

Coagulation of a Carboxylated Latex with Polyethylenimine

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Synopsis

The coagulation of a carboxylated styrene/butadiene latex, using polyethylenimine (PEI), was investigated using a light transmission technique and microelectrophoresis. Two charge-reversal regions were observed as the polyelectrolyte concentration was increased from 10^{-4} to 1 wt-%. During each of these regions, the latex was destabilized and then restabilized. The addition of HCl to the PEI solution can eliminate the second coagulation region completely while the first region is hardly affected. The second region was found to be dependent on the degree of protonation of the polyethylenimine and occurred in a pH range where the latex surface charge increases drastically as a function of increasing pH due to the ionization of surface carboxyl groups.

INTRODUCTION

The destabilization of colloids by polymeric flocculants has been widely studied. The organic polyelectrolytes can be categorized into nonionic, anionic, and cationic flocculants. Other coagulating agents used involve inorganic polymers such as hydrolyzed polymeric forms of aluminum. For instance, the adsorption of hydrolyzed metal ions and their coagulating efficiency have been extensively studied.¹⁻⁹ High molecular weight anionic polymers in the presence of small amounts of electrolyte can also effectively flocculate negative inorganic sols.^{10,11} In this case, flocculation occurs at electrolyte concentrations much smaller than those necessary in the absence of polymers. This type of flocculation, where the sol and polymeric flocculant are of like charge, is usually explained in terms of adsorption of the polymer at the colloid-solution interface and bridging of the polymer chains between particles.

Polystyrene latexes were studied in the presence of cationic flocculants, and particle size effects were demonstrated.¹² The flocculant concentration needed for destabilization increased as a function of surface area. This shows the importance of neutralization of charge in this type of destabilization. LaMer and his co-workers studied the flocculation of silica with several cationic polymers.¹³⁻¹⁵ These authors found that high molecular weight PEI neutralized the charge on the particles quite effectively. High

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polymer concentrations reversed the charge and redispersed the system. It was found, however, that very low molecular weight PEI polymers could not cause restabilization. Ries and Meyers¹⁶ studied the flocculation of silica and polystyrene latex colloids with cationic and anionic polyelectrolytes. They concluded that the cationic agents operated by a twofold mechanism: charge neutralization and bridging. This resulted in a decrease in negative zeta potential and ensuing flocculation. Higher additions of cationic flocculant produced positive zeta potentials and eventual restabilization. These authors showed electron micrographs of flocculated systems and interpreted a fibrous interlinking system between particles which they presented as evidence of bridging.

Gregory¹⁷ studied the flocculation of a carboxylated polystyrene latex with two cationic polyamine flocculants of differing molecular weight. He found the higher molecular weight polymer to flocculate the latex at higher negative particle mobilities (-2.5 microns/sec/V/cm). He attributed this to a greater possibility of bridging between particles. An important observation was that restabilization occurred at quite low positive mobility values. This was attributed to steric repulsion due to large amounts of adsorbed polymer. In this work, the decrease in critical flocculation and stabilization concentrations with decreasing pH was attributed to a lower particle surface charge density. Any enhanced protonation of the polyamines was not discussed.

James and Healy⁹ have shown that multiple charge reversal can occur when an inorganic colloid such as silica is studied as a function of pH at a fixed metal ion concentration. A first reversal is attributed to the point of zero charge (PZC) of the colloidal SiO_2 . A second charge reversal is usually described as being caused by the adsorption of highly charged hydrolyzed metal ion complexes. James and Healy⁹ propose that this reversal region happens at a pH where surface precipitation of the metal hydroxide takes place. A third charge reversal region is due to a coating of metal hydroxide nucleated on the surface and the electrokinetic properties describe a PZC approaching that of the metal hydroxide colloid itself.

