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EVA DOBROVOLNY

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# Table of Contents

**ABSTRACT**

INTRODUCTION .............................................. 1

DISCUSSION AND THEORY .................................. 2

  Serum Replacement ....................................... 2
  Zeta Potential .......................................... 3
  Double Layer Theory .................................... 4
  Repulsion ................................................ 9
  Attraction .............................................. 9
  Born Repulsion ......................................... 10
  The Total Energy of Interaction ...................... 10
  Kinetics of Coagulation ................................ 12
  Turbidity Measurements ................................ 14

PROCEDURE ................................................. 17

  Characterization ....................................... 17
  Standardization ........................................ 17
  Coagulation ............................................ 17

DISCUSSION OF RESULTS .................................. 19

  Characterization ....................................... 19
  Calibration Curves ..................................... 19
  Coagulation Studies ................................... 20

CONCLUSIONS .............................................. 22

REFERENCES .............................................. 23

ACKNOWLEDGMENTS ........................................ 25

DATA AND CALCULATIONS .................................. 26

  1. Zeta Potential ...................................... 26
  2. Cross-sectional Area ................................ 26
  3.a) Surface Potential .................................. 30
  3.b) Rate Constant of Coagulation ...................... 31

TABLES ...................................................... 33-46

FIGURES ..................................................... 47-77

APPENDICES ............................................... 78

  A. Concentration Profile of adsorbable Species ...... i
  B. Debye-Hückel Approximation ........................ iv
  C. Zeta Potential ...................................... vi
  D. Kinetics of Coagulation ............................. vii
Characterization and coagulation studies were conducted using a monodispersed polystyrene latex. Measurements of the Zeta Potential of the latex particles varied inversely with the square root of the suspending electrolyte. Comparison of the scattering cross-sectional areas found experimentally with those predicted from literature tables showed close similarity. The coagulation of a suspension of polystyrene particles was analyzed by measuring its change in absorption with time upon the addition of an electrolyte. The resulting experimental values for the rapid coagulation constant were generally lower on the order of ten, from the values predicted theoretically.
INTRODUCTION

Because of its homogeneity with respect to particle size, a monodisperse polystyrene latex is a good model for characterization and coagulation studies. There are several characterization methods available: The Serum replacement method, measurement of the \( \zeta \)-potential and comparison of the scattering cross-sectional areas. The latter two of these were investigated in this study, primarily as tools for characterizing the electrochemical properties of importance in stability considerations. The coagulation of the polystyrene particles was analyzed in view of the Double Layer theory with awareness on the size, nature and spherical shape of the latex particles.
DISCUSSION AND THEORY

A latex system is comprised of a polymer phase and an aqueous phase, and a subsequent air/aqueous phase interface and a polymer particle/aqueous phase interface. Since the size of the latex particle is quite small (10^2 to 10^4 Å), its specific surface area (or polymer particle/aqueous interface) becomes the dominant factor in controlling the behavior of the latex system as a whole. The characterization of the polymer particle/aqueous interface as to the number of functional groups and their corresponding acidic (or basic) strength can be achieved by "cleaning" the latex using ion exchange or a serum replacement method, followed by conductometric or potentiometric titration with base (or acid). In application these techniques remove the adsorbed species on the particle surface and the dissolved species in the serum phase. Adsorbed species may consist of physically adsorbed emulsifier molecules, water soluble polymer molecules, and chemically bound initiator fragments. Dissolved species may consist of an emulsifier, water soluble polymer, residual initiator and its decomposition products, and buffer (1).

Serum Replacement

The most simple and promising cleaning technique, here to be discussed, is the serum replacement method. This method utilizes a cell, a cylindrical polycarbonate reservoir held between two polyacetal plates. The cell contains a Nucleopore filtration membrane which confines the latex particles and allows the passage of a pumped or free flowing distilled deionized water along with the unwanted species. The purity of the filtrate is determined by comparison of the conductance of the filtrate with that of the feed water. The equations dealing with the concentration profile of the adsorbable species undergoing "cleaning" are derived in Appendix A. In this particular study, however, it was assumed that the latex solutions were sufficiently diluted (wt% x 10^-7), such that "cleaning" was not required.
Zeta Potential

The surface charge density of a latex particle can be approximated by the so-called Zeta Potential. This potential is evaluated at the spherical boundary which distinguishes the particle as a migrating unit. One way to experimentally evaluate the Zeta Potential is to observe the movement of the particle in an electric field, thus measuring its electrophoretic mobility. Stigter (2) derived a relationship between the electrophoretic velocity, $v$, and the Zeta Potential for the motion of a charged spherical colloid through an aqueous salt solution under the influence of a uniform field $E$. In the following equation, $v$ is expressed with respect to the solution at infinite distance as:

$$v = \frac{\phi E}{4\pi \eta} + \frac{\Delta E}{3\eta} \frac{1}{a} \int_0^a \varphi r dr$$ ..........................(1)

where "a" is the particle radius with an electric charge, $Q$, uniformly distributed over its surface. $\eta$ is the viscosity of the solution, $\varphi$ is the electric charge density in the double layer, and "r" is the distance from the center of the sphere. Then substituting the following definitions for the electric charge and electric charge density,

$$Q = -\pi e a^2 (d\phi/dr)r = a$$ ..........................(2)

$$\varphi = -\varepsilon \nabla \cdot \phi = -(\varepsilon / \varepsilon) d^2(r \phi) dr$$ ..........................(3)

where $\phi$ is the potential in the double layer, and $\varepsilon$ is the dielectric constant of the particular system. The expression for the electrophoretic velocity becomes:

$$v = \frac{2 \varepsilon e (\varepsilon / \varepsilon^2) E}{3 \eta}$$ ..........................(4)

where $\phi_{r=a} = (\varepsilon / \varepsilon^2)$

This relationship holds for relatively small spheres, $\kappa a \ll 1$, where $\kappa$ is the reciprocal thickness of the double layer (see Appendix B). For thin double layers, $\kappa a >> 1$, the following von Smoluchowski equation is valid:

$$v = \frac{\Delta (\varepsilon / \varepsilon^2) E}{\eta}$$ ..........................(5)

The factor $2/3$ in the original eq. 4 is due to the deformation of the electric field, $E$, by the thicker spherical layer.
It can be shown, that the Zeta Potential of a particle is a function of the bulk concentration of the suspending electrolyte. For this purpose, it is necessary to have an understanding of the double layer theory, which deals with the distribution of co-ions and counter-ions about a charged surface in an electrolytic medium. Figure 1 shows how the electric potential varies with distance from the particular surface. At close enough approach, thermal agitation prevents counter-ions from becoming firmly attached to the surface, thus neutralizing their charge. Instead, it allows for the formation of a double layer around the surface having a certain surface potential. Further away from the charged particle surface, counter-ions are screened from electrostatic attraction by excess counter-ions near the surface. Thus they are more diffuse, and the potential drops off with increasing distance to zero at infinity. The addition of an electrolyte magnifies the screening effect and leads to a greater compacting of the diffuse double layer, and thus a more rapid potential decay.

Double Layer

The two theories describing the average charge distribution and the corresponding potential function in the double layer around a charged particle are the Gouy-Chapman theory and the Debye-Hückel theory (for solutions of strong electrolytes) (3). The Debye-Hückel approximation begins with the Poisson equation, which gives the relationship between charge density and the electrostatic potential in the medium as

$$\nabla^2 \psi = \frac{j_x}{\varepsilon} + \frac{j_y}{\varepsilon} + \frac{j_z}{\varepsilon} = -\frac{4\pi}{\varepsilon} \rho$$

where, $\rho$ is the charge density in the electrolyte phase of the system and a function of $x,y,$ and $z$.

$\psi$ is the potential and specifically $\psi_s$ is the potential at the interface.

$\varepsilon$ is the relative permittivity of the medium.

