\gamma \equiv \frac{e^{\varphi/2}-1}{e^{\varphi/2}+1} \quad \text{and} \quad \varphi = \frac{ve\Psi_d}{kT} \tag{2}$$

and, ε is the dielectric constant, z is the valence of the counter-ion and e_o is the protonic charge.

The Debye-Hückel parameter, κ, is given by:

$$\kappa = \sqrt{\frac{8\pi \mathrm{c} \mathrm{N}_\mathrm{A} z^2 e_0^2}{\varepsilon k T}} \tag{3}$$

where c is the concentration of the electrolyte, N_A is Avogadro's number and e_o is the protonic charge.

The van der Waals attraction is calculated from (Pailthorpe and Russel 1982):

$$\Phi_{vdW} = -\frac{A_{eff}}{6}\left[\frac{2a^2}{r^2-4a^2}+\frac{2a^2}{r^2}+\ln\left(1-\frac{4a^2}{r^2}\right)\right] \tag{4}$$

where a is the radius of the sphere, r is the center to center separation distance, and A_{eff} is the effective Hamaker constant from Lifshitz theory (Pailthorpe and Russel 1982).

The absolute stability ratio is the quotient of the rate of flocculation when interactive forces between particles are absent, and the rate at any other electrolyte concentration:

$$W_{abs}(c_e) = \frac{rate\ when\ \Phi_T = 0}{rate\ when\ \Phi_T \neq 0} \tag{5}$$

where c_e is the electrolyte concentration. The numerator of this equation represents the case of rapid flocculation where every collision results in particles sticking together (Smoluchowski kinetics); it is most nearly realized at high electrolyte concentrations.

2.2 THE EXPERIMENTAL STABILITY RATIO

An experimental absolute stability ratio can be directly calculated from small angle light scattering (SALS) data using the following equation (Young 1991):

$$W = \frac{2}{\tau}\left(\frac{1}{I_0}\frac{dI}{dt}\right)^{-1} \quad and \quad \tau = \frac{3\eta}{4kTn_0} \tag{6}$$

where I_o and dI/dt are the intercept and slope, respectively, of the scattering intensity versus time profile, η is the viscosity of the dispersion, k is the Boltzmann constant, T is the temperature and n_o is the initial concentration of particles (singlets).

2.3 THE THEORETICAL STABILITY RATIO

2.3.1.1 HOMO-FLOCCULATION

Fuch's equation for homo-flocculation can be used to calculate the theoretical stability ratio:

$$W = 2a\int_{2a}^{\infty} \frac{D_{\infty}}{D(u)} \exp\left[\frac{\Phi_T(r)}{kT}\right]\frac{dr}{r^2} \tag{7}$$

where u is the dimensionless center-to-center separation distance between the particles at their closest point of contact, and D_{∞} and $D(u)$ are the bulk and local diffusion coefficients, respectively. The ratio of diffusion coefficients in the above equation represents a hydrodynamic correction proposed by Spielman (1970) to account for the viscous drainage of solvent from between particles as they approach one another:

$$\frac{D_{\infty}}{D(u)} = \frac{6u^2 + 13u + 2}{6u^2 + 4u} \tag{8}$$

$$where \quad u = \frac{r - 2a}{a}$$

2.3.1.2 HETEROFLOCCULATION

The equations for heteroflocculation allows one to account for variations in properties such as zeta potential and particle size. In the limit of monodisperse particles with no deviation in zeta potential, the equations describing heteroflocculation reduce to Fuch's equation given above. Ofoli (1994) showed that the variation in zeta potential is important in the calculation of the theoretical absolute stability ratio. As a result, it has been incorporated into the theoretical calculations in this study.

Prieve and Lin (1982) derived the following equation to account for variations in particle size and surface potential:

$$W_{ij} = R_{ij} \int_0^{\infty} \frac{\exp(\Phi_{ij}(h)/kT)}{(h+R_{ij})^2 D(h)/D_{\infty}} dh \tag{9}$$

where $\Phi_{ij}(h)$ is the total energy of interaction between particles i and j, $h + R_{ij}$ is the center-to-center separation distance, and $R_{ij} = a_i + a_j$. For the case of a distribution in surface potential, the following equation for the mean stability ratio can be used (Prieve and Lin 1982):

$$\langle W_{\Psi} \rangle = \frac{\int_{-\infty}^{\infty} \int_{\Psi_1}^{\infty} p(\Psi_1) p(\Psi_2) d\Psi_1 d\Psi_2}{\int_{-\infty}^{\infty} \int_{\Psi_1}^{\infty} \frac{p(\Psi_1) p(\Psi_2)}{W(\Psi_1, \Psi_2)} d\Psi_2 d\Psi_1} \tag{10}$$

where $<W_{\psi}>$ is the mean stability ratio due to a distribution in surface potential, $p(\Psi_i)$ is the probability density for Stern potential Ψ_i and $W(\Psi_1, \Psi_2)$ is the heterogeneous stability ratio defined in Eq. (9).

2.4 SMALL ANGLE LIGHT SCATTERING

Light scattering is well suited to measuring the rate of flocculation because of its high sensitivity to small changes in particle size. Lord Rayleigh (1918) laid the foundation for the theory of light scattering in the early 20th century by applying the electromagnetic theory of light to small, non-absorbing particles in a gaseous medium. He showed that if a particle is smaller than 1/20th of the wavelength of the incident radiation, it will scatter light in proportion to the square of its volume. To extend the applicability of Rayleigh scattering, Debye and Gans introduced a correction to this theory by incorporating a form factor that accounts for interparticle scattering from different volume elements within a particle larger than the Rayleigh limit (Kerker, 1969; Oster and Riley, 1952). Debye also argued that, at small angles, the Rayleigh limit can be further relaxed because interference effects in the forward scattering direction become negligible. Recently, Ofoli (1994) produced experimental evidence that, at small angles (2° or less), the regime of Rayleigh scattering can be extended to $D \leq 0.95$ μm for probing polystyrene spheres in water with a helium-neon (HeNe) laser.

The small angle scattering of light from a dispersion of identical primary particles with time-varying floc sizes is (Lips and Willis, 1973; Zeichner and Showalter, 1979):

$$I(\theta,t) = \sum_{j=1}^{\infty} n_j(t) j^2 I_s(\theta) \tag{11}$$

where $n_j(t)$ is the number of flocs at time t containing j primary particles. For a flocculating dispersion of primary particles, the rate of disappearance of singlets from the system $-dn_1 / dt$, based on Eq. (11) is (Lips and Willis, 1973; Zeichner and Showalter, 1979):

$$-\frac{\mathrm{d}n_1}{\mathrm{d}t} = \frac{n_0}{I_0} \frac{\mathrm{d}I(\theta,t)}{\mathrm{d}t} \tag{12}$$

where n_0 is the initial number of singlets and I_0 is the intensity of the incident radiation (Lips and Willis, 1973; Zeichner and Showalter, 1979). The experimental flocculation rate can be calculated by substituting the initial intensity and slope dI/dt of the intensity vs. time plot for the flocculating dispersion into Eq. (12).

2.5 ELECTROPHORETIC MOBILITY

The repulsive forces between colloidal particles are described by a model of the electrical double layer (EDL). The theory of the EDL deals with the distribution of counter-ions and co-ions at the surface. Helmholtz (1879) first proposed a model of a fixed layer of counter-ions adsorbed to the surface of the colloid. This was modified by the Gouy-Chapman model which assumed that the electrical properties at the surface of a colloidal particle are a balance between electrical forces which tend to attract counter-ions, and thermal motion which tends towards a uniform distribution of the ions (Gouy, 1910; Chapman, 1913). The model predicts that the combined effect of this competition is to produce a "diffuse" electrical double layer rather than a fixed layer of ions at the surface.

The two schools of thought were combined by Stern (1924) who proposed that the electrical double layer is a combination of adsorbed and diffusing ions. Stern introduced a correction for the finite size of the ions in the first layer adjacent to the charged surface, and argued that electrostatic and van der Waals forces near the surface might be enough to overcome the thermal motion of the ions in the vicinity of the surface. The EDL in Stern's model is, therefore, divided into two parts: a compact layer of attached counter ions at the surface, surrounded by a diffuse collection of co- and counter-ions extending from the particle surface into the bulk fluid (Figure 2-1). The "thickness" of the diffuse layer is given by the Debye length ($1/\kappa$) (Laidler and Meiser, 1982):

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\, k\, T}{8\pi\, c\, N_A z^2 e_0^2}} \qquad (13)$$

where c is the concentration of the electrolyte, N_A is Avogadro's number and e_o is the protonic charge. It can be seen from Eq. (13) that the Debye length decreases as the electrolyte concentration increases, leading to a decrease in the diffuse double layer.

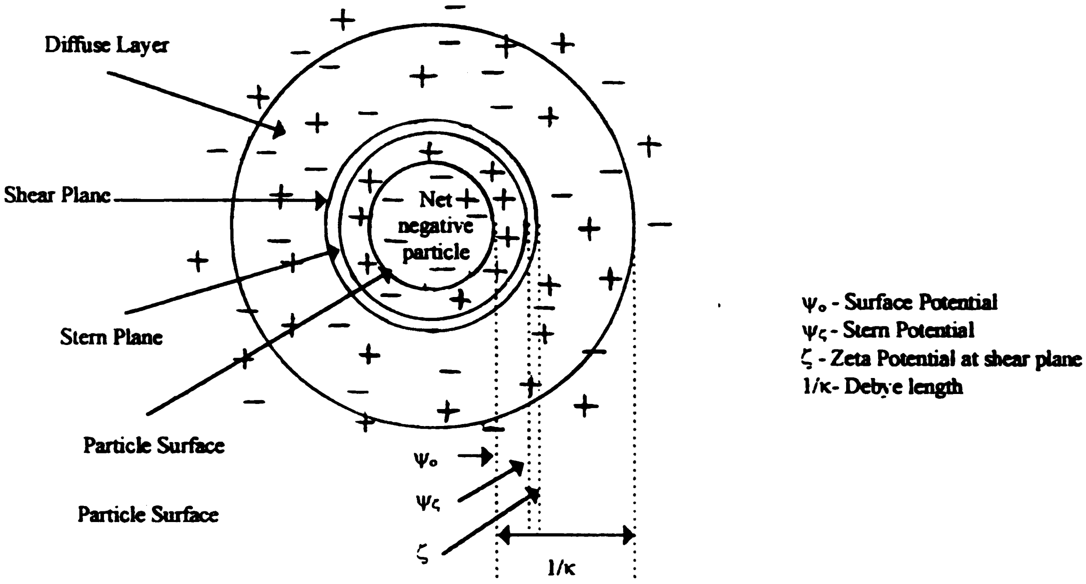


Figure 2-1: Stern model of the electrical double layer

If an electric field is applied to an aqueous colloidal dispersion, a force is created in both parts of the double layer. The charged surface of the colloid and the solvent inside the shear plane tend to move in the attractive direction, while the ions outside the surface of shear move in the opposite direction. The movement of the colloidal particle in response to this applied potential gradient is the electrophoretic mobility.