The terms "flocculation" and "coagulation" have been used interchangeably in the literature, as shown in this review. Many authors use "flocculation" when the destabilizing agent is polymeric. This usage stems from industry where most polymers sold for this purpose are termed "polymeric flocculants." In this context, the present authors believe that the term "flocculation" should be reserved only for destabilization mechanisms which are caused by the polymeric nature of the agent. This would involve screening of charge and bridging. This would also mean that "flocculation" should be employed for reversible colloidal destabilization where the aggregates can be broken under low shear rates as evidenced in the phenomenon of pseudoplasticity. On the other hand, the term "coagulation" is employed when dealing with electrolytic destabilization of a lyophobic colloid by an inorganic electrolyte or destabilization by a charge neutralization phenomenon. The later was most important in our studies, and

consequently the mechanism of destabilization in the present work will be referred to as a "coagulation" phenomenon.¹⁸

This study will describe the appearance of two charge reversal regions as a carboxylated styrene/butadiene latex is coagulated with increasing concentration of polyethylenimine and the pH is left to drift.

EXPERIMENTAL

Materials

The latex used in these studies had been prepared as a copolymeric composition of styrene (42%), butadiene (56%), and acrylic acid (2%). The latter is usually referred to as the vinyl acid comonomer and contributes extensively to the colloidal stability of the dispersion. The particle size, as measured by light scattering, was 1895 Å in diameter. The latex was filtered through a 60-mesh copper sieve and then through an 80-mesh varnish filter to remove any large-size waste which may have been present. At this point, the latex pH was 3.5 and the concentration of the dispersion was 50.6% solids. A 0.6% solids dispersion was prepared from this latex by diluting an aliquot with distilled water. When this was diluted to 0.06% solids as a blank for spectrophotometric measurements, the absorbance increased slowly with time, indicating instability of the latex sol. Consequently, a fresh 0.6% latex dispersion was prepared and the pH was adjusted immediately to 8.5 with NH_4OH . This 0.6% dispersion was used as a stock for the coagulation studies reported here.

The coagulating agent used in these studies was PEI-18 (Dow Chemical Company), a polyethylenimine product with a molecular weight (\bar{M}_n) of approximately 1800.

Apparatus and Procedure

The procedure for the coagulation studies was as follows: Two sets of test tubes were prepared. The first set contained 5 ml of 0.12% latex; the second, 5 ml of PEI-18 solution of varying concentrations. These were mixed by pouring the PEI solution into the latex sol, then pouring back and forth between test tubes several times. The final dispersions, containing 0.06% latex, were left standing for a period of 18 hr. A 1-ml aliquot was then withdrawn from the mixture, then diluted to 10 ml. The absorbance was measured using a Beckman DB-G Grating Spectrophotometer at a wavelength of 546 nm. The absorbance did not change after the 18-hr waiting period, except in some cases very near the critical coagulation concentration (c.c.c.) and critical stabilization concentration (c.s.c.), where the coagulation rate was very sensitive.

Electrophoretic mobilities were measured on a Rank Brothers Mark II particle microelectrophoresis apparatus. The measurements were done at the actual concentrations of the coagulation experiments, namely, 0.06% latex solids with varying PEI concentrations. In the latex characteriza-

tion studies, however, the latex concentrations covered a range of 10^{-5} to $10^{-1}\%$ by weight. The highly diluted latexes were made more visible by using a Spectra-Physics Model 134 He/Ne 3 milliwatt laser. This laser is not linearly polarized and gave a wide enough beam for producing good measurements. The more concentrated latexes ($>10^{-3}\%$ solids) are more easily observed with a quartz-iodine lamp. The instrument has facilities for the use of two kinds of cells. A flat cell (rectangular cross section), made of silica, is preferred when the colloid sediments appreciably under gravity and when nonaqueous electrophoresis work is being done. In these studies, a thin-walled cylindrical cell, made of Pyrex, was used. Measurements were checked at the high and low stationary levels. More information as to the calibration of the instrument and further capabilities can be found in the manufacturer's instruction manual written by Smith.¹⁹

Zeta potential and surface charge density calculations were not made since the essential reason for electrokinetic measurements, in this study, was to establish whether restabilization was accompanied by charge reversal.