The above equation is further manipulated in Appendix B, resulting in a general expression which shows that the diffuse double layer is compressed when an electrolyte is added, or when the valence of $+ve$ counter-ion is larger. This becomes a significant observation in the coagulation experiments which will be discussed later.
Figure 1: Variation of potential $\varphi_0$ with distance.
A treatment of the electric double layer, as done by Gouy-Chapman, (3) assumes that ions are point sources of charge at low concentrations. The equations developed account for the variation in the potential with distance from the surface for the diffuse double layer:

\[ \psi = \psi_0 \exp \left( -\frac{k}{\lambda} \right) \]

\[ \lambda = \frac{\psi_0 \left( \frac{ze}{kT} \right)}{\psi_0 \left( \frac{ze}{kT} \right) + 1} \]

where, \( k \) = Boltzmann's constant
\( T \) = Temperature
\( z \) = Electrolyte valence
\( \psi \) = Surface potential
\( \lambda \) = Double Layer thickness (See Appendix B for comparison)

The charge density as a function of the potential at the surface, whose value is subjected to no limitation, is expressed by,

\[ \sigma = \frac{\psi_0}{4\pi} \left( \frac{8\pi kTn}{e} \right)^{1/2} \left[ \lambda \psi_0 \left( \frac{ze}{kT} \right) - \lambda \psi_0 \left( \frac{ze}{kT} \right) \right] \]

or

\[ \sigma = \frac{\psi_0}{2\pi kT} \left( \frac{ze}{kT} \right) \]

However, the Gouy-Chapman theory breaks down as ion crowding occurs, because it predicts unrealistic charge densities at the surface. The Stern theory, on the other hand, accounts for the volume of the ions by dividing the aqueous part of the double layer with a Stern surface. The Stern surface separates an adsorbed layer of ions at the surface of the particle from the rest of the diffuse layer, (see Fig. 2). One of the consequences of this assumption is a Langmuir isotherm, which allows for surface saturation:

\[ \theta = \frac{k^s n_0}{1 + k^s n_0} \]

where \( \theta \) is the fraction of surface adsorption sites occupied, \( n_0 \) is the concentration of the adsorbed ions in the solution, and \( K \) is a constant. This constant is proportional to a Boltzmann
$\psi_0$ - surface potential

$\psi_c$ - Stern potential

$\gamma$ - zeta potential

Figure 2: Double layer in Stern Theory
factor in which the energy term consist of the contribution from the electrical energy associated with the ion in the Stern layer, \( \mathcal{E}_c \gamma_s \), and the specific chemical energy associated with the adsorption, \( \phi \).

Therefore,
\[
\kappa = \frac{\mathcal{E}_c \gamma_s + \phi}{\kappa \tau} \tag{11}
\]

Another consequence is that the Stern layer resembles a parallel plate capacitor model, so,
\[
\frac{\gamma_s - \gamma_i}{\delta} = \frac{4\pi}{\varepsilon_i} \Gamma_i \tag{12}
\]
where \( \delta \) is the Stern distance.

If the fraction of surface sites occupied equals \( \frac{\gamma_s}{\gamma_i} \), where \( \gamma_s \) is the charge density at surface saturation, then one can show that the potential drop in the Stern layer increases with the concentration of the adsorbed ion ending at some limiting value, (3)
\[
\frac{\gamma_s - \gamma_i}{\delta} = \frac{4\pi}{\varepsilon_i} \frac{\gamma_s \kappa \eta_s}{1 + \kappa \eta_s} \tag{13}
\]

All this is of direct importance when trying to find a theoretical value for the Zeta Potential, knowing the surface charge density. From Fig. 2, if the distance of \( \gamma_s \) and \( \gamma \) from \( \gamma_i \) are small, one can assume that \( \gamma_s \approx \gamma_i \approx \gamma \).

Equation 9 could then be expressed as:
\[
\sigma = \frac{\mathcal{E}_c \gamma_s - \phi}{2\pi \varepsilon_i} \sinh \left( \frac{\mathcal{E}_c \gamma_s}{2\pi \varepsilon_i} \right) \tag{14}
\]
and under specific assumptions (see Appendix C), equation 14 would reduce to,
\[
\sigma = \mathcal{C} \sqrt{\eta_i} \tag{15}
\]
where \( \mathcal{C} \) is some constant. This would mean that the Zeta Potential is inversely proportional to \( \sqrt{\eta_i} \), the electrolyte concentration.
Forces between Particles

Repulsion

When two particles approach each other, their electrical double layers begin to interfere, changing the ion distribution in the double layer. Hiemenz(3) defines the total potential energy of repulsion between two spheres by:

\[ V_R = \frac{64\pi R n_0 kT \lambda^2}{\lambda} \exp(-\lambda s_o) \] ..........................(16)

where \( R \) is the radius of the spheres, and \( s_o \) is the distance of closest approach of their surfaces. Assuming uniform spheres of large radius and low potentials, equation 16 simplifies to,

\[ V_R = \frac{\pi \kappa R \lambda^2}{2} \exp(-\lambda s_o) \] ..........................(17)

This shows that the repulsion increases with \( R \) and decreases exponentially with \( s_o \). Since it was shown previously, that the presence of an electrolyte compressed the double layer on the particle surface, the range of double layer repulsion would be reduced consequently.

Attraction

Attraction forces can be basically classified into short range and long range van der Waals forces. Short range forces can stem from permanent dipoles, induced dipoles, polarizability and London dispersion forces which arise between individual particles. In general, these forces are proportional to \( 1/r^6 \), \( r \) being the distance of separation. Attraction potential, unlike repulsion, is independent of electrolyte concentration. The equation of the potential energy due to the long range attractive forces between two spherical particles has been developed by Hamaker and is found in reference (18).

\[ V_A = \frac{A}{6} \left[ \ln\left( \frac{s_o + 2a}{s_o} \right) - \frac{8}{s_o} \left( \frac{s_o + 2a}{s_o} \right) \right] \] ........(19)

where \( a \) is the particle radius

\( s_o \) is the distance of closest approach

\( A \) is the Hamaker constant which for particles of material 1 in the medium of material 2 is given as,
\[ A = \left( \sqrt{A_{11}} - \sqrt{A_{22}} \right)^2 \] ..........................(20)

Under conditions where \( s_0 \ll a \),

\[ V_A = A \frac{A}{\delta} \left[ \ln(1 + \frac{2a}{s_0}) - \frac{2a}{s_0} \left( \frac{a}{2a} \right) \right] ..............(19) \]

\[ V_A = - A \frac{A}{\delta} \left( \frac{2a^2 - a}{s_0^2} \right) \] ..........................(21)

**Born Repulsion**

Another force which becomes significant at small distances is the Born repulsion between electronic clouds as they interpenetrate each other, (18)

\[ V_B = \frac{A}{\gamma} \left[ \frac{8a + s_0}{(2a + s_0)^2} + \frac{6a - s_0}{s_0^2} \right] ..............(22) \]

**Total energy of interaction**

On the basic assumption, that the total energy of interaction can be obtained by the summation of all pertinent energies, Derjaguin and Landau, as well as Verwey and Overbeek developed the full theory of stability (DLVO theory). The total energy of interaction, \( V_T \), between colloidal bodies is given by:

\[ V_T = V_R + V_A + V_B \] ..........................(23)

A schematic representation of the total potential of interaction indicates a resultant energy profile (Fig. 3), with a primary maximum and two minima. One minimum is the deep primary minimum and the other is the shallow secondary minimum. Such a total energy profile becomes important when understanding the coagulation process between two spheres. According to the DLVO theory, if the primary maximum is low (\( \leq 5kT \)), particles may overcome it and become permanently attached at the primary minimum. This is called irreversible coagulation. However, if the maximum is sufficiently high, the particles may attain an equilibrium at the secondary minimum, which would correspond

* \( \gamma \) is the collision diameter
Figure 3: Potential Interaction between two spheres
to a reversible coagulation (7).

Kinetics of Coagulation

The kinetics for this purpose will therefore depend upon the potential profile and any factors which affect it. Since the rate of any ordinary chemical reaction is described in terms of an energy profile along a reaction coordinate, the activation energy for the flocculation may be regarded as equivalent to the height of the potential energy barrier described above. This activation energy is fixed by the nature of the reactants and can be studied in terms of the effects on the rate with temperature variations. Similarly, the colloidal particle's ability to overcome the potential energy barrier will depend upon its thermal energy.

The theory of slow coagulation was developed by Fuchs and is based on Smoluchowski's theory of rapid coagulation, where the coagulation process is treated as a diffusion problem toward a central particle, (diffusion being temperature controlled). Furthermore, the expression for $J$, the total number of particles colliding per unit time is developed in appendix D.

$$J_1 = kn_0, \text{ where } k = \frac{4 \pi}{\int_{a, r} \exp(V/kT) \, dr}$$

where $V$ is the potential of interaction as defined by equation 23.

Because the rate $= \frac{J_1 n_0}{2} = \frac{kn_0^2}{2}$ ...................................................(25)

In a bimolecular process, $r_T = \frac{dN_T}{dt} = -k_s N_T^2 = -\frac{kN_T^2}{2}$ ..............(26)

which upon integration becomes $N_T = \frac{N_{T_0}}{1 + k_s N_{T_0}t}$ .............(27)

where $k_s$ is the slow coagulation constant.