3. OBJECTIVES

DLVO theory, generally accepted as the pre-eminent theoretical model for particle-particle interactions, has been shown by many researchers to predict a steeper stability ratio curve than is obtained experimentally during the slow flocculation of colloidal particles. Two of the more likely reasons for this classical discrepancy are that 1) due to surface roughness, particles do not conform to the smooth, perfectly spherical shape assumed by the classical theories; and 2) particles are subject to heterogeneities in surface potential and cannot be characterized by a single constant potential.

While both of these factors are difficult to account for directly in theoretical calculations, experimental techniques are available which enable one to evaluate their effects. For example, in a recent study, Ofoli and Prieve (1997) annealed polystyrene particle surfaces by heat treating for six hours to reduce the degree of surface roughness, and showed that this resulted in a marked reduction in the discrepancy between theory and experiment. One of the goals of the current study was to extend the work of Ofoli and Prieve (1997) to evaluate how the extent of heat treatment affects the discrepancy between theory and experiment during slow flocculation of colloidal species.

In another study, Litton and Olson (1995) showed that surface charge heterogeneities can be reduced by adding a surfactant to a dispersion at a concentration below the critical micelle concentration (cmc). They reported that experimental attachment efficiencies of carboxyl latexes onto granular quartz sand in the presence of 10^{-3}M sodium dodecyl sulfate were closer to the theoretically derived values. The second goal of this study was to investigate the effect of adding a surfactant to the colloidal dispersions prior to measuring the initial rate of flocculation.

Specifically, the objectives of the study are:

1. To evaluate the effect of the extent of heat treatment beyond six hours on the agreement between experimental flocculation rates and those calculated on the basis of DLVO theory; and
2. To assess the effect of adding sodium dodecyl sulfate (SDS) to mask surface charge heterogeneities on this classical discrepancy

4. MATERIALS AND METHODS

4.1 EXPERIMENTAL DESIGN

Clean, surfactant-free polystyrene particles were purchased from Interfacial Dynamics Corporation (IDC, Portland, OR). Table 4-1 lists the experiments performed to evaluate the effects of heat treatment and stabilization with a surfactant. Electrophoretic mobility measurements could not be completed on all samples due to time constraints. The 24 hour samples were chosen for electrophoresis measurements because they would provide the largest potential beneficial result of surface annealment.

4.2 SAMPLE PREPARATION

4.2.1 HEAT TREATMENT OF COLLOIDAL DISPERSIONS

The dispersion, originally at a number concentration of $5.9\text{x}10^{12}$ particles/mL, was diluted to make a $3.34\text{x}10^{10}$ particles/ml stock solution (subsequently referred to as "stock colloid"). The concentration of the stock colloid (0.05 vol%) was chosen based on evidence presented by Rosen and Saville (1991) that suspensions above 0.5 vol% tended to flocculate during heating. The samples to be heat treated were taken directly from this stock and sealed in a Parr bomb (Parr Bomb Corp., Moline, IL). The bomb was placed in an oven at 120°C and heated for 6, 12 or 24 hours. The heated dispersions were slowly cooled,

Table 4-1: Experimental Design

Designation	Treatment	Light scattering	Electrophoresis
Native	none, diluted directly from IDC stock	yes	yes
6 hour heat treated	native particles were heated for 6 hours	yes	no
12 hour heat treated	native particles were heated for 12 hours	yes	no
24 hour heat treated	native particles were heated for 24 hours	yes	yes
Stabilized	native dispersion was stabilized with SDS below the cmc	yes	yes
6 hour heat treated	native particles were heated for 6 hours, then stabilized with SDS below the cmc	yes	no
12 hour heat treated	native particles were heated for 12 hours, then stabilized with SDS below the cmc	yes	no
24 hour heat treated	native particles were heated for 24 hours, then stabilized with SDS below the cmc	yes	yes

with the oven temperatures successively stepped down to 90°C for four hours, 60°C for four hours, and room temperature for four hours. Since there was no sedimentation at the bottom of the sample vial after heat treatment, it was assumed that flocculation did not occur during the process. The dispersions for light scattering and electrophoresis were prepared directly from these samples.

4.2.2 STABILIZATION OF DISPERSIONS WITH SODIUM DODECYL SULFATE (SDS)

A stock solution was prepared from solid sodium dodecyl sulfate (Boehringer Mannheim Laboratory Reagents, electrophoretic grade) by adding the appropriate weight of dry solid to a clean, dry volumetric flask. Double filtered distilled water was then added. The resulting solution was sonicated for 30 minutes to insure complete mixing. After cooling, the solution was brought to volume. An aliquot was taken from this stock solution to bring the final SDS concentration in the stock colloid solutions to a concentration of 1×10^{-5} M. This concentration was used to insure that micelles did not form (the cmc of SDS is 1×10^{-3} M at 30°C). The heat treated samples were stabilized only after the heat treatment procedure described above.

4.3 SMALL ANGLE LIGHT SCATTERING

4.3.1 LIGHT SCATTERING SETUP

Small angle light scattering (SALS) was used to measure the absolute flocculation rate, using the setup described by Young and Prieve (1991 (Figure 4-1). In this setup, light from a 1 mW Helium-Neon (HeNe) laser (λ =633 nm) passes through a 10x beam expander (2) to

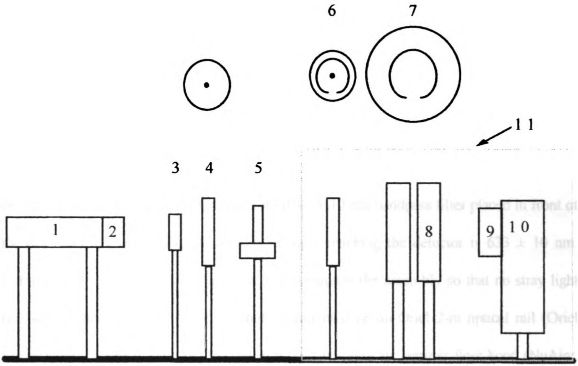


Figure 4-1: Small angle light scattering setup

increase the diameter of the beam from 0.6 to 6.0 mm, a neutral density filter (3) to reduce the incident intensity, a 3mm aperture plate (4) to eliminate all but the peak intensity of the Gaussian distributed incident light, and into a 1 cm cuvette containing the sample (5). To insure that only the light scattered at small angles is detectable, two 270° annular slit plates in series (6 and 7) configured to produce an angle of 2° were placed in the path of the scattered light. The direct incident light was attenuated at the first slit plate with a Rayleigh horn mounted in its center.

The light scattered at an angle of 2° from the horizontal passes through a plano-convex lens (8) which focuses the beam on the detector (10). A 10 nm bandpass filter placed in front of the detector (9) assures that the only wavelength reaching the detector is 633 ± 10 nm. Component 11 is a light tight black box that surrounds the assembly so that no stray light reaches the detector. The entire assembly is mounted on an Oriel 2-m optical rail (Oriel Corporation, Stratford, CT) and housed in a NuAire clean air laminar flow hood (NuAire, Plymouth, MN) to alleviate dust contamination. The output of the photomultiplier tube detector is monitored by an Oriel Model 7070 combination ammeter and high voltage power supply (Oriel Corporation, Stratford, CT) which is connected to a National Instruments data acquisition board (AT MIO 16XE-50) using a standard PC. A LabView (Version 3.1, National Instruments, Austin, TX) data acquisition software was used to collect the intensity measurements.

The configuration of the annular slits to produce the scattering angle of 2° is shown in Figure 4-2. The angle is defined by θ in the figure and is obtained by taking the average of the angle formed by a line extending from the bottom of the first slit to the top of the second slit, and the angle formed by a line running from the top of the first slit to the bottom of the second slit. In our set-up, the scattering angle is 1.6° +/- 0.08.

4.3.2 NECESSITY OF CLEAN EXPERIMENTS

Since the intensity of light scattered is proportional to the square of the volume of a particle, dust, dirt, crystals or entrapped air bubbles will scatter much more light than the colloidal particles. A speck of dust, for example, is on the order of 1 μm in diameter while the particles are 0.3 μm. In relative terms, a speck of dust will scatter more than one thousand times as much light as each of the particles. Consequently, many precautions were taken to insure that no foreign particles were incorporated into the samples.

All work, including mixing of dispersions, was performed in a NuAire laminar flow hood. Aliquots of the samples were measured using an Eppendorf pipette (Brinkmann, Westbury, NY) fitted with sterile disposable pipette tips. The tips were first blown free of contaminants using compressed air (Aero-Duster, Miller Stephenson, Danbury, CT). All water used in the preparation of samples or cleaning of glassware was double filtered through a 0.02 μm filter prior to use. Glassware was washed with filtered water, then shaken dry inside the laminar flow hood. Salt solutions were filtered after preparation and again before use. In addition, all data sets were examined for intensity spikes, generally an indication of foreign matter contamination.