In a few cases, the latex was diluted in its own serum for electrokinetic studies. Actually, a diluted serum was used. The 55% solids latex was diluted down to 15% with deionized water and 0.2 g CCl_4 per g of latex solids was added to the latex to make the particles denser for centrifugation. The mixture was shaken for 2 hr and the latex centrifuged at 19,000 rpm for 1 hr. The slightly turbid supernatant was carefully withdrawn from the centrifuge tubes with a syringe and then filtered successively through Gelman Metrical GA-9 filters with a pore size of $0.10\ \mu\text{m}$. A second filtration was made through Millipore Pellicon permeable membranes, Type PS. The resulting filtrate was clear to the eye, but gave a Tyndall scattering beam in the laser similar to a $10^{-4}\%$ latex dispersion in water. The original latex was diluted to $10^{-2}\%$ and $3 \times 10^{-2}\%$ in this serum, and the mobilities are shown in Figure 1.

Our initial aim was to study the coagulation domain where c.e.c. and c.s.c. values would be followed as a function of pH. However, one of our first observations was that the pH of the latex-PEI mixtures was very difficult to measure reproducibly and even more difficult to regulate. The difficulty in measuring the pH was found to be due to the PEI. Whenever the pH of a PEI solution (especially a concentrated one) was measured, the pH reading drifted with time. A recheck of the calibration using a buffer was then poor. If the electrodes were allowed to soak in water, the response reverted to the original calibration level. Consequently, during pH measurements, calibration of the electrodes was checked frequently.

RESULTS AND DISCUSSION

The effect of dilution on the electrokinetic properties of the latex is shown in Figure 1. The curve demonstrates how the mobility decreases rapidly when the dispersion is diluted with deionized water from $10^{-1}\%$ to $3 \times$

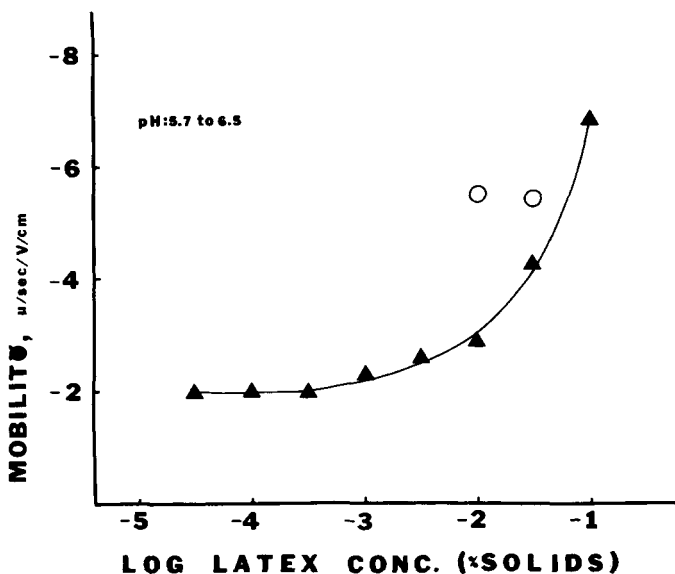


Fig. 1. Electrophoretic mobility as a function of latex concentration: (▲) dilution in distilled water; (○) dilution in latex serum.

$10^{-5}\%$ solids. At $10^{-4}\%$ solids and below, the latex mobility remained constant at -2.0 microns/sec/V/cm. This indicates that the particles must reach a constant surface charge density at high dilution. The decrease in mobility with dilution is, in all probability, caused by the desorption of the emulsifier (sodium lauryl sulfate) as well as some soluble carboxylated oligomeric species. The circles depict mobility values for the same latex diluted in its own serum. In this case, the mobilities are extensively greater and fairly constant. The water diluted samples had pH values in the range of 5.7 to 6.5. The serum- and water-diluted systems give widely different mobilities, as would be expected since the media differ so much in soap and electrolyte content. The serum diluted systems registered a current of app. 470 microamps at an applied potential of 60 volts. Latex systems diluted with water registered less than 1 microamp current.