Substituting, one obtains an expression for $k_s$,

$$k_s = \frac{k}{2} = 2 \pi \left( \int_{a, r} \frac{\exp(V/kT)}{r^2} \, dr \right)$$

The ratio of the coagulation rates in the absence and in the
presence of an energy barrier, i.e. the stability ratio, is expressed as:

\[ W = \frac{k_r}{k_s} \quad \text{(29)} \]

where \( k_r \) is the fast rate constant, and \( k_s \) is the slow rate constant. When no potential barriers are present to interfere with the flocculation process, the coagulation rate becomes faster and therefore,

\[ k_r = \frac{2\pi}{\int_{a_1}^{a_2} \frac{dr}{D r^2}} \quad \text{(30)} \]

Stokes-Einstein equation gives the expression for \( D \) for a sphere as follows,

\[ D = \frac{kT}{6\pi \eta a_1} \quad \text{(31)} \]

Substituting into equation (30), and assuming that \( a_1 = a_2 \),

\[ k = \frac{2\pi}{\int_{a_1}^{a_2} \frac{dr}{kT \frac{r^2}{6\pi \eta a_1}}} \quad \text{(32)} \]

which upon integration yields,

\[ k = \frac{4}{3} \left( \frac{kT}{\eta} \right) \quad \text{(33)} \]

For reaction in water at 298 K, this equals \( 1.2 \times 10^{-12} \text{ cm}^3 \) particle second

Substitution yields a complete expression for the stability ratio,

\[ W = \int_{a_1}^{a_2} \frac{\exp(V/kT)}{r^2 D} \quad \text{(34)} \]

As discussed in the paragraph dealing with the double layer theory, adding of an electrolyte to a colloidal solution decreases the size of the potential layer surrounding each particle. When two
such particles interact, the overall effect becomes a lowered energy barrier, and thus a faster coagulation rate. Furthermore, for a particular salt, a fairly sharply defined concentration is needed in order to induce coagulation. This is called the critical coagulation concentration, c.c.c.

According to Peirink and Overbeek (9), in the slow coagulation region, a log-log plot of the stability ratio, $W$ versus the electrolyte concentration should be a linear line, whose slope is related to the particle radius, the surface potential and the electrolyte valence by:

$$\frac{-d(A_{\text{c.c.}} - W)}{d(\log C)} = 2.65 \times 10^{-7} \frac{A_{\text{c.c.}}}{A_{\text{c.c.}}} \tanh \left( \frac{1}{4A_{\text{c.c.}}} \right)$$  \hspace{1cm} (35)

At the point of critical coagulation, the function $W$ goes to 1, because $k_s^* = k_r$ and the slope becomes zero. Here, the DLVO theory, agreeing with the Rule of Schulze and Hardy* (3), gives:

$$c.c.c. = \frac{1}{A_{\text{c.c.}}} \tanh \left( \frac{1}{4A_{\text{c.c.}}} \right)$$  \hspace{1cm} (36)

for $\psi = 50 mV$, the hyperbolic tangent can be approximated by its argument, and at $T = 25^\circ C$

$$c.c.c. = \frac{6.98 \times 10^{-30}}{A_{\text{c.c.}}^4} \psi^4$$  \hspace{1cm} (37)

which shows an inverse second power dependence on the valence of the electrolyte, (7).

Turbidity experiments

The reaction rate constant $k_r$ for coagulation under specified conditions can be found experimentally by measuring the turbidity of solution as a function of time. An equation which handles this situation by assuming that multiple scattering of light does not occur is as follows (21).

$$T = \sum_{i=1}^{n} n_i R_i L \hspace{1cm} (38)$$

where $T$ is the turbidity of the dispersion, $R_i$ is the scattering

* Schulze-Hardy rule states that the valence of the ion of the opposite charge to the colloid has the principal effect on the stability of the colloid.
cross section of an i-multiplet and L is the diameter of the cuvette holding the sample, and

\[ n_i = \frac{n_0 \left( \frac{t}{\theta} \right)^{i-1}}{(1 + \frac{t}{\theta})^{i+1}} \]

where \( \theta = 1/(n_0 k_r) \) is the half life time of the colloidal system. Substituting into equation 38, and taking the derivative with respect to time yields,

\[ \frac{d\tau}{dt} = n_i h L \sum \left\{ \frac{\left( \frac{t}{\theta} \right)^{i-1} R_{i-1}}{(1 + \frac{t}{\theta})^{i+2}} - \frac{i-1}{i-2} \left( \frac{t}{\theta} \right)^{i-2} R_i \right\} \]

......(40)

and for two particle collision, at \( t = 0 \)

\[ \frac{d\tau}{dt} = n_i^2 h L R_2 \left( \frac{R^2}{R_i^2} - 2 \right) \]

......(41)

where \( R_2 \) is the scattering cross section of the resulting two-particle sphere.

The choice of procedure for calculating \( P \) depends upon the system being studied. The Mie theory for light scattering is more accurate for a coagulating latex system than the Rayleigh scattering theory since it is not restricted to particles with dimensions less than the wavelength of light being used, and the particles can either be absorbing or nonabsorbing. In the Mie theory (8), for linearly polarized light and any value of \( a \) or \( m \),

\[ \frac{i(\theta)}{I_0} = \frac{\lambda n^2}{4 \pi^2 r^4} \left( j_j^2 + j_H^2 \right) \]

......(42)

where \( j_j \) and \( j_H \) are complex functions of \( m \) and \( \alpha \) (see calculations 2a-c for the calculation of the cross sectional area)

The scattering cross-section is defined as,

\[ R_s = \frac{\lambda n^2}{4 \pi} \sum_i \left( 2 \pi r_i \right) \left( |a_i|^2 + |b_i|^2 \right) \]

......(43)

If absorption occurs, then,

\[ R_{ext} = R_{scat} + P_{abs} \]

......(44)

\( n_0 \) is the initial number density
The values of these expressions may be looked up in the tables of references 10, 11, and 12 (see calculations).
PROCEDURE

1. Characterization

The characterization of latex surface charge was achieved by measuring the Zeta Potential as a function of the bulk concentration of the suspending electrolyte. The instrument used was a Zeta-Meter, which measures the rate of movement of charged particles in a DC voltage filed. The suspension to be tested was placed in an electrophoresis cell having an electrode on either side connected to a power unit. The cell was then placed under a microscope whose eyepiece contained a tracking grid (ocular micrometer). After proper adjustments, the DC voltage was applied, and the particles were timed as they traversed one grid division. The mobility and Zeta Potential were then calculated or determined graphically from the obtained rates (see Fig.). Due to optical limitation, only two particles of the largest diameter size were able to be analyzed, i.e. 11,000 Å and 20,200 Å. The latex suspensions, initially 25% by weight, were diluted 1 x 10^6 fold.

2. Standardization

Standardization of the photometer was carried out with the variance of known size by the generation of calibration curves; optical density vs. weight percent, and subsequent calculation of the scattering cross-sectional area Å. The calculated scattering cross sections were compared to theoretical values from literature tables (12). For each particle diameter, the optical density was recorded at approximately five different concentrations, on the order of 1 x 10^-3 wt%. This procedure utilized a Cary-14 spectrophotometer, operating with a visible light source of 500 nm. The following particle sizes were studied: (in Å) 910, 1090, 1760, 2340, 3570, 11,000, 20,200 and 7940 Å.

3. Coagulation

Coagulation studies involving NaCl and Ba(NO_3)_2 were performed on the following particle diameters: 910, 1090, 1760, 2340, 3570 Å. The remaining particles were too large for experimental purposes, i.e. they were not subjected to Brownian motion. The optical density was recorded at 500 nm using a Cary-14 spectrophotometer.
The schematic diagram of the Cary-14 spectrophotometer (Fig 4) shows a double cell (test cell and reference cell) set up, which enabled the measurement of the relative changes in O.D. as a function of time. The quartz sample cells had 1 cm path length and 5 ml capacity.