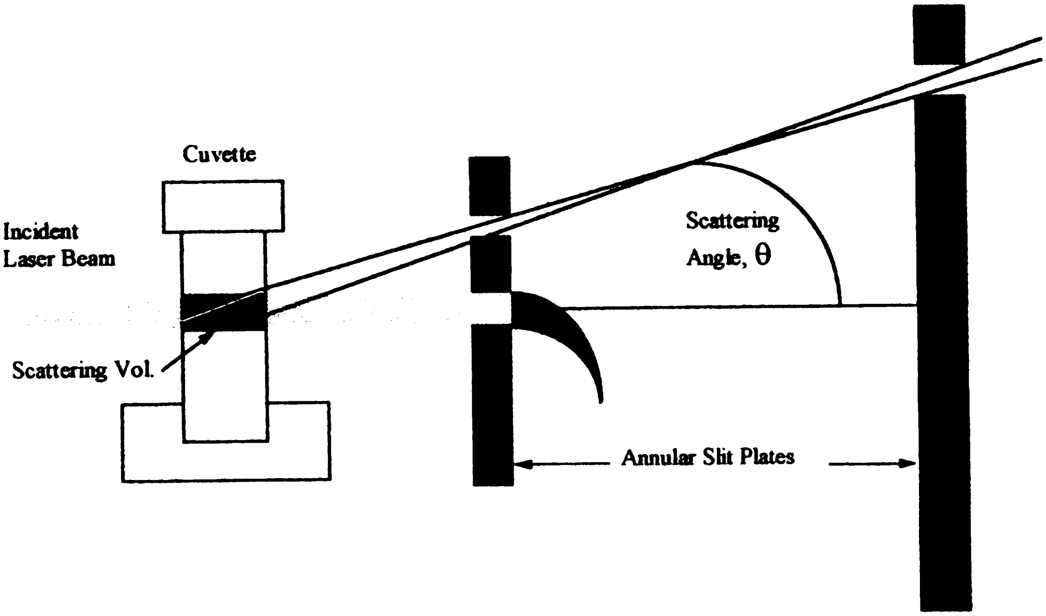


Figure 4-2: Determination of scattering angle

4.3.3 DETERMINATION OF SINGLE SCATTERING LIMIT

Using the definition proposed by Ofoli (1994), the single scattering limit was determined by the following procedure. A cuvette was filled with two milliliters of double filtered distilled water and placed in the sample holder of the SALS apparatus. The shutter of the photomultiplier tube was opened and the scattering intensity was measured for a period of 2 minutes at 2 scans/second. The average intensity over this time period was used for the background reading.

An aliquot of the stock solution was then added to the blank solution to produce a colloidal dispersion. The scattering intensity of the dispersion was measured for 10 minutes at 2 scans/second. The background reading was subtracted from the average intensity of the dispersion to obtain the scattering intensity at that number concentration (data point). These data were collected in the absence of electrolytes.

It should be noted here that the ten minutes of scanning for the colloidal dispersion was probably unnecessary. It was determined by repeated experiments that 2 minutes was sufficient for a baseline reading in the absence of colloidal flocculation. Ten minutes was chosen only as a precautionary measure to make sure that enough data points were obtained.

4.3.4 INITIAL FLOCCULATION RATE EXPERIMENTS

Scattering intensity measurements were obtained by SALS over electrolyte concentrations ranging from 0.0001 to 0.2M KCl for unstabilized samples and 0.01 to 0.025M KCl for stabilized samples. Lower salt concentrations were used for the native particles because they are inherently less stable; therefore, smaller amounts of electrolyte are required to achieve flocculation. The following procedure was used to obtain the measurements. A stock electrolyte solution with no particles was prepared by adding potassium chloride (KCl) (Fisher Scientific, 99% pure) to double filtered distilled water. An aliquot of this solution was diluted to the appropriate electrolyte concentration, and 2 mL was placed in a cuvette. Intensity measurements were collected on the blank solution for 3 minutes at a rate of 2 scans per second. Here again, the three minutes for a background measurement was only a precautionary measure. The measurements were averaged to obtain a background reading.

With the shutter on the photomultiplier tube closed, one milliliter of the colloidal dispersion was added to the blank solution, and the data acquisition system started. The cuvette was gently tipped back and forth to assure complete mixing of the particles in the electrolyte solution, taking care to not introduce air bubbles. After the colloid was added, the cuvette was placed back into the sample holder, the shutter on the PMT was pulled open, and intensity measurements were collected for 30 minutes at a rate of 2 scans per second. The average value obtained from the blank measurement was then subtracted from each of the intensity readings to obtain the scattering profile of the flocculating dispersion.

A Laser Zee Model 501 (Pen Kem, Bedford Hills, NY) was used to measure the electrophoretic mobility of the particles. It uses the Smoluchowski model to convert electrophoretic mobility to zeta potential. The measurements were taken at the upper stationary layer of the instrument. A standard colloid was measured before each set of runs, to insure correct operation of the instrument. The sample aliquot was carefully added to the electrophoresis cell with a syringe to avoid introducing air bubbles. The cell was then placed on the Laser Zee and the zeta potential and conductivity were measured according to instrument instructions. The temperature and pH were also recorded.

Zeta potential data were obtained for four sets of treatments: native, 24 hour native heated, stabilized, and 24 hour heat treated stabilized dispersions. For each treatment, mobility measurements were made at five electrolyte concentrations as described earlier.

5. RESULTS AND DISCUSSION

5.1 SINGLE SCATTERING LIMIT

To determine the single scattering limit, data were collected over a concentration range of $3\text{x}10^7$ to $7\text{x}10^9$ particles/mL, using SALS as described earlier. A regression line was computed using the first five data points. Since the scattering intensity is proportional to the incident radiation, the total scattering intensity must be linear with respect to particle concentration when all particles see the same incident light with little or no attenuation of the laser beam.

Based on this concept, the first deviation of the experimental scattering data from this line was defined by Ofoli (1994) as the termination of the single scattering regime, and is considered to mark the onset of multiple scattering (Figure 5-1). For this data, the relationship between particle concentration and scattering intensity remains quite linear until a concentration of about $1.5\text{x}10^9$ particles/ml, which is in agreement with the scattering concentration limit established by Ofoli (1994) for this particle size. Based on this limit, a concentration of $8\text{x}10^8$ particles/mL was chosen for all flocculation experiments, to insure that the single scattering limit is not exceeded.

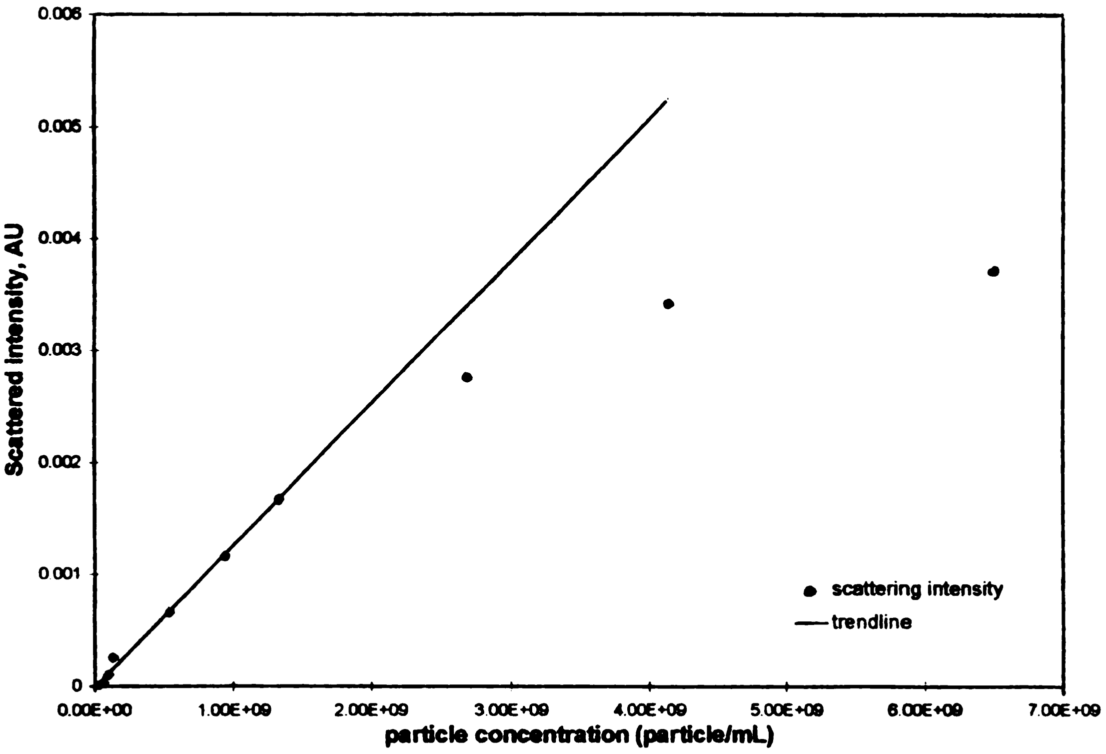


Figure 5-1: Single scattering limit for 0.3 μm polystyrene particles

5.2 ELECTROPHORESIS

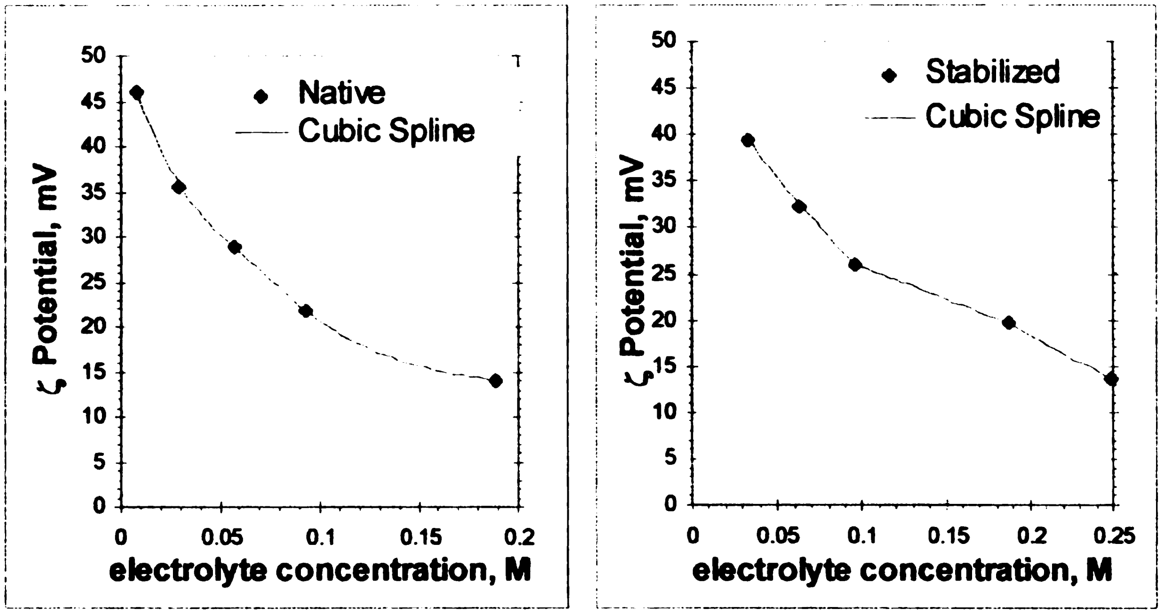
Electrolyte solutions were prepared to give a final concentration spanning a range of about 0.01 M KCl to 0.25 M KCl. The 25 mL aliquot necessary for electrophoresis experiments was prepared by mixing 23 mL of the stock solution with 2 mL of electrolyte solution. The stock solutions were sonicated for 15 seconds to break up any flocs that might have formed during refrigeration. The concentration of electrolytes in the final solution was determined by plotting a standard curve of conductivity versus concentration for five electrolyte solutions. The standard curve was then used to calculate the electrolyte concentrations.