The effect of comonomeric acid on the electrokinetic properties of the latex dispersion is shown in Figure 2, where the mobility is plotted as a function of pH at a latex concentration of $10^{-3}\%$ solids. The pH was varied by the addition of HCl or NaOH. The increase in mobility with an increase in pH is usually indicative of surface carboxylation.^{20,21} The curve shows that, even at a bulk pH of 11, complete ionization of the carboxyl groups had not occurred. This is evidenced by the fact that the mobility was still increasing at this highest pH investigated. Another important observation is the mobility at low pH (3 to 6). The constant value in this region shows that the pK_a will be quite high. A mobility value of -2.6 microns/sec/V/cm in this low pH range denotes a fairly extensive surface charge density contribution which is due to surface sulfation.

The difficulty in regulating the pH of the PEI-latex mixtures stems from the complicated acid-base behavior of polyethylenimine²² (and polyelectrolytes in general²³). The considerable change in pH over a large concentration range of PEI meant that it was impractical to try to establish the c.c.c. as a function of pH. Therefore, the coagulation of the latex with PEI-18 was studied as a function of the degree of neutralization of PEI (or the equivalents of added HCl per equivalent of amino groups in PEI). Figure 3 shows the measured pH of PEI solutions as a function of dilution

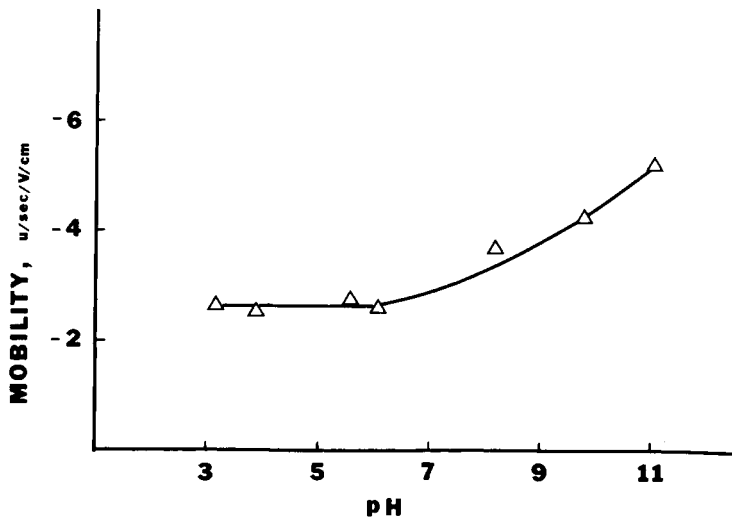


Fig. 2. Electrophoretic mobility as a function of pH at $10^{-3}\%$ solids.