A 1.5 ml latex suspension of known composition was placed in the reference cell as well as the sample cell and the optical density was adjusted to zero. One ml of distilled, deionized water was injected into the reference cell, the spectrophotometer was turned on and 1 ml of selected electrolyte was injected into the sample cell, marking the point of injection. Optical density was followed as a function of time. The concentration range of NaCl electrolyte used was 0.117 M to 1.0 M and that of Ba(NO$_3$)$_2$ was 0.0133 M to 0.0833 M. This is comparable to the concentration range of Ba(NO$_3$)$_2$ used by Schild, ElAasser and Poehlein (15), which was 0.003 M to 0.025 M. The concentration range of NaCl and Ba(NO$_3$)$_2$ as used by Greens and Saunders (6) was 0.3 to 1.0 M and 0.005 to 0.015 M respectively.
DISCUSSION OF RESULTS

1. Characterization

The results of -Z.P. vs. concentration of NaCl, found in Table I are plotted in Figures 1 and 2. The shapes of the curves suggest an inverse square root relationship and in fact when \( 1/\sqrt{n_0} \) is plotted vs. -Z.P. (Fig 3), the result is basically a straight line. This behavior, as already explained in the "theory section", is caused by the decrease of the double layer (decrease in Z.P.) upon the addition of electrolyte.

Experimental results show that the slope of \( 1/\sqrt{n_0} \) vs. the Zeta Potential of a larger size particle (20,200 A diameter) is less steeper than that of a smaller particle (11,000 A diameter). This points to the fact that the surface charge density of 11,000 A latex is 2.74 times as large as that of the 20,200 A latex. Theoretical calculations show that the Zeta Potential is independent of the particle size (see Appendix C).

Problems encountered in the experiment: At higher concentrations, major difficulties have been encountered when trying to measure the migration rates of the particles. These difficulties stemmed from erratic (eddie-type movement) behavior of the particles when they were subjected to an applied potential. One could postulate that the voltage also induced the migration of Na\(^+\) and Cl\(^-\) ions to the opposite electrodes and at higher salt concentrations the flow of ions enwrapped the flow of the individual particles.

2. Calibration curves

Experimental as well as literature values of the scattering cross-sectional area for each particle size are given in Table II. Both values are comparable in magnitude, i.e. for particle diameter 11,000 A, \( R_{\text{exp}} = 3.38 \times 10^{-8} \text{cm}^2 \) and \( R_{\text{lit}} = 3.39 \times 10^{-8} \text{cm}^2 \).
3. Coagulation Studies

Table VI shows both, the theoretical and experimental slope of the stability curve at slow coagulation. The theoretical values, based on the surface charge density of the particle, increase proportionally with the particle diameter. On the other hand, the experimental values obtained with Ba(NO₃)₂ as an electrolyte tend to decrease, and those obtained with NaCl electrolyte are random with an average value around -2.1. The decrease in stability with increasing particle size may be attributed to coagulation in the secondary minimum, since the secondary minimum of larger size particle is deeper (7).

Experimental values for the Hamaker constant A (Table VII) are lower by approximately 20% from the predicted literature value. Of course, this value may or may not be exactly representative of the particular system studied. * Also, the calculation of the Hamaker constant is based on a flat plate model, which could contribute to the observed variations.

Although theoretically, the c.c.c. should vary inversely with the sixth power of the valence of the counter-ion as stated in ref.(6),

\[
c_{\text{c.c.}} = \frac{9.0 \times 10^{-22}}{A^2 v^6}
\]

the experimental values display a range of 0.76 to 5.52 inverse power dependence (Table VIa). Comparison of results of similar particle sizes to those done by Silebi (7) shows the power for particle diameter = 2340Å to be 3.12 and for diameter=3570Å to be 3.12 also. Experimental values obtained for these two sizes are 4.60 and 0.76 respectively. It is hard to pinpoint the reason for the discrepancy of these results, although it might be worth to mention that the values of c.c.c. were obtained graphically. This at times presented problems, because in certain instances more than one line could have been drawn through the data points (see -logW vs. logC plot for D=1760 in Ba(NO₃)₂),(fig 1).

*The value for A, 5 x10⁻¹⁴ ergs (13), is listed under Polystyrene in water at 20°C. No mention is made of the size, surface charge density of the particles nor the manufacturer of the Polystyrene. Therefore, this value cannot be taken as absolute for the particular system studied.
Table VIIIb shows the ratio of theoretical to experimental rate constant for fast coagulation. Generally, the experimental values are found to be lower than the predicted (with the exception of two). One possible explanation could be that the formed doublet scatters less light than the sphere of comparable volume. However, this would account only for 25% decrease in the scattering efficiency (7). Also the fact that the rate constant was calculated with experimental values for \( \frac{dT}{dt} \) and literature values for \( R_1 \) and \( R_2 \) could contribute to the observed discrepancy. A definite source of error, however, would be the established weight% concentration given for each particle size. Through evaporation or accidental "dry-up", this concentration could be drastically altered. Since the calculation of \( k_r \) requires the exact number of particles present initially in the suspension \( N_{T0} \), an erroneous concentration would yield the wrong rate constant, especially when the \( N_{T0} \) term appears squared in the equation (see sample calculations 3b).
CONCLUSIONS

1. The Zeta Potential of monodisperse latex particles varied inversely with the square root of the suspending electrolyte concentration. The surface charge density of particles \( D=11,000 \ \text{Å} \) was found to be 2.74 times as great as of particles \( D=20,200 \ \text{Å} \).

2. The scattering cross-sectional areas for a range of latex particle diameters (910 Å to 20,000 Å) found experimentally were comparable to the values found in literature tables.

3. While the DLVO theory predicted an increase in the slopes of the stability curve with increasing particle size, experimental results showed the opposite. Such an effect was contributed to the coagulation in the secondary minimum.

4. Experimental values for the Hamaker constant were lower by approximately 20% from the predicted literature value. This value, however, may or may not have been representative of the system under study.

5. Experimental values for c.c.c. displayed a range in the orders of inverse power dependence on the valence of the counter-ion. This was attributed to the graphical estimation of c.c.c. values.

6. Experimental values for \( k_T \) were generally lower on the order of 10 than the value predicted theoretically. The effect was accounted to the decreased light scattering by a doublet than by a sphere of comparable volume and to the doubtful values of established initial latex concentrations.
REFERENCES


2. Olphen H. and Myers K., Physical Chemistry. Enriching Topics from Colloid and Surface Science, IUPAC Commission, No. 1.6, 1975,
   a. Chapt 2, H van Olphen, "Theories of the Stability of Lyophobic Colloidal Systems"
   b. Chapt 13, Hansen R., "Coagulation Kinetics and Bimolecular Reaction Kinetics"
   c. Chapt 15, van den Esher and Pieper, "Critical Coagulation concentration of latexes"
   d. Chapt 20, Stigter D., "Electrophoresis"


ACKNOWLEDGMENTS

I wish to thank Professor McHugh for his critical advice and patience, especially during those times when things looked hopeless. Also, I wish to thank Professor Schaeiwitz for the use of his Zeta Meter, Steve Ulrich for the help with the Cary-14, and Elmer Lash for making a special cover for the spectrophotometer.
DATA AND CALCULATIONS

1. Zeta Potential

Electrophoretic Mobility from the Zeta Meter measurement is defined as:

\[
EM = \frac{160 \text{ microns}}{t} \times \frac{10 \text{ cm}}{V}
\]

where 10 cm is the length of the electrophoresis cell, and \( t \) is the time needed to traverse one full grid division. Knowing the electrophoretic mobility, the Zeta Potential can be obtained through the following Helmholtz-Smoluchowski equation found in the Zeta-meter Manual (20):

\[
7.P. = \frac{4V_t}{D_t} \times EM
\]

where \( V_t \) is the viscosity of the suspending liquid in poises and \( D_t \) is the dielectric constant of the suspending liquid. This equation reduces to

\[
7.P. = C_t \times EM
\]

where the values for the constant \( C_t \) in pure water are found in Table IVa(20).