5.3 ELECTROPHORETIC MOBILITY

Zeta potential data were obtained for four of the treatments defined earlier: native, 24 hour heat treated native, stabilized, and 24 hour heat treated stabilized dispersions. A cubic spline was fit to the five data points (Figure 5-2) to obtain an expression to be used in the calculation of the theoretical stability ratios. The zeta potentials decrease monotonically with increasing electrolyte concentration, as predicted by the Gouy-Chapman equation, which applies in the limit as $\kappa a \to \infty$ (Hunter, 1981):

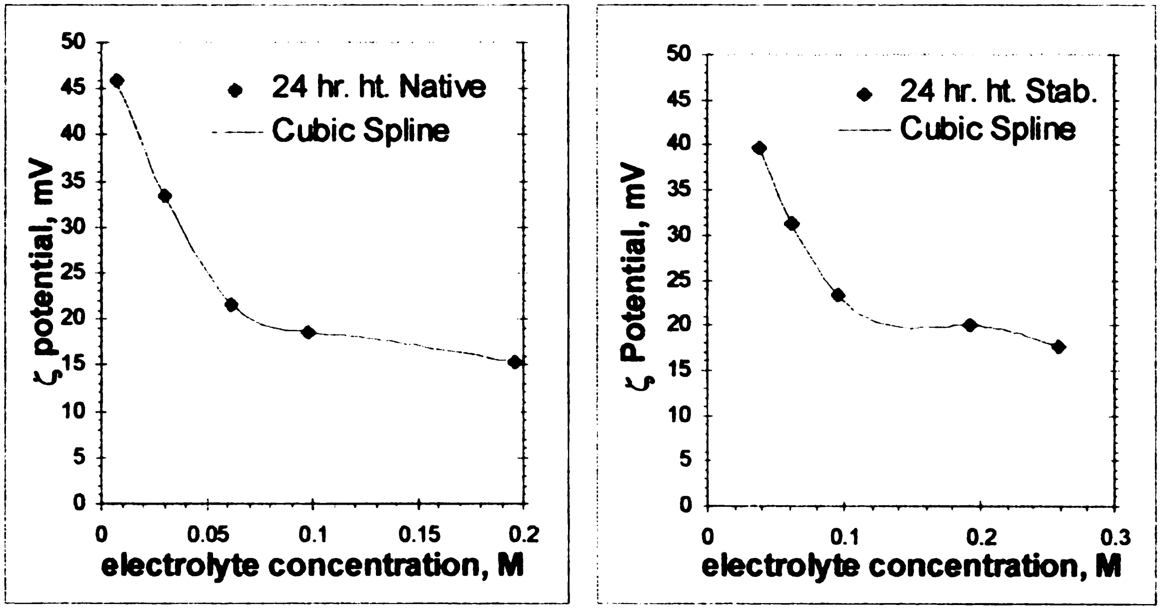
$$\sigma = A\sqrt{c}\sinh\frac{e\zeta}{2kT} \tag{14}$$

Assuming that the surface charge (σ) is constant, it is obvious from Eq. (14) that the ζ potential must decrease as the electrolyte concentration (c) increases. The trend in the mobility data is consistent with that reported by other researchers (Seebergh and Berg, 1995; Ofoli, 1994).



(a) Native

(b) Stabilized



(c) 24 hour heat treated native

(d) 24 hour heat treated stabilized

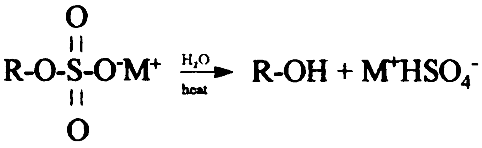
Figure 5-2: ζ potential for polystyrene particles.

The Lazer Zee only gives an average zeta potential, and is not capable of resolving the distribution of zeta potentials for the dispersion. Since this distribution is essential in our theoretical calculations, we have assumed an average standard deviation in the zeta potential of 12% for native unstabilized particles, and a 15% for heat treated particles, based on data from Ofoli (1994). In the absence of additional data, the same values were used in the theoretical calculations for stabilized particles, although Ofoli (1994) did not use these in his work.

A maximum was observed in the electrophoretic mobility profiles at very low electrolyte concentrations for the native and the native heat treated particles. There were no maxima in the profiles of either of the stabilized particles. The fact that a maximum was not observed for the stabilized particles was most likely due to the fact that readings were not taken at a low enough electrolyte concentration. The observed maxima occurred well below the range of electrolyte concentrations required for the theoretical stability ratio calculations in this study, therefore, it will not be a factor in any comparisons between theory and experiment.

The ζ potentials for the four cases studied are presented in Figure 5-3. Stabilization increases the ζ potential (Figure 5-3 a and b), which is to be expected, and is consistent with the assumption that the hydrophobic tail of the surfactant adsorbs onto uncharged regions of the colloid (Kayes, 1976; Kandori, et. al., 1989). The hydrophilic head of the surfactant would then extend from the surface, adding steric as well as electrostatic stabilization, thus increasing the magnitude of the ζ potential. These observations are consistent with other electrokinetic studies of anionic surfactants added to polymer latex particles (Litton and Olsen, 1994; Kandori, et al, 1989; and Kayes, 1976).

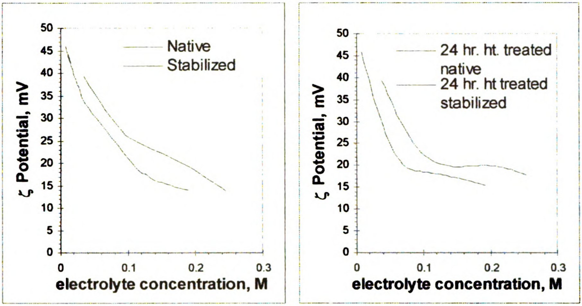
Heat treating the colloidal dispersions results in a lowering of the ζ potential, as can be seen in Figure 5-3 c and d. This is consistent with what has been reported by other researchers (Rosen and Saville, 1990; Seebergh and Berg, 1995; Elimelech and O'Melia, 1990). Seebergh and Berg (1995) have shown that the surface charge density on polystyrene particles decreases upon heat treatment, most likely due to hydrolysis of the sulfate groups on the polystyrene particle surface by the following reaction:



$$\text{R-O-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}\text{-O}^{-}\text{M}^{+} \xrightarrow[\text{heat}]{H_2O} \text{R-OH} + \text{M}^{+}\text{HSO}_4^{-}$$

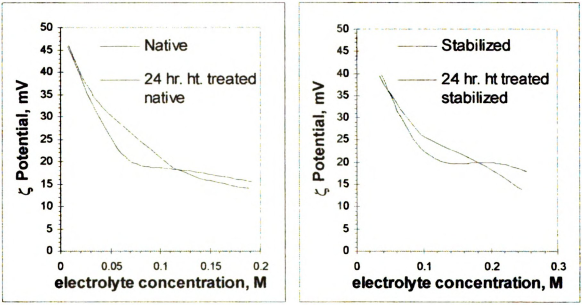
They reported that half of the sulfate functional groups were converted to uncharged hydroxyl groups after 12 hours of heat treatment.

The reason for the crossover in the zeta potential profiles of native and heat treated particles Figure 5-3 c and d is not clear. Fortunately, the crossover points occur well below the theoretical critical coagulation concentration (ccc), as will be shown later. Therefore, they do not affect the comparison of theoretical and experimental stability ratios in the slow flocculation regime.



(a) Native and Stabilized

(b) 24 hour heat treated native and 24 hour heat treated stabilized



(c) native and
24 hour heat treated native

(d) stabilized and
24 hour heat treated stabilized

Figure 5-3: ζ potential trend

5.4 CRITICAL COAGULATION CONCENTRATION

The experimental critical coagulation concentration (ccc) for the native particles was found to be 0.15M KCl, which is in agreement with results reported by other researchers (see Ofoli 1994, for example). No data were collected beyond an electrolyte concentration of 0.2 M KCl for the unstabilized surface annealed particles because it was not apparent that this value would be less than the ccc. Since the focus of this research is on the slow flocculation regime, not having data beyond the ccc should not present any particular difficulties.

The critical coagulation concentration for the stabilized particles, both native and heat treated, was calculated as 0.4M KCl. The increase in ccc relative to the value for the native particles appears to be a logical trend. Assuming the surfactant alkyl chains adhere to the polymer with the ionic head sticking out into solution, this would add electrostatic stability to the dispersion. Therefore, a higher concentration of electrolyte would be required to fully depress the electrical double layer.

5.5 THE STABILITY RATIO

Figure 5-4 and Figure 5-5 are typical scattering intensity profiles for slow and rapid flocculation, respectively. The sharp rise in intensity after one minute is due to the fact that data collection was initiated immediately upon adding the colloid to the electrolyte solution as described earlier; however, the shutter to the photomultiplier tube was opened only after the dispersion had been completely mixed and the cuvette had been placed into the sample holder. The slope *(dI/dt)* and intercept *(I_o)* of each scan were obtained from a regression of the initial part of the data. Using these values, the experimental stability ratio was calculated from Eq. (6).