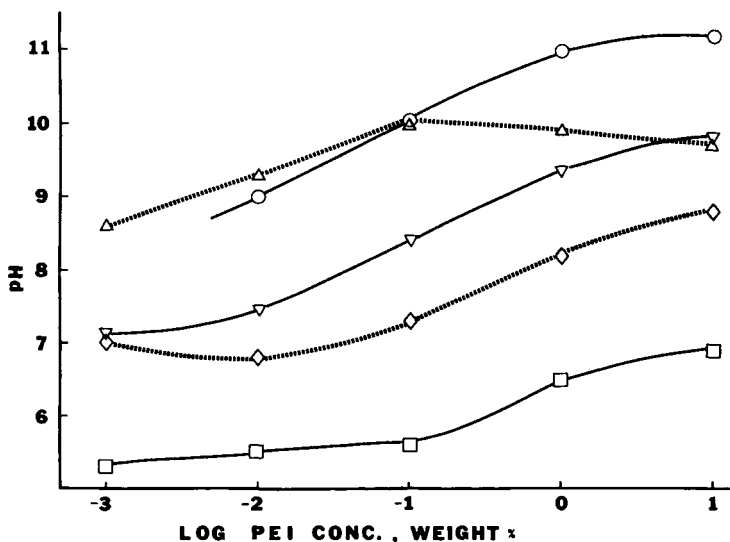


Fig. 3. The pH of PEI solutions as a function of concentration: (O) no added acid; (Δ) $\alpha = 0.035$; (∇) $\alpha = 0.174$; (\diamond) $\alpha = 0.362$; (\square) $\alpha = 0.490$.

at differing degrees of neutralization (α). In all cases, there is an increase in pH as the PEI concentration increases over the range of 10^{-3} to 10% by weight. This pH enhancement is decreased as the degree of neutralization is increased. Hence, the degree of protonation of the PEI molecules is controlled by the addition of HCl. Notice, at 1% PEI, how the pH is decreased from 11 to 6.5 with increasing HCl concentration.

The absorbance curve of the 0.06% latex mixed with varying concentrations of PEI is shown in Figure 4. Also shown are the measured pH values of these mixtures. No HCl was added to the PEI; the degree of protonation of the PEI was due solely to its hydrolysis. Two areas of destabilization were observed. The first one occurred at PEI concentrations between 3×10^{-4} and $10^{-3}\%$. Above the latter concentration, the dispersion was restabilized. The electrophoretic mobility at $5 \times 10^{-5}\%$ PEI was measured at -3.4 microns/sec/V/cm. At $2 \times 10^{-3}\%$ PEI, where restabilization has occurred, the mobility was found to be $+1.8$ microns/sec/V/cm. Hence, the restabilization is due to charge reversal and must occur by a specific adsorption of protonated PEI species onto the latex-solution interface. Such adsorption decreases the surface charge density and the dispersion coagulates when this charge approaches zero. If further adsorption occurs, the charge is reversed and restabilization can take place. This adsorption increases even beyond the first critical stabilization concentration as evidenced by a mobility of $+2.7$ microns/sec/V/cm at $2 \times 10^{-2}\%$ PEI.

The second region of coagulation occurs between $10^{-1}\%$ and 1% PEI. The restabilized sol at 1% PEI yielded an electrophoretic mobility value of -0.4 microns/sec/V/cm. This second charge reversal can be explained by the two following phenomena which can happen at higher pH: (1) the negative surface charge at the latex-solution interface is enhanced due to ionization of the surface carboxyl groups (refer to Fig. 2); (2) deprotonation of polyethylenimine with increasing pH.

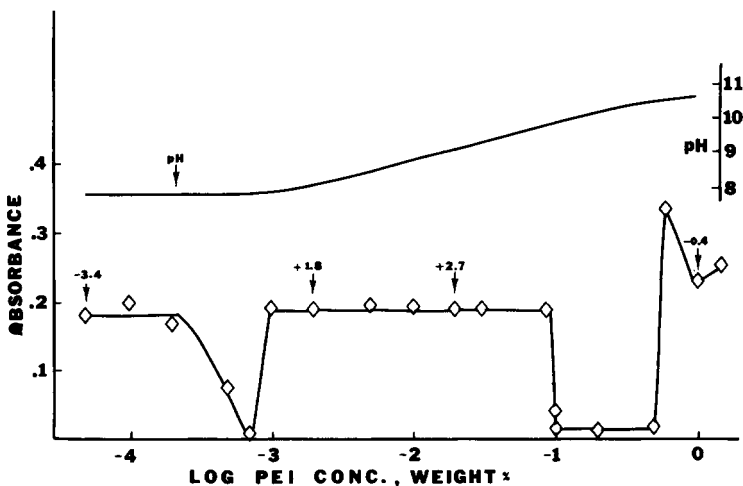


Fig. 4. Absorbance as a function of PEI concentration (no added acid).