Sample calculations for 20,200 Å latex particles, applied voltage 150 V

<table>
<thead>
<tr>
<th>trial</th>
<th>time over two full grids (sec)</th>
<th>trial</th>
<th>time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.1</td>
<td>6</td>
<td>6.4</td>
</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>7</td>
<td>6.8</td>
</tr>
<tr>
<td>3</td>
<td>8.7</td>
<td>8</td>
<td>6.8</td>
</tr>
<tr>
<td>4</td>
<td>7.1</td>
<td>9</td>
<td>5.7</td>
</tr>
<tr>
<td>5</td>
<td>5.3</td>
<td>10</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Average time per grid = 3.22

Consulting Table IV(b) (20) \[ EM = -3.5 \text{ microns per second/volt per cm} \]

\[ Z.P. = -3.5 (13.4) \]

\[ = -46.9 \text{ millivolts} \]
The slopes of $1/n_0$ vs. Zeta Potential equal \[ \frac{\sqrt{\frac{\varepsilon A T}{c e}}}{2\pi} \]
(from Appendix C)
Therefore, 
\[ \text{slope}_{11,000A} = 1.2 \]
\[ \text{slope}_{20,200A} = 0.4375 \]
Thus the ratio of the surface charge densities for the two particle sizes can be found by comparing the slopes, since all other terms are constant.
\[ \frac{\frac{\varepsilon A T}{c e}}{11,000A} = \frac{1.2}{0.4375} = 2.74 \]
2a. Calculation of cross-sectional area (experimental)

Concentrations of latex particles were calculated under the following assumption:

\[
\text{wt}\% = \frac{w_o v_p}{w_o v_p + v_{H_2O}} = \frac{w_o v_p}{v_{H_2O}}
\]

where \(w_o\) is the original wt\%  
\(v_p\) is the volume of the polymer sample  
\(v_{H_2O}\) is the volume of water added

Given that,  
\[\tau = SRX = 2.303 \log(I_o/I) = 2.303\] (O.D.)

where  
\[N = \left(\frac{\% wt/100}{v_p}\right) \frac{1}{c_m} = \left(\frac{c_m}{c_p v_p}\right) (\% wt/100)\]

where \(v_p, c_p\) are the volume and density of particle under study and \(c_m\) is the density of the medium.

Substitution yields,  
\[\frac{c_m}{v_p c_p} (\text{wt}\%/100) \text{ RX } = 2.303 \text{ (O.D.)}\]

then  
\[R = \frac{2.303 \tau \left(D_p\right)^3}{\left(c_m/c_p\right)^6 (\text{wt}\% x 10^{-2})}\]

where \((\text{O.D.}/\text{wt}\% x 10^{-2})\) is the slope of the calibration curve and  
\[c_p = 1.05 \text{ g/cm}^3\]  
\[c_m = 1.00 \text{ g/cm}^3\]  
\[X = 1 \text{ cm (width of cell)}\]

Simplification yields,  
\[P = 1.21 \ D_p^3\] (slope of calibration curve)

Therefore, for \(D=910\)  
\[R = 1.21 (910 \times 10^{-3})^3 (9.48 \times 10^4)\]  
\[R = 8.644 \times 10^{-11} \text{ cm}^2\]
2b. Calculation of cross-sectional area (literature)

Table IV (12) gives the necessary information for the calculation of $R$,

$$ R = c(\lambda_o) \sum_{n=1}^{\infty} \frac{|a_n|^2 + |b_n|^2}{(2n+1)} $$

where $c(\lambda_o) = \lambda_o^2 / \sum_n^{\infty} (\lambda_o)^{2n} n^n$

$$ \hat{n}_p = 1.566 + \frac{0.0078}{\lambda_o} + \frac{0.000334}{\lambda_o^2} $$

$\lambda_o = 500 \text{ nm}$, $n_p = 1.50$, $T = 27^\circ C$

$n_{ref} = 1.336 \text{ (water)}$, $m = n_p / n_{ref}$

Also $\alpha = \frac{n_p D_p \hat{n}_p}{\lambda_o}$ where $D_p$ is the particle diameter in nm

For $\lambda_o = 500$, $n_{ref} = 1.336$

$n_p = 1.602$

$m = 1.198$

$c = 2.224 \times 10^{-11}$

Table V lists the values of $\alpha$ at $\lambda_o = 500$ and $m = 1.20$ as a function of $D_p$.

The summation $\sum_{n=1}^{\infty} \frac{|a_n|^2 + |b_n|^2}{(2n+1)}$ is a function of $\alpha$ and $m$.

Table V lists the summation value for each particle size.

The resulting $R$ values are in Table II.

* $n_p$ is the index of refraction of the polymer under study.
  $\lambda_o$ is the wavelength of source.
3a. Calculation of surface potential, $\Psi$, d log$W$/d log$C$ (theoretical)

(For results see Tables VI and VII) \[ \sigma = \frac{e}{4\pi} \frac{\Psi_0}{\lambda^{-1}} \]

where \[ \frac{e}{4\pi} = 78.3 \]
\[ \lambda^{-1} = 9.61 \times 10^{-8} \text{ cm} \]
\[ \kappa \equiv \frac{3\pi e N_c \bar{Z}}{1000 \varepsilon kT} \]

Then \[ \sigma = \frac{71.3}{(9 \times 10^8 \text{ cm}^{-1})} \frac{\Psi_0}{(9.61 \times 10^{-8} \text{ cm})} \times \frac{1W}{1000 \text{ m}} \times \frac{1m}{100 \text{ cm}} \]

$\Psi_0$ is in mV and $\sigma$ is in coulombs/cm$^2$

(Values for $\sigma$ were found in Ahmed's and Silebi's theses (7) & (17))

Solving for $\Psi_0$,
\[ \Psi_0 = \sigma (1.105 \times 10^6) \]

\[ \delta = \frac{\ln(2\pi e \Psi_0/2kT-1)}{\ln(2\pi e \Psi_0/2kT+1)} \]

where \[ kT = (1.38 \times 10^{-23})(298)(1000) \text{ mV } \text{C} \]
\[ e = 1.602 \times 10^{-19} \text{ C} \]
\[ v = \text{electrolyte valence} \]

Then dlog$W$/dlog$C = -2.06 \times 10^7 \left( \frac{a^2}{v^2} \right)$

where $a$ is the radius in cm, $C$ is the electrolyte concentration

\[ \text{c.c.c.} = \frac{8 \times 10^{-22}}{A^2 v^6} \text{ in millimoles/liter} \]

\[ \text{valid when } A^4 \gg 1 \text{, particles are large in comparison to the Double Layer thickness} \]
Jb. Calculation of rate constant of coagulation

\[
\frac{d\tau}{dt}_c = N_{To}^2 k_r L R_1 \left( \frac{R_2}{R_1} - 2 \right)
\]

where \( R_2 \) is the cross-sectional area of a doublet whose
\( r_2 = \sqrt{\frac{2}{3}} r_1 \)

Solving for \( k_r \),

\[
k_r = \frac{\frac{d\tau}{dt}_c}{N_{To}^2 L R_1 \left( \frac{R_2}{R_1} - 2 \right)}
\]

when \( \frac{d\tau}{dt}_c = dO.D./dt \), at critical coagulation, the rate constant \( k_r \) becomes the rapid coagulation constant.

\( L = 1 \) cm (width of cell)

\( N_{To} \) = number of particles/ ml at \( t=0 \)

\( C_0 \) = initial wt% x \( 10^{-2} \)

\( v_p \) = particle volume

\( N_{To} \) is given by, \( N_{To} = \frac{C_0}{v_p} \)
Given Data:

Monodisperse Polystyrene particles manufactured by Dow Chemical. The particles have a negative surface charge from sulfonation by Potassium Persulfate.

<table>
<thead>
<tr>
<th>Diameter (Å)</th>
<th>Volume (cm$^3$)</th>
<th>Initial Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.568 x 10^{-16}</td>
<td>18.83</td>
</tr>
<tr>
<td>2</td>
<td>3.95 x 10^{-16}</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>6.781 x 10^{-16}</td>
<td>41.45</td>
</tr>
<tr>
<td>4</td>
<td>2.855 x 10^{-15}</td>
<td>29.68</td>
</tr>
<tr>
<td>5</td>
<td>6.71 x 10^{-15}</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>2.382 x 10^{-14}</td>
<td>31.07</td>
</tr>
<tr>
<td>7</td>
<td>2.661 x 10^{-13}</td>
<td>29.80</td>
</tr>
<tr>
<td>8</td>
<td>9.69 x 10^{-13}</td>
<td>25.64</td>
</tr>
<tr>
<td>9</td>
<td>3.16 x 10^{-12}</td>
<td>25</td>
</tr>
</tbody>
</table>
### TABLE I

<table>
<thead>
<tr>
<th>NaCl (Moles/liter)</th>
<th>-Z.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11,000 Å</td>
</tr>
<tr>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>0.001</td>
<td>24</td>
</tr>
<tr>
<td>0.003</td>
<td>19</td>
</tr>
<tr>
<td>0.005</td>
<td>24</td>
</tr>
<tr>
<td>0.007</td>
<td>22</td>
</tr>
<tr>
<td>0.009</td>
<td>37</td>
</tr>
</tbody>
</table>