The experimental stability ratios were lower than those reported in the literature. Ofoli (1994), for example reported a value of about 1000 for 0.301 μm polystyrene latexes at electrolyte concentrations of 0.01M NaCl. Additionally, Kihara (1994) reported a stability ratio of about 1000 at 0.001M KNO_3 for 0.26 μm polystyrene particles, which is also significantly higher than the ratio measured in this work. These differences are most likely due to problems with establishing a unique slope for scans at very low salt concentrations, as discussed later.

The theoretical stability ratios were calculated using Eqs. (9) and (10), incorporating the zeta potentials determined from electrophoretic mobility measurements, and the assumed standard deviation, using a MathCad program developed by Ofoli (1994). The theoretical stability ratio shows a much higher sensitivity to electrolyte concentration than the experimental data, which is consistent with the trends reported in other flocculation and deposition experiments (see Ofoli 1994, for example).

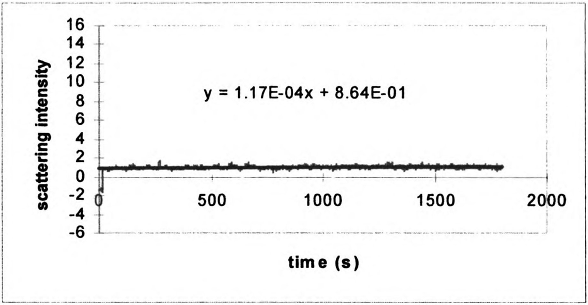


Figure 5-4: Typical SALS scan during slow flocculation

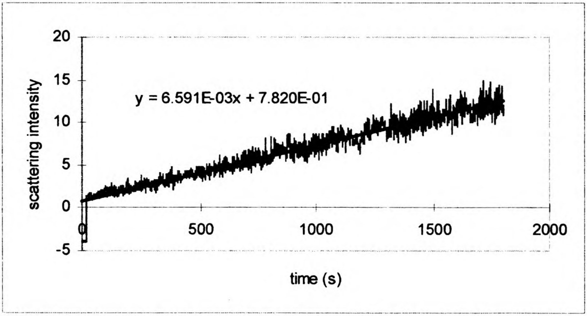


Figure 5-5: Typical SALS scan during rapid flocculation

5.5.1 EFFECT OF THE EXTENT OF HEAT TREATMENT

These results have confirmed that the overall effect of heat treatment is to reduce the stability of the given colloidal dispersion. It is generally accepted that heat treatment also anneals the surface, making the particle smoother by collapsing any polymeric hairs that may have extended into the solution. It has also been shown that the surface charge density on polystyrene particles decreases upon heat treatment, most likely due to hydrolysis of the sulfate groups on the polystyrene particle surface.

To demonstrate the effect of the extent of heat treatment on both experimental and theoretical calculations, the stability ratios at the lowest electrolyte concentration measured are plotted as a function of the duration of heat treatment for both native and heat treated particles (Figure 5-6). The percent change in stability ratio with respect to heating time is also tabulated in Table 5-1.

Table 5-1: Relative reduction in stability ratio upon heating, %

	6 hours of heating	12 hours of heating	24 hours of heating
native	89	-2	2
stabilized	70	39	76

The change in the stability ratio is very substantial after 6 hours of heating for both the native and stabilized particles. After 6 hours, the stability ratio of the native particles shows no further reduction in stability, while the stability ratio of the stabilized particles shows only limited further loss in stability.

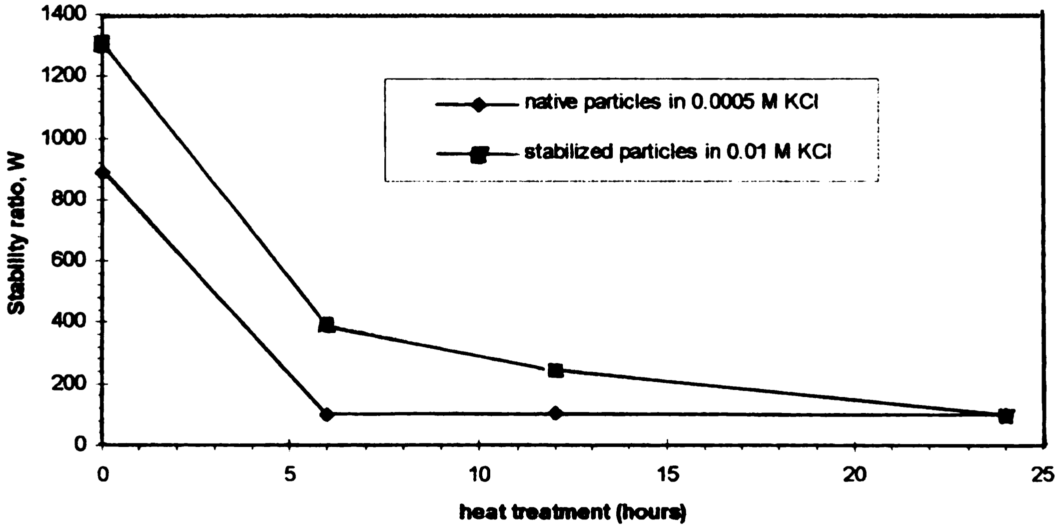
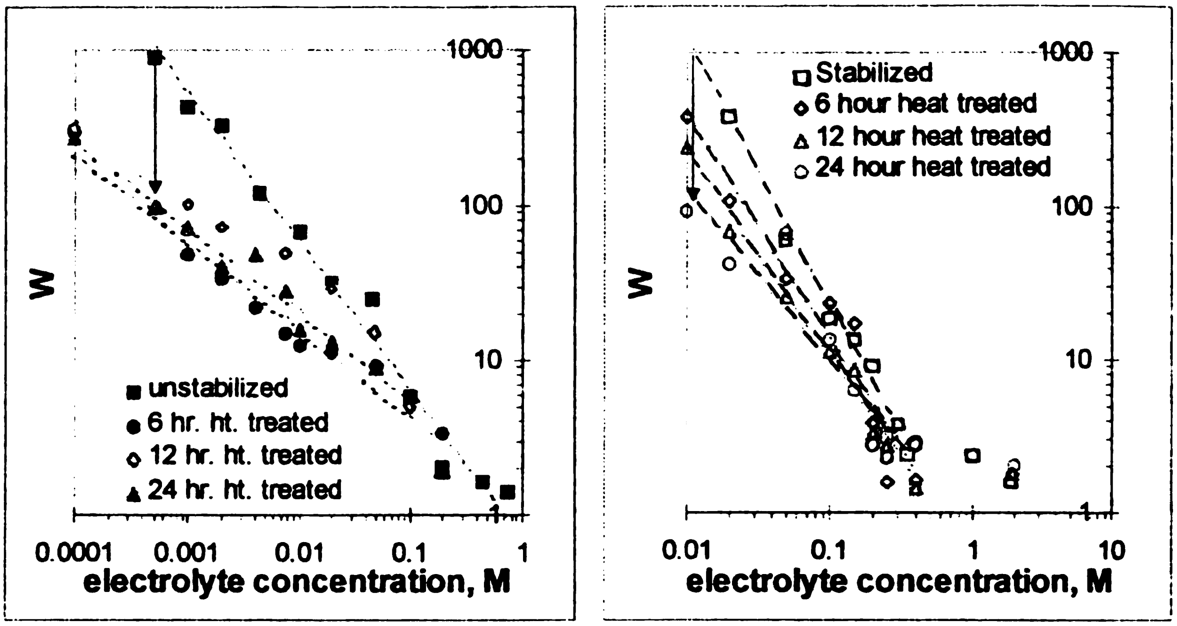


Figure 5-6: Effect of extent of heat treatment on dispersion stability

Clearly, there is a competition between the destabilization effect caused by heat treatment and the re-stabilizing influence of adding surfactants to the dispersion. For native particles, heat treatment destabilizes the particles completely after 6 hours, and further heating has little or no effect on reducing the stability ratio. When SDS is added after heating, some degree of stability is regained by the dispersions. But even adding SDS has its limit, because after 24 hours of heating, the stability ratio is the same for both the native and stabilized particles.

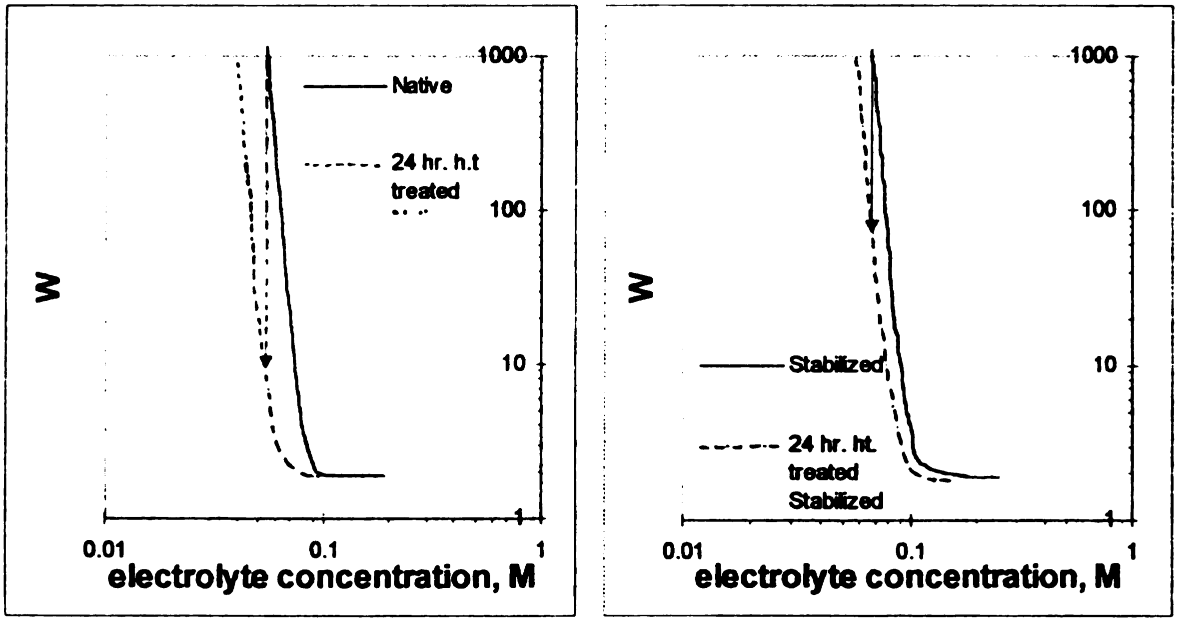
The same information can be seen in a different way by examining Figure 5-7. Here both the experimental and theoretical stability ratios have been plotted for comparison. The arrows are meant to aid in comparison of stability ratios at a given electrolyte concentration. A decrease in stability is observed for the native particles in both the experimental (Figure 5-7a) and theoretical (Figure 5-7c) curves. It appears that the decrease in the theoretical stability ratio at a given point with heat treatment is primarily due to a decrease in the ccc of the dispersion (from 0.82 to 0.057). The decrease is most likely attributable to a reduction of the steric barrier to coagulation following surface annealment. The fact that this is not observable in our experimental study is probably because enough data points were not collected around the ccc, as explained earlier.