Shepherd and Kitchener²² calculated α -values of 0.306 and 0.032 at pH values of 9.0 and 10.5, respectively. During this pH change in Figure 4, the mobility went from +2.7 to -0.4 microns/sec/V/cm. With no PEI present, the mobility would increase from -3.8 to -4.8 microns/sec/V/cm during the same pH change (Figure 2).

Therefore, at higher pH, the charge to be neutralized is greater and the counterion charge on the polymeric adsorbate is decreased, leading to a return of the original negative surface charge and a lack of charge neutralization.

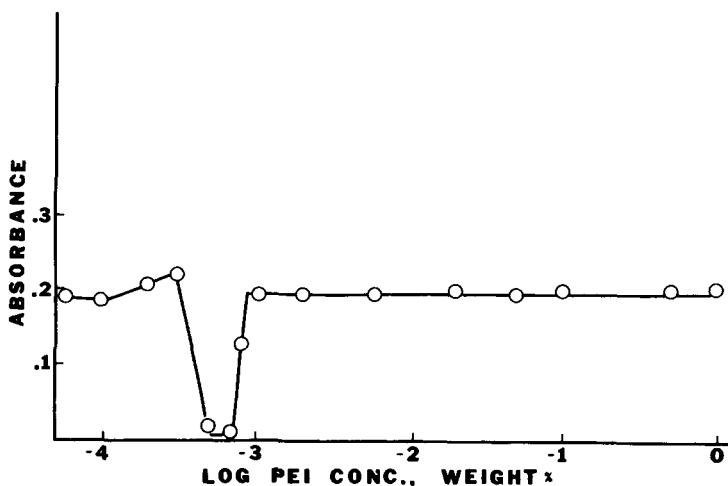


Fig. 5. Absorbance as a function of PEI concentration ($\alpha = 0.007$).

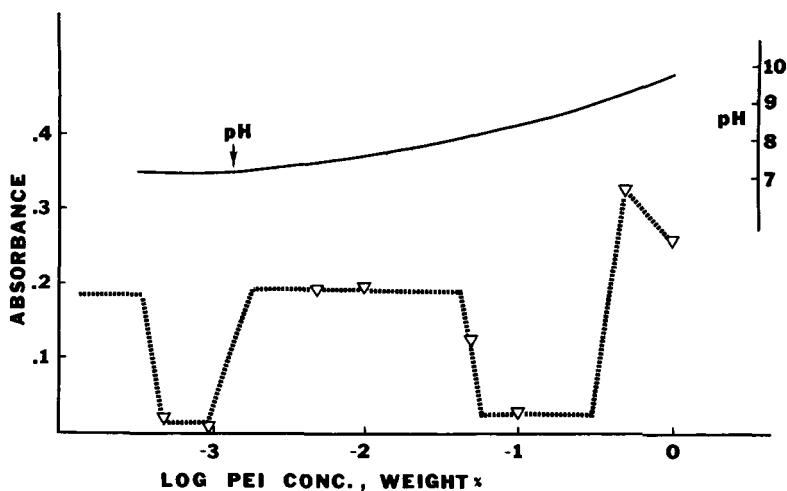


Fig. 6. Absorbance as a function of PEI concentration (0.021 equiv NH_4OH /equiv PEI added).

The effect of PEI protonation was investigated further by adding varying amounts of HCl to the PEI and observing the coagulation phenomena. At a degree of neutralization (α) of 0.0007 the second coagulation region still existed. At α -values of 0.007 and greater, this second coagulation region did not appear. Figure 5 gives a good example of this behavior. The first coagulation region remained essentially the same. Hence, the addition of HCl eliminated the second region of coagulation by increasing the degree of protonation on the PEI and decreasing the negative surface charge density at the latex-solution interface. The opposite effect can be seen in Figure 6, where 0.021 equivalents of NH_4OH per equivalent of PEI have been added. As can be seen by the few points plotted, the second charge reversal region has reappeared.

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