### TABLE II

<table>
<thead>
<tr>
<th>Particle Diameter (Angstrom)</th>
<th>Experimental R (cm²)</th>
<th>Literature R (cm²)</th>
<th>R for (2r/Å² r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>910</td>
<td>8.644 x 10⁻¹¹</td>
<td>9.2 x 10⁻¹²</td>
<td>3.29 x 10⁻¹²</td>
</tr>
<tr>
<td>1090</td>
<td>0.55 x 10⁻¹¹</td>
<td>0.271 x 10⁻¹¹</td>
<td>0.85 x 10⁻¹¹</td>
</tr>
<tr>
<td>1760</td>
<td>5.13 x 10⁻¹¹</td>
<td>2.82 x 10⁻¹¹</td>
<td>7.909 x 10⁻¹¹</td>
</tr>
<tr>
<td>2340</td>
<td>3.079 x 10⁻¹⁰</td>
<td>1.03 x 10⁻¹⁰</td>
<td>3.069 x 10⁻¹¹</td>
</tr>
<tr>
<td>3570</td>
<td>7.13 x 10⁻¹⁰</td>
<td>6.53 x 10⁻¹⁰</td>
<td>1.722 x 10⁻⁹</td>
</tr>
<tr>
<td>7940</td>
<td>1.81 x 10⁻⁸</td>
<td>1.43 x 10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>11,000</td>
<td>3.38 x 10⁻⁸</td>
<td>3.39 x 10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>20,200</td>
<td>7.68 x 10⁻⁸</td>
<td>6.45 x 10⁻⁸</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE III

**Calibration Curves**

1. **910 Å**

<table>
<thead>
<tr>
<th>% wt</th>
<th>absorbance (O.D.)</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.499 \times 10^{-4}$</td>
<td>0.418</td>
<td>$9.48 \times 10^4$</td>
</tr>
<tr>
<td>$1.25 \times 10^{-3}$</td>
<td>1.168</td>
<td></td>
</tr>
<tr>
<td>$6.25 \times 10^{-4}$</td>
<td>0.611</td>
<td></td>
</tr>
<tr>
<td>$1.25 \times 10^{-4}$</td>
<td>0.253</td>
<td></td>
</tr>
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</table>

2. **1090 Å**

<table>
<thead>
<tr>
<th>% wt</th>
<th>absorbance</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.14 \times 10^{-4}$</td>
<td>1.11</td>
<td>$3.5 \times 10^3$</td>
</tr>
<tr>
<td>$1.38 \times 10^{-4}$</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>$8.28 \times 10^{-5}$</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>$2.76 \times 10^{-5}$</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>$1.66 \times 10^{-5}$</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

3. **1760 Å**

<table>
<thead>
<tr>
<th>% wt</th>
<th>absorbance</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.48 \times 10^{-3}$</td>
<td>too dense</td>
<td></td>
</tr>
<tr>
<td>$3.70 \times 10^{-4}$</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>$9.25 \times 10^{-5}$</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>$2.41 \times 10^{-5}$</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>$5.78 \times 10^{-6}$</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>$1.45 \times 10^{-6}$</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE III con't

#### 4. 2340 %

<table>
<thead>
<tr>
<th>% wt</th>
<th>absorbance (O.D.)</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.166 x 10^{-5}</td>
<td>0.799</td>
<td>1.986 x 10^4</td>
</tr>
<tr>
<td>5.77 x 10^{-5}</td>
<td>1.127</td>
<td></td>
</tr>
<tr>
<td>1.19 x 10^{-5}</td>
<td>0.264</td>
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<tr>
<td>9.37 x 10^{-5}</td>
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</tr>
<tr>
<td>5.95 x 10^{-6}</td>
<td>0.137</td>
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</table>

#### 5. 3570 %

<table>
<thead>
<tr>
<th>% wt</th>
<th>absorbance</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.17 x 10^{-4}</td>
<td>too dense</td>
<td>1.3 x 10^4</td>
</tr>
<tr>
<td>1.04 x 10^{-4}</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>2.07 x 10^{-5}</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>4.14 x 10^{-6}</td>
<td>0.04</td>
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</tr>
<tr>
<td>5.74 x 10^{-5}</td>
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</table>

#### 6. 7940 %

<table>
<thead>
<tr>
<th>% wt</th>
<th>absorbance</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.96 x 10^{-4}</td>
<td>too dense</td>
<td>3.0 x 10^4</td>
</tr>
<tr>
<td>1.19 x 10^{-4}</td>
<td>too dense</td>
<td></td>
</tr>
<tr>
<td>2.38 x 10^{-5}</td>
<td>0.86</td>
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</tr>
<tr>
<td>6.62 x 10^{-5}</td>
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</tr>
<tr>
<td>1.32 x 10^{-5}</td>
<td>0.50</td>
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</table>
### Table III cont.

<table>
<thead>
<tr>
<th>7. 11,000 mg</th>
<th><strong>absorbance (O.D.)</strong></th>
<th><strong>slope</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>% wt</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.13 x 10^{-4}</td>
<td>too dense</td>
<td>2.1 x 10^4</td>
</tr>
<tr>
<td>8.54 x 10^{-5}</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>1.71 x 10^{-5}</td>
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<td></td>
</tr>
<tr>
<td>7.70 x 10^{-5}</td>
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</tr>
<tr>
<td>1.14 x 10^{-5}</td>
<td>0.39</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>8. 20,200 mg</th>
<th><strong>absorbance</strong></th>
<th><strong>slope</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>% wt</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.00 x 10^{-4}</td>
<td>too dense</td>
<td>7.7 x 10^{-3}</td>
</tr>
<tr>
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<td>5.56 x 10^{-5}</td>
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<tr>
<td>2.00 x 10^{-5}</td>
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</tr>
<tr>
<td>1.36 x 10^{-4}</td>
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<td></td>
</tr>
<tr>
<td>Temperature °C</td>
<td>C_t</td>
<td>Temperature °C</td>
</tr>
<tr>
<td>---------------</td>
<td>------</td>
<td>----------------</td>
</tr>
<tr>
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<td>19.6</td>
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<td>10</td>
<td>17.6</td>
<td>40</td>
</tr>
<tr>
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These values are valid for most aqueous systems. Their viscosity and dielectric constant should be reasonably close to that of distilled water.
TABLE V (a)

**Summations**

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TABLE V(a) cont'

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| Page 115 |
| s\m | 1.06 | 1.10 | 1.15 | 1.20 | 1.25 | 1.30 |
| 0.2 | 0.4153 | 0.1806 | 0.3961 | 0.6876 | 0.9667 | 0.1486 |
| 0.4 | 0.7048 | 0.5736 | 0.6179 | 0.6416 | 0.6368 | 0.2544 |
| 0.6 | 0.2286 | 0.1328 | 0.2991 | 0.5228 | 0.6399 | 0.1131 |
| 0.8 | 0.0561 | 0.0189 | 0.6668 | 0.81428 | 0.92868 | 0.24487 |
| 1.0 | 0.0166 | 0.0342 | 0.010864 | 0.034088 | 0.053868 | 0.077488 |
| 1.2 | 0.0874 | 0.214861 | 0.34487 | 0.51875 | 0.697396 | 0.14119 |
| 1.4 | 0.0733 | 0.023898 | 0.063496 | 0.086359 | 0.13241 | 0.22082 |
| 1.6 | 0.0197 | 0.034412 | 0.076387 | 0.13708 | 0.21591 | 0.31399 |
| 1.8 | 0.019899 | 0.044631 | 0.10194 | 0.18370 | 0.29120 | 0.42674 |
| 2.0 | 0.014094 | 0.067561 | 0.13233 | 0.24094 | 0.36728 | 0.57048 |
### TABLE V (b)

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<td>Diameter (Anfs)</td>
<td>$u$ mC/cm²</td>
<td>$v$ mV</td>
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<tr>
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<td>------------</td>
<td>--------</td>
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$$d\log W / d\log C$$