The same decrease in stability with heat treatment is observed in the both the experimental (Figure 5-7b) and theoretical (Figure 5-7d) stability ratios for stabilized particles. The



(a) Experimental Native

(b) Experimental Stabilized



(c) Theoretical Native

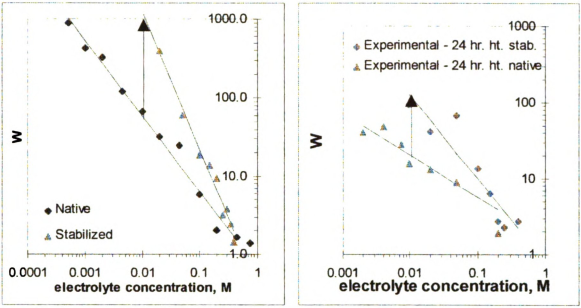
(d) Theoretical Stabilized

Figure 5-7: Effect of Heat Treatment on Polystyrene particles change in stability ratio is not as drastic as that predicted for the native heat treated particles, however (from 0.096 to 0.089). Once again this is probably due to the competition between heat treatment and stabilization. Once the particles are heat treated, it is assumed that all of the polymeric hairs that contributed to the steric stabilization have collapsed to the surface. The addition of the surfactant, however, reintroduces some steric interactions because of the hydrophillic head groups sticking out from the surface. Thus, the overall effect of the heat treatment is reduced, as is reflected in the ccc.

5.5.2 EFFECT OF STABILIZATION WITH SODIUM DODECYL SULFATE

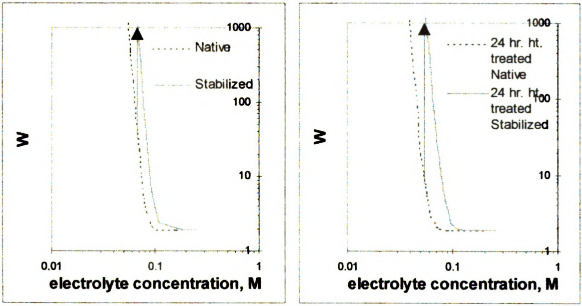
The consensus of various researchers is that the addition of a surfactant stabilizes a particle by the adsorption of the hydrophobic tail onto the surface of the colloid, adding both steric and electrostatic stabilization to the dispersion. To examine the effects of adding a surfactant to a colloidal dispersion, the stability ratio of the stabilized particles are compared to their native counterparts in Figure 5-8. Again, the arrows are meant to aid in the comparison of stability ratios at a given electrolyte concentration.

A similar increase in stability upon addition of the surfactant was observed for both the experimental (Figure 5-8 a) and theoretical (Figure 5-8 c) curves. The slight increase in ccc that is apparent in the theoretical stability ratio (from 0.082 to 0.096 M KCl) would not be easy to detect experimentally, particularly in light of not having enough data points in the immediate vicinity of the ccc.



(a) Experimental native

(b) Experimental heat treated



(c) Theoretical native

(d) Theoretical heat treated

Figure 5-8: Effect of Stabilization on polystyrene particles

The same increase in stability upon addition of surfactant is observed in both the native (Figure 5-8 b) and theoretical (Figure 5-8 d) heat treated particles as well. The change in stability of the theoretical stability ratio of the particles is much more drastic than that seen for the experimental ones. The increase is apparently primarily due to a change in the ccc for the particles (from 0.57 to 0.89 M KCl). That this is the largest change in ccc seen for any of the dispersions is explained by thinking about the hypothesized effects of each treatment. The heat annealment of the particles is expected to collapse the hairy layer of the particle thereby reducing the ccc. On the other hand, the stabilization of the particles is expected to add stability to the dispersion because of the steric and electrostatic interactions between stabilized particles. The combination of these two effects should result in the largest difference in ccc, which is observed in the theoretical measurements.

5.6 DIFFICULTY IN CHARACTERIZING SLOPES OF SCATTERING INTENSITY PROFILES

It is difficult to obtain a unique value for the stability ratio at small electrolyte concentrations because the scattering intensity scans are very flat. It is obvious from the scan of the scattering intensity with time measurements that there is some increase in intensity with respect to time. Determining exactly what this increase is, however, is complicated by the fact that the slopes are very small. Additionally, due to the nature of the samples and the detection system used, there is always some scatter and drift in the data.

Take, for example, the determination of the experimental stability ratio for the native particles tabulated in Table 5-2. At high electrolyte concentrations (>0.02 M KCl) the deviation in the stability ratio is small, and so it is easy to calculate a reliable stability ratio.

Table 5-2: Typical deviation in experimental stability ratio

electrolyte concentration	Experimental stability ratio				
	50-1000	50-2000	50-3000	50-3600	actual
0.0005	129.0	175.0	101.0	158.0	889.3
0.001	70.0	601.0	296.0	7912.0	432.7
0.002	57.0	113.0	95.0	101.3	323.6
0.0045	194.1	81.1	97.3	82.8	118.9
0.01	24.4	66.9	100.3	82.0	66.8
0.02	121.8	131.8	119.8	142.3	32.0
0.045	12.7	22.4	47.9	61.2	24.9
0.1			27.0	44.8	5.8
0.2	4.2	3.1	2.9	2.6	2.0
0.45	2.2	2.0	1.7	1.5	1.6
0.75	1.8	1.5	1.4	1.4	1.4
slope	-0.68	-0.61	-0.85	-0.77	-0.93

However, at smaller electrolyte concentrations, the deviations can become large, depending on what segment of the data is used to obtain a regression line.

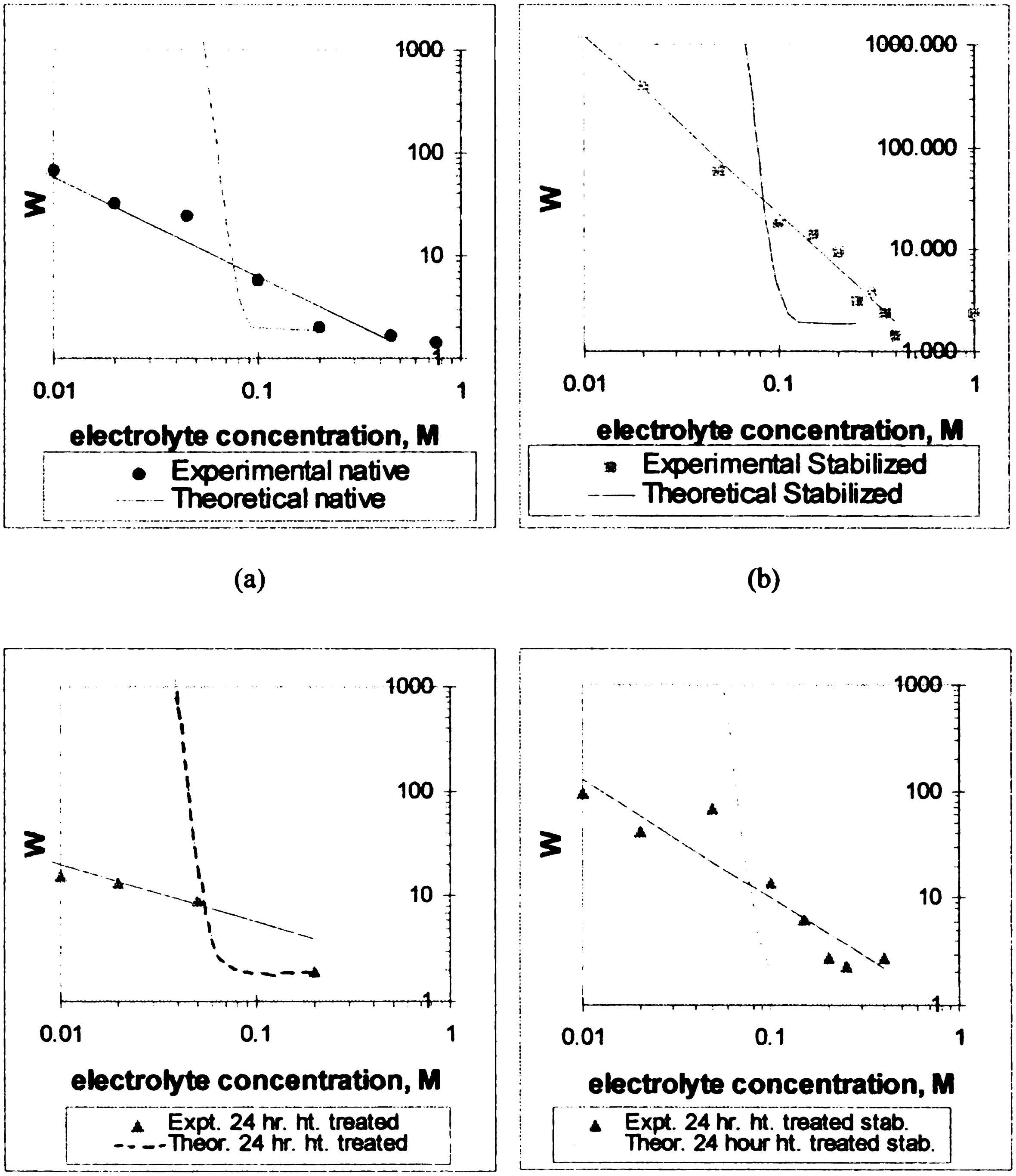
Table 5-2 shows an example of the variation that is possible in the determination of the experimental stability ratio. This is a slightly exaggerated example because no care was taken in selecting the "smooth" regions of the intensity profiles. However, it does illustrate the point that variation exists depending on what region of the intensity profiles are used. For example, at 0.001M KCl, using the intensity measurements from 50-1000 scans gives a stability ratio of 70;. An increase of two orders of magnitude is observed, however, if the data from 50-3000 scans is used. The slope of the curves is affected too. Depending on the area of the intensity measurements used, the slope varies from -0.6 to -0.9.

5.7 COMPARISON OF THEORETICAL AND EXPERIMENTAL STABILITY RATIOS

The theoretical and experimental stability ratio are best compared by looking at the slope of a line drawn through the stability ratio in the slow flocculation regime. To aid in this comparison, shows the slope of all of the curves as well as a ratio (E/T) between experimental (E) and theoretical (T) slopes. The higher this ratio, the closer the agreement between experiment and theory. A value of unity would indicate that the experimental and theoretical curve are in complete agreement. Based on this value, the order of agreement between experiment and theory is as follows: stabilized (Figure 5-9b), 24 hour stabilized (Figure 5-9d), native (Figure 5-9a) and 24 hour heated stabilized (Figure 5-9b).

Table 5-3. Comparison between theoretical and experimental stability ratios

	Theoretical (T)	Experimental (E)	Ratio (E/T)
Stabilized	-15.41	-1.77	.115
24 hour heat treated stabilized	-12.18	-1.15	.094
Native	-14.09	-0.96	.068
24 hour heat treated native	-12.87	-0.549	.043



(a) (b)

(c) (d)

Figure 5-9: Stability Ratios of Native and Stabilized Particles.

The improvement between theory and experiment upon the addition of a surfactant is not surprising because it has been reported in the literature that such an improvement occurs in deposition studies (Kayes, Litton and Olsen, 1995). However, the reduction in improvement was a little startling. The ratio E/T decreased with heat treating from 0.115 to 0.094 for the stabilized particles and 0.068 to 0.043 for native particles. Many studies exist that point out the improvement upon heat treating (Rosen and Saville, 1991; Ofoli, 1994; Elimelech and O'Melia, 1990).

To see why this might be so, a closer look at the data is warranted (Table 5-4). For comparisons between theory and experiment, it is wise to use the same range of concentrations. A look at the data, however, shows that data was not collected over the same concentrations ranges to result in the same comparison. I, therefore, had to resort to comparing over the same range of stability ratio, which might not be as accurate.

Another possibility for the disagreement with other researchers lies in the analysis of the experimental stability ratio. To aid in a direct comparison between curves, all electrolyte concentrations were normalized by their individual ccc in Figure 5-10. It is interesting to note that the theoretical (T) stability ratios are basically the same for all data represented. The only variation comes from the experimental stability ratio. Therefore, any error in calculating the experimental stability ratio would detract from the improvement between theory and experiment.

Table 5-4: Unstabilized particles

Unstabilized native			
	Experimental		Theoretical
conc.	W	regr. W	W
0.0005	889.3	1034.1	
0.0010	432.7	531.2	
0.0020	323.6	272.9	
0.0045	118.9	125.2	
0.010	66.8	58.1	
0.020	32.0	29.9	
0.030			2.61E+07
0.045	24.9	13.7	
0.050			4811.0
0.052			2601.0
0.053			1645.0
0.055			951.7
0.057			547.8
0.058			438.2
0.059			321.1
0.061			191.4
0.063			118.1
0.066			51.0
0.068			32.8
0.070			21.9
0.075			8.2
0.081			3.9
0.085			2.8
0.093			2.0
0.100	5.8	6.4	
0.103			1.9
0.189			1.9
0.200	2.0	3.3	
0.450	1.6	1.5	
0.750	1.4	0.9	

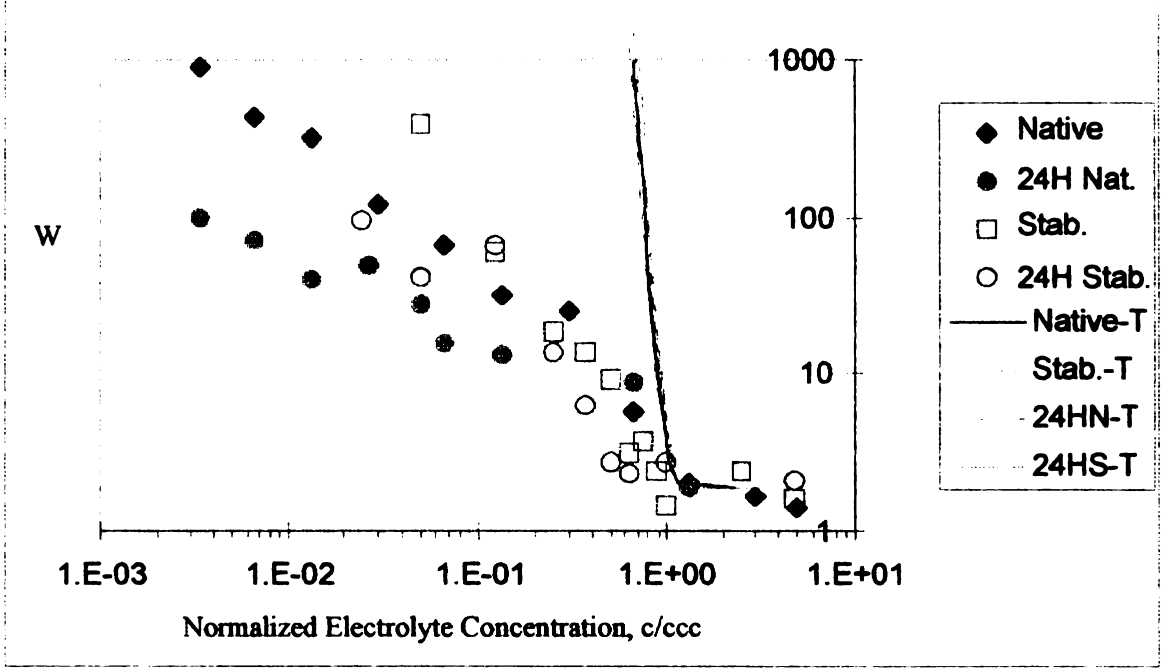


Figure 5-10: Normalized stability ratio

6. SUMMARY AND CONCLUSIONS

6.1 SUMMARY

This purpose of this work was twofold: to examine the effect of masking surface charge heterogeneities with a surfactant on the discrepancy between theoretical and experimental stability ratios and the effect of heat treating the surface of the colloid on that same disparity. Sulfate stabilized, surfactant free, polystyrene latex particles were used as a model colloid since they are monodisperse with well characterized surface functional groups.

Heat treatment of the particles has been shown to improve the agreement between experiment and theory (Rosen and Saville, 1990; Ofoli, 1994). It was achieved in this study by heating a 0.05 vol% fraction of the particles for 6, 12 and 24 hour at 120°C followed by a slow cooling. The resulting dispersions were then tested by low angle light scattering and electrophoresis to get an experimental and theoretical stability ratio.

Surface charge heterogeneities on the colloid have been shown to affect the theoretical stability ratio (Kayes, 1990). Litton and Olsen (1995) showed that adding a surfactant to a polystyrene dispersion reduces the discrepancy between theory and experiment. Therefore, a surfactant was added to some of the dispersions to achieve a final concentration of $1\text{x}10^{-5}$ M SDS. Surfactant was added to the heat treated dispersions only after the heat treatment regime was completed. These samples were also tested by light scattering and electrophoresis to obtain an experimental and theoretical stability ratio.

The light scattering setup used was that described by Prieve and Young (1991) with the intensity of the scattered light measured at 1.6°. Electrophoresis was completed on a Penn Kem Model 501 Lazer Zee instrument. Zeta potential was obtained from the electrophoretic mobility using the Smoluchowski equation.

The experimental stability ratio was determined by obtaining a light scattering intensity vs. time plot from the small angle light scattering apparatus. A regression line is then drawn through data to obtain the slope and intercept of the data. These values, as well as the temperature and the initial singlet concentration of the dispersion, are then substituted into equation 6. The theoretical stability ratio was obtained by using the equation proposed by Prieve and Lin (1982) which takes into account variations in size and surface charge. The Hammaker constant was obtained from Lifshitz theory using no adjustable parameters. The standard deviation was also incorporated into the calculations using a MathCad program designed by Ofoli.

The data show that there is a decrease in overall stability upon heat treatment while the addition of a surfactant serves to increase the stability of a system which is in agreement with data reported by other researchers. However, this study did not show the increase in agreement between theory and experiment with heat treatment that has been reported by so many other researchers.

6.2 CONCLUSIONS

Heat annealment of the particles did not improve the agreement between theory and experimental values. However, the experimental stability ratios of the stabilized colloidal dispersion were in better agreement with theory. The decrease in stability ratio seen upon heat treatment and the increase observed upon stabilization of the dispersions were in line with those reported in the literature.

It was surprising, however, that heat annealment did not improve the discrepancy between theory and experiment as has been reported by other researchers. A possible explanation for this is that the distribution in zeta potentials of the polystyrene particles had a higher standard deviation than the 15% assumed. Ofoli (1994) showed that taking the deviation of zeta potential into account greatly reduces the slope of the theoretical stability ratio curve. Therefore, if the standard deviation in zeta potential of the dispersions used was larger than 15%, the slope of the theoretical heat treated native stability ratio curve would be lower than that reported.

In a similar vein, if the effect of stabilizing the particles is to mask the surface charge heterogeneities, then the deviation for the stabilized particles would be lower than that for the native particles. This would increase the slope of the theoretical stability ratio curve for the stabilized particles, thereby decreasing the agreement with experiment. Further studies should be done using an electrophoresis instrument capable of measuring the deviation in zeta potential so that a careful analysis of the standard deviation can done.