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* $u = \log \frac{c.c.c. (\text{Ba(NO}_3\text{)}_2)}{c.c.c. (\text{NaCl})}$
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Literature value [13] $A = 5 \times 10^{-14}$ ergs
### TABLE VIII (a)

| Diameter (Å) | \( N_{To} \) | \( \frac{dT}{dt} \), at e.c.c. (sec\(^{-1}\)) | \( k_R \) (cm\(^3\)/sec) | \( k_R \) (cm\(^3\)/sec) |
|--------------|--------------|-----------------------------|----------------|-----------------|----------------|
|              | NaCl         | Ba(NO\(_3\))\(_2\)         | NaCl           | Ba(NO\(_3\))\(_2\) |
| 910 6.10 x 10\(^{10}\) | 6.10 x 10\(^{10}\) | 7.0 x 10\(^{-3}\) | 4.0 x 10\(^{-3}\) |
| 1090 3.06 x 10\(^{11}\) | 1.02 x 10\(^{11}\) | 8.00 x 10\(^{-3}\) | 1.0 x 10\(^{-2}\) |
| 1760 1.2 x 10\(^{10}\) | 1.73 x 10\(^{10}\) | 6.00 x 10\(^{-3}\) | 9.0 x 10\(^{-3}\) |
| 2340 2.94 x 10\(^9\) | 5.88 x 10\(^9\) | 3.0 x 10\(^{-3}\) | 1.20 x 10\(^{-3}\) |
| 3570 1.09 x 10\(^9\) | 2.17 x 10\(^9\) | 5.0 x 10\(^{-2}\) | 1.20 x 10\(^{-3}\) |

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<th>Diameter (Å)</th>
<th>( k_R ) (cm(^3)/sec)</th>
<th>( k_R ) (cm(^3)/sec)</th>
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<td>Ba(NO(_3))(_2)</td>
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Theoretical value (eq. 24, Theory of Coagulation) \( k_R = 2.71 \times 10^{-12} \) cm\(^3\)/sec
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Figure 1: Z.P. vs. Concentration of NaCl
Figure 2: 2.8% Concentration of NaCl

particle diameter 20,000 Å
Figure 3: -2.8 as the (concentration of NaCl)^2
Figure 4: Calibration Curve, D = 910 A
Figure 5: Calibration Curve, D = 1090 Å
\( D = 1760 \text{ Å} \)

Figure 6: Calibration Curve, \( D = 1760 \text{ Å} \)
Figure 7: Calibration Curve, D = 2.340 Å
Figure 6: Calibration Curve, \( \lambda = 3570 \text{ Å} \)
Figure 9: Calibration Curve, $D = 7940\,\text{A}$
Figure 10: Calibration Curve, $D = 11,000 \text{ Å}$
Figure 11: Calibration Curve, $D = 20,200\, \text{A}$
Figure 12: Stability Curve, $D = 910 \, \text{A}$ in NaCl
Figure 13: Stability Curve, $D = 1090 \text{Å}$ in NaCl
Figure 14: Stability Curve, $D = 1760\,\text{Å}$ in $\text{NaCl}$
Figure 15: Stability Curve, $D = 2340A^2$ in NaCl.
Figure 16: Stability Curve, $D = 3570 \text{ Å}$ in NaCl.
Figure 17: Stability Curve, $D = 9108$ in $Ba(NO_3)_2$
Figure 18: Stability Curve, $D = 1090 \text{Å}$ in $\text{Ba(NO}_3\text{)}_2$. 

$D = 1075 \text{Å}$ 

$\text{Ba(NO}_3\text{)}_2$
Figure 19: Stability Curve, $D = 1760\text{A'}$ in $\text{Ba(NO}_3\text{)}_2$.
Figure 20: Stability Curve, $D = 2340 \text{ Å}$ in $\text{Ba(NO}_3\text{)}_2$.
Figure 21: Stability Curve, \( D = 3570 \text{#/cm}^2 \) in \( \text{Ba(NO}_3\text{)}_2 \).
Figure 22: Turbidity vs. Time, $D = 910^\circ$ in NaCl
Figure 13: Initial vs. Time Curves, D = 1090 Å in NaCl
Figure 24: Turbidity vs. Time. \( D = 2340 \, \text{Å} \) in NaCl
Figure 25: Turbidity vs. Time, \( D = 1.76 \times 10^{-6} \text{m} \) in NaCl
Figure 26: Turbidity vs. Time, D = 3570Å in NaCl

Diameter = 3570 Å
Figure 28: Turbidity vs. Time, $D = 1090 \, \text{nm}$ in $\text{Ba(NO}_3)_2$
Figure 29: Turbidity vs. Time, $D = 1760\mu$ in $Ba(NO_3)_2$
Figure 30: Turbidity vs. Time, $D = 2.340 \text{ Å}$ in $\text{Ba(NO}_3\text{)}_2$.
Figure 31: Turbidity vs Time, D = 3570 Å in Ba(NO₃)₂
APPENDICES
APPENDIX A

Concentration profile of adsorbable species

1) $C_A \rightarrow C_{A\text{sat}}$

- $C_{Ao}$: concentration of species A at $t=0$
- $C_{aw}$: concentration of species A in water

Assume $F_{in} = F_{out}$ ($F$ is the volumetric flow rate)

For a constant volume process, the material balance is:

amount in - amount out = accumulation

\[
\dot{F} C_{aw} \Delta t - \dot{F} C_A \Delta t = \dot{C}(t/C_A)
\]

\[
(\dot{F} C_{aw} - \dot{F} C_A) \Delta t = \int \dot{C} \, dt
\]

\[
\frac{dC_A}{C_a - C_{aw}} = \left( \frac{\dot{F}}{V} \right) \, dt
\]

\[
- \ln \frac{C_{sat} - C_{aw}}{C_a - C_{aw}} = \frac{\dot{F}}{V} \Delta t
\]

Assuming that the distilled water is A free: $C_{aw} = 0$, then

\[
- \ln \frac{C_{sat}}{C_a} = \frac{\dot{F}}{V} \Delta t
\]

or

\[
C_a = C_{sat} \exp \left( \frac{\dot{F}}{V} \Delta t \right)
\]

In a more general case, as long as $C_a > C_{sat}$

\[
C_{ao} = C_a \exp \left( \frac{\dot{F}}{V} \Delta t \right)
\]

or

\[
C_a = C_{ao} \exp (-\frac{\dot{F}}{V} \Delta t) \text{ at some time } t
\]

2) Assuming an equilibrium between the adsorbable species on the particle surface and aqueous phase described by the Langmuir isotherm, one can write the following equation.
\[ k_a C_a (s_o - s) = k_d s \]  \hspace{1cm} (5)

where
- \( s_o \) is the total surface area
- \( s \) is the surface area covered with adsorbable species
- \( k_a \) is the rate constant for adsorption
- \( k_d \) is the rate constant for desorption

**Mass Balance**

\[ \text{Amount in} - \text{Amount out} = \text{Accumulation} \]

\[ F(C_{aw} \Delta t) - F(C_a \Delta t) - \Delta \left( \frac{s}{N_a a_s} \right) = \Delta (V C_a) \]  \hspace{1cm} (6)

where \( \frac{s}{N_a a_s} \) are the species going in or out according to the equilibrium, and \( a_s \) is the molecular area of adsorbable species, \( N_a \) is the Avogadro's number.

From Langmuir's isotherm, \( s = s_o \left( \frac{b C_a}{1 + b C_a} \right) \)  \hspace{2cm} (7)

where \( b = k_a / k_d \)

Substituting equation 7 into equation 6,

\[ F(C_{aw} - C_a) \Delta t - d \left( \frac{s}{N_a a_s} \left( \frac{b C_a}{1 + b C_a} \right) \right) = d V C_a \]

\[ F(C_{aw} - C_a) \Delta t = V d C_a + \frac{s_o b}{N_a a_s} d \left( \frac{C_a}{1 + b C_a} \right) \]  \hspace{1cm} (8)

Letting \( u = \frac{C_a}{1 + b C_a} \), so

\[ \frac{du}{dC_a} = \frac{1}{(1 + b C_a)^2} \]

\[ d \left( \frac{C_a}{1 + b C_a} \right) = \frac{d C_a}{(1 + b C_a)^2} \]

Then,

\[ F(C_{aw} - C_a) \Delta t = V d C_a + \frac{s_o b}{N_a a_s} \left[ \frac{1}{(1 + b C_a)^2} \right] d C_a \]  \hspace{1cm} (9)

Integrating from some initial concentration \( C_{a_0} \) to \( C_a \)

\[ \int \frac{F}{V} \, dt = \int \left[ \frac{1 + \frac{s_o b}{N_a a_s} \frac{1}{(1 + b C_a)^2}}{C_{a_0} (C_{aw} - C_a)} \right] \, d C_a \]  \hspace{1cm} (10)
\[
\frac{t}{\tau} = - \frac{c}{(c - c_{aw})} + \frac{S_e b}{V a_s N_a} \left[ \frac{1}{(1 - b c)^2} \cdot \frac{d c_a}{(c - c_{aw})} \right]
\]