7. SUGGESTIONS FOR FUTURE RESEARCH

Exploring the effect of stabilization in more detail would be enlightening. If the reduction in discrepancy seen in this study is real, then the possibility exists for even greater reduction at higher SDS concentrations. However, further studies should deal with polystyrene particles stabilized with sulfonate groups as they do no hydrolyze on heat treating. SDS is also subject to hydrolysis, therefore, another surfactant such as Cetyl Triammonium Bromide or sodium dodecyl sulfonate should be used.

APPENDICES

APPENDIX A - STOCK SOLUTION CALCULATIONS

1. APPENDIX A: STOCK SOLUTION CALCULATIONS

Table 8-1: Concentration calculator for stock colloid

Stock Colloid				
Original concentration	***concentration units***	***Final Volume (ml)***	***concentration desired***	***ml to add***
8.8	%	250	0.05	1.42E+00
5.87E+12	particles/mL	250	3.33E+10	1.42E+00

Table 8-2: Calculator for stock SDS solution

	SDS Solution			
MW	***units***	***inal Volume (m***	***oncentration desire***	***g to add***
288.38	g/mol	50	2.219E-04	0.0032

Table 8-3: Calculator for high molarity KCl stock solution

KCl calculator

Desired Molarity: 3.00
mL of solution: 100.00

calculated g KCL: 22.365

Actual Molarity: 3.00
mL of solution: 100.00

actual g KCL: 22.3554

Table 8-4: Calculator for low molarity KCl stock solution

KCl calculator	
Desired Molarity:	0.15
mL of solution:	100.00
calculated g KCL:	1.11825
Actual Molarity:	0.1507
mL of solution:	100.00
actual g KCL:	1.1234

Table 8-5: Worksheet used for typical colloidal dispersions

The unstabilized particles were prepared directly from stock colloid				
Original conc.	***units***	***Final Vol.(ml)***	***conc. desired***	***ml to add***
3.3E+10	particles/mL	50	2.34E+09	3.51
Sample as run				
Original conc.	***units***	***Final Vol.(ml)***	***conc. desired***	***ml to add***
2.3E+09	particles/mL	3	7.8E+08	1.0
Concentration Calculator for final samples				
	Electrolyte concentration		0.1507	M
mLKCl	**mL water**	**ml particles**	**total volume**	**final conc.**
0.002	1.998	1.000	3.000	1.00E-04
0.010	1.990	1.000	3.000	5.00E-04
0.020	1.980	1.000	3.000	1.00E-03
0.050	1.950	1.000	3.000	2.50E-03
0.100	1.900	1.000	3.000	5.00E-03
0.149	1.851	1.000	3.000	7.50E-03
0.199	1.801	1.000	3.000	1.00E-02
0.249	1.751	1.000	3.000	1.25E-02
0.299	1.701	1.000	3.000	1.50E-02
0.348	1.652	1.000	3.000	1.75E-02
0.995	1.005	1.000	3.000	5.00E-02
2.000	0.000	1.000	3.000	1.00E-01
0.817	1.183	1.000	3.000	4.50E-01
1.362	0.638	1.000	3.000	7.50E-01

APPENDIX B

9. APPENDIX B: LABVIEW

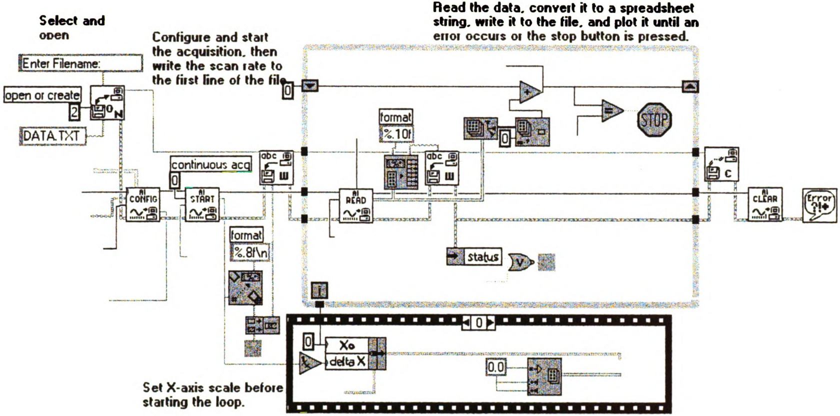


Figure 9-1: Labview data acquisition program

APPENDIX C

1. APPENDIX C: RESULTS

Table 10-1: Stability ratio data sheet for native colloidal dispersion

Unstabilized native			
	Experimental		Theoretical
conc.	W	regr. W	W
0.0005	889.3	1034.1	
0.0010	432.7	531.2	
0.0020	323.6	272.9	
0.0045	118.9	125.2	
0.010	66.8	58.1	
0.020	32.0	29.9	
0.030			2.61E+07
0.045	24.9	13.7	
0.050			4811.0
0.052			2601.0
0.053			1645.0
0.055			951.7
0.057			547.8
0.058			438.2
0.059			321.1
0.061			191.4
0.063			118.1
0.066			51.0
0.068			32.8
0.070			21.9
0.075			8.2
0.081			3.9
0.085			2.8
0.093			2.0
0.100	5.8	6.4	
0.103			1.9
0.189			1.9
0.200	2.0	3.3	
0.450	1.6	1.5	
0.750	1.4	0.9	

Table 10-2: Stability Ratio data sheet for stabilized colloidal dispersion

Stabilized			
	Experimental		Theoretical
conc.	W	regr. W	W
0.010	1310.9	1230.7	
0.020	385.6	367.6	
0.050	60.3	74.4	
0.063			5097.0
0.066			2052.0
0.068			1103.0
0.069			828.9
0.073			310.0
0.075			188.2
0.079			68.1
0.081			43.7
0.086			19.6
0.088			13.6
0.092			7.7
0.096			5.2
0.099			4.0
0.100	18.5	22.2	
0.110			2.3
0.125			2.0
0.150	13.8	11.0	
0.187			1.9
0.200	9.3	6.6	
0.249			1.9
0.25	3.1	4.5	
0.3	3.7	3.3	
0.35	2.4	2.5	
0.4	1.4	2.0	
1	2.4	0.4	
1.95	1.6	0.1	

Table 10-3: Stability ratio data for 24 hour heat treated native dispersion

24 heat treated			
	Experimental		Theoretical
conc.	W	regr. W	W
0.0001	269.0	255.6	
0.0005	98.1	105.7	
0.0010	71.2	72.2	
0.0020	40.6	49.4	
0.0040	48.3	33.8	
0.0075	28.0	23.9	
0.010	15.7	20.4	
0.020	13.1	14.0	
0.031			39170.0
0.033			8920.0
0.038			1509.0
0.040			681.7
0.042			314.4
0.044			153.1
0.046			79.0
0.047			46.1
0.049			22.9
0.050	8.9	8.4	
0.051			16.1
0.055			7.1
0.057			5.2
0.059			4.0
0.062			2.8
0.076			1.9
0.098			1.9
0.196			1.9
0.2	1.9	3.9	

Table 10-4: Stability ratio data for 24 hour heat treated stabilized colloidal dispersion

24 hour heat treated			
	Experimental		Theoretical
conc.	W	regr. W	W
0.010	94.380	127.823	
0.020	41.970	59.456	
0.050	66.822	21.615	9236.00
0.055			1821.00
0.057			1177.00
0.058			756.56
0.060			439.90
0.061			361.01
0.065			124.29
0.068			63.55
0.071			34.44
0.075			17.02
0.080			8.28
0.085			4.79
0.095			2.49
0.100	13.648	10.054	2.20
0.125			1.89
0.150	6.271	6.425	
0.193			1.89
0.200	2.755	4.677	
0.250	2.299	3.655	
0.259			1.89
0.400	2.750	2.175	
1.980	2.057	0.372	

Table 10-5: Stability ratio data for 6 and 12 hour heat treated native and stabilized colloidal dispersions

6 hour heat treated		
conc.	W	regr. W
0.0001	301.704	215.787
0.0005	100.127	86.766
0.0010	48.718	58.605
0.0020	33.669	39.585
0.0040	21.819	26.737
0.0075	14.873	18.732
0.0100	12.300	15.917
0.0200	11.398	10.751
0.0500	9.238	6.400
0.2000	3.340	2.920

(a) 6 hour heat treated native

12 hour heat treated		
conc.	W	regr. W
0.0001	313.261	319.933
0.0005	102.398	139.389
0.0010	102.050	97.460
0.0020	72.126	68.144
0.0040	43.707	47.646
0.0075	49.095	34.442
0.0200	29.744	20.758
0.0500	15.460	12.935
0.1005	5.055	9.023
0.2000	1.780	6.324

(b) 12 hour heat treated native

6 hour heat treated		
conc.	W	regr. W
0.01	391.856	398.645
0.02	110.385	144.093
0.05	33.812	37.534
0.1	23.892	13.567
0.15	17.307	7.481
0.2	3.910	4.904
0.25	1.604	3.534
0.4	1.638	1.773
1.95	1.783	0.173

(c) 6 hour heat treated stabilized

12 hour heat treated		
conc.	W	regr. W
0.01	240.297	221.428
0.02	69.994	87.569
0.05	26.115	25.690
0.1	11.265	10.160
0.15	8.492	5.905
0.2	3.314	4.018
0.25	2.792	2.981
0.4	1.463	1.589
1.95	1.765	0.191

(d) 12 hour heat treated stabilized

Table 10-6: Zeta Potentials

Native	
KCl conc.	ζ potential
0.007656	46
0.02979	35.60
0.05769	28.90
0.09303	21.80
0.18882	14.10

Stabilized	
KCl conc.	ζ potential
0.03351	39.4
0.06327	32.30
0.09582	26.00
0.18696	19.60
0.24927	13.60

24 hour native	
KCl conc.	ζ potential
0.007396	45.8
0.03072	33.30
0.06234	21.50
0.09768	18.60
0.19626	15.30

24 hour stabilized	
KCl conc.	ζ potential
0.03816	39.6
0.06141	31.30
0.09489	23.30
0.19254	20.00
0.25857	17.70

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