The general solution to equation 11 can be found in CRC pg. 399 and the formula 54, it is:

\[
\frac{t}{\tau} = \ln \left( \frac{c_a}{c_{aw}} \right) - \frac{b S_e}{a_s V N_a} \left[ \frac{b (c_a - c_a) - b c_{aw}}{(1 + b c_a)(1 - b c_a)} \right] - \ln \left( \frac{c_a - c_{aw}}{c_a} \right)
\]

Special cases

1) \( c_{aw} = 0 \)

\[
\frac{t}{\tau} = \frac{c_a}{c_{aw}} - \frac{b S_e}{a_s V N_a} \left[ \frac{b (c_a - c_a)}{(1 + b c_a)(1 - b c_a)} \right] = \ln \left( \frac{c_a}{c_{aw}} \right)
\]

2) \( b = 0 \)

\[
\frac{t}{\tau} = \ln \left( \frac{c_a}{c_{aw}} \right)
\]

which is the same as equation 4.
Debye - Hückel Approximation

The potential distribution, described by the Poisson equation, shall be for simplicity considered a function of $x$ direction only, so that,
\[
\frac{d^2 \psi}{dx^2} = -\frac{4\pi \rho}{\varepsilon} \tag{1}
\]

The charge density can be expressed as a function of the potential by means of the Boltzmann equation,
\[
\frac{n_i}{n_{i0}} = \exp \left( \frac{-z_i e \psi}{kT} \right) \tag{2}
\]

where, $n_i$ is the number of ions of type $i$ per cubic centimeter near the surface,
$n_{i0}$ is the concentration far from the surface (bulk conc.),
$z_i$ is the valence of the counter-ions.

Since the charge density $\rho = \sum_i z_i e n_i$, then by substitution of equation 2,
\[
\rho = \sum_i z_i e n_i \cdot \exp \left( \frac{-z_i e \psi}{kT} \right) \tag{3}
\]

The combination of eq. 1 and 3 yields the Poisson - Boltzmann equation:
\[
\frac{d^2 \psi}{dx^2} = -\frac{4\pi e}{\varepsilon} \sum_i z_i n_i \cdot \exp \left( \frac{-z_i e \psi}{kT} \right) \tag{4}
\]

which upon the approximations:
1) $z_i e < kT$ (low surface potentials)
2) additive ion potentials

becomes,
\[
\frac{d^2 \psi}{dx^2} = \frac{4\pi z^2 e \psi}{kT} \sum_i z_i n_i \tag{5}
\]
where \[ k^2 = \frac{4\pi^2 e^2 \hbar}{\hbar c T} \] \hspace{1cm} \ldots (6)

so that \[ \frac{d^2 \psi}{dx^2} = \lambda^2 \psi \] \hspace{1cm} \ldots (7)

The solution to equation 7 is just,
\[ \psi = \psi_0 \exp(-\lambda x) \] \hspace{1cm} \ldots (8)

Here \( \lambda \) is the Debye characteristic length, a measure for the thickness of the diffuse double layer.

According to equation 8,
\[ \psi \rightarrow \psi_0 \] \hspace{1cm} \text{as} \hspace{1cm} \lambda \rightarrow 0

and \[ \psi \rightarrow 0 \] \hspace{1cm} \text{as} \hspace{1cm} \lambda \rightarrow \infty \]
APPENDIX C

Zeta Potential as a function of the electrolyte concentration

From Gouy - Chapman theory and Stern theory, the surface charge can be expressed as:

\[ \tau = \frac{\varepsilon kT \chi}{2\pi \varepsilon \kappa} \sinh \left( \frac{e \kappa}{2kT} \right) \] .................................(1)

Assuming that the surface potential can be approximated by the Zeta Potential, \( \zeta \approx \tau \), and that the argument \( \frac{e \kappa}{2kT} \) is small,

\[ \tau = \frac{\varepsilon kT \chi}{2\pi \varepsilon \kappa} \left( \frac{e \kappa}{2kT} \right) \] .................................(2)

But,

\[ \chi = 2 \varepsilon \sqrt{\frac{\tau \varepsilon Z^2 \kappa}{\varepsilon kT}} \] .................................(3)

(see Appendix B)

which upon substitution into eq. 2 yields:

\[ \tau = \frac{\varepsilon kT \chi}{2\pi \varepsilon \kappa} \left( \frac{e \kappa}{2kT} \right) \left( e \sqrt{\frac{\tau \varepsilon Z^2 \kappa}{\varepsilon kT}} \right) \] .................................(4)

which reduces to

\[ \tau = \frac{e \varepsilon J}{2\tau} \sqrt{\frac{\tau \varepsilon Z^2 \kappa}{\varepsilon kT}} \] .................................(5)

If the electrolyte is univalent, or \( z_1 = 1 \), equation 5 can be written as:

\[ \tau = \frac{e \varepsilon J}{2\tau} \sqrt{\frac{2\tau \kappa}{\varepsilon kT}} \] .................................(6)

This shows that \( \tau \) is proportional to \( J \sqrt{\kappa} \), therefore

\[ J \sim \frac{1}{\sqrt{\kappa}} \] .................................(7)
APPENDIX D

Kinetics of Coagulation

(From reference 19)

Consider a volume element of latex suspension. A total material balance is described by the Equation of Continuity as,

\[ \frac{f(N)}{f \Delta} + \frac{f'(N)}{f \Delta y} + \frac{f(N)}{f \Delta r} = 0 \tag{1} \]

where \( N \) is the number flux of particles and \( n \) is the number concentration, at steady state \( \frac{dn}{dr} = 0 \), and using spherical coordinates,

\[ \mathbf{v} \cdot \mathbf{N} = 0 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 N_A \right) \tag{2} \]

where \( N \) is the flux in \( R \) direction and \( r \) is the distance from the center. Then \( J_i \), the total number of particles colliding per unit time with some central particle is given by:

\[ J_i = 4\pi r^2 N_A \tag{3} \]

By definition,

\[ D \mathbf{v} = \frac{D n}{kT} \mathbf{F} \]

where \( D \) is the diffusion coefficient

\( k \) is the Boltzmann coefficient

\( T \) is the absolute temperature

\( \mathbf{F} \) is the force of interaction due to the potential \( v \)

Using spherical coordinates and substituting \( \frac{dv}{dr} \) for \( \mathbf{F} \)

\[ N_A \frac{dN_A}{dr} + \frac{D}{kT} \frac{dv}{dr} \tag{4} \]

Equation 3 then becomes,

\[ J_i = 4\pi r^2 \left( D \frac{dN_A}{dr} + \frac{nD}{kT} \frac{dv}{dr} \right) \tag{5} \]

Reducing equation 5,

\[ \frac{J_i}{4\pi r^2} = \frac{D dN_A}{dr} + \frac{nD}{kT} \frac{dv}{dr} \]
\[
\frac{J}{4\pi r^2} \exp\left(\frac{v}{\Delta T}\right) = \mathcal{D} \frac{d}{dr} \left( n \exp\left(\frac{v(r)}{\Delta T}\right) \right)
\]
\[
\frac{J}{4\pi} \int_{0}^{\infty} \frac{\exp\left(\frac{v}{\Delta T}\right)}{Dr^2} = \int_{0}^{a} d \left[ n \exp\left(\frac{v(r)}{\Delta T}\right) \right]
\]

Since at \( n_0 \), \( v(r) = 0 \)

Then
\[
J_1 = \frac{4\pi n_0}{\int_{0}^{\infty} \frac{\exp\left(\frac{v}{\Delta T}\right)}{Dr^2}}
\]

\[\text{(6)}\]

where \( a \) is the particle radius.
\[ \frac{J}{4\pi r^2} \exp \left( \frac{v}{kT} \right) = D \frac{dr}{dr} \left( \frac{\exp \left( \frac{v(r)}{kT} \right)}{r} \right) \]

\[ \int_{a}^{\infty} \frac{\exp \left( \frac{v(r)}{kT} \right)}{Dr^2} dr = \int_{a}^{\infty} \left[ -D \exp \left( \frac{v(r)}{kT} \right) \right] dr \]

Since at \( n_0 \), \( v(r) = 0 \)

Then

\[ J = \frac{4\pi n_0}{r^2 D} \]

\[ \dot{J} = \frac{4\pi n_0}{r^2 D} \]

\[ .............(6) \]

where \( a \) is the particle radius.