# THE OBSERVED STABILITY OF PVC PARTICLES
# IN n-BUTYLCHLORIDE

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# ABSTRACT

The mechanism by which PVC particles remained stable in n-butylchloride was investigated.

The PVC particles were made by aqueous emulsion polymerization with benzoyl peroxide initiator and polyvinyl alcohol surfactant. The particles were cleaned by ion exchange and their surface charge was found to be 0.068 ± 0.005 $C/m^2$. Dispersions of PVC in n-butylchloride were prepared by two methods. In the first, the particles were dried in an oven. The dried particles were redispersed in n-butylchloride via sonication. This produced a dispersion consisting of 0.26 $kg/m^3$ of PVC particles with an arithmetic volume average diameter of 317 nm and a standard deviation of 93 nm. The second method involved dialyzing the cleaned aqueous latex with methanol and then with n-butylchloride. The dialysis method was inferior to the sonication method. The dialysis method was time consuming, it produced a dispersion with large particle diameter, the dispersion was contaminated with water and methanol and surface species were removed by the methanol.

The particles were found to be stabilized by an electrostatic mechanism. This was verified by observing that the particles migrated to the positive electrode when exposed to a potential difference of 1000 V. A surface potential of 0.203 V was calculated for the particles from mobility measurements and the Huckel equation.

The charge separation that must occur to allow the particles to have the negative charge is hypothesized to be a result of organic molecules such as PVC-PVA oligomers that dissolve from the particles and form micelles. These molecules were readily soluble in methanol and only slightly soluble in n-butylchloride. As a result, when the dispersion was washed with methanol, the particles flocculated. The presence of these species in the dispersant was supported by evidence from ultra-violet, infra-red and nuclear magnetic resonance spectroscopy. The electronegative groups in the micelles provide a reasonably polar environment for hydrogen ions to exist. These hydrogen ions became the countercharge for the negatively charged particles.

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# CHAPTER 1

# INTRODUCTION

## 1.1 General Issues And Background

Processing of PVC involves uniformly blending additives into the resin. Additives vary in nature and function. They may be liquids, sticky or waxy solids, or dry powders. Typical additives include plasticizers, fillers, flame retardants, colorants, lubricants and solid reinforcements. Matthews [19] had observed that particle size, size distribution and shape greatly affect the flow behaviour of particles and the way in which they compact together, soften and melt. Particles with a wide size distribution tend to pack closer and will resist intimate mixing with additives to a greater extent than monodisperse particles. As a result, the particle size distribution of aggregates is likely to have a significant effect on solids blending.

Zichy [38] studied the morphology of polymerizing vinylchloride droplets and concluded that the colloidal stability of the precipitated polymer is the dominant influence on internal aggregate formation. Zichy also concluded by observing the size of the internal grains that there must be a repulsive force between the precipitated polymer particles. More attention should therefore be paid to the control of the particle size distribution of PVC resins through an understanding of the colloidal stability of the particles.

PVC is a very viscous polymer which is difficult to process in commercial equipment [12]. The difficulty occurs mainly because the polymer degrades above 200°C where the temperature is high enough to give good flow. PVC resin producers are constantly seeking new ways to improve the processability of the resin. Commercially attractive blend times of PVC resin should be two to four minutes or less [12].

In North America, PVC resin is produced mainly by suspension polymerization. In this process, droplets of vinylchloride monomer are suspended in water by agitation, and the droplets are stabilized with a surfactant, usually polyvinyl alcohol. The initiator dissolves into the monomer to start the polymerization reaction. As the polymer grows, it reaches a critical size that is no longer soluble in the monomer. Polymer particles therefore precipitate out. To make polymer that will have a small blend time, the precipitated particles must not flocculate. Thus, the control of particle stability within the monomer droplets is a key issue.

It is important to understand the factors that affect the stability of PVC particles formed within the vinylchloride monomer droplets during suspension polymerization. If the particles are stable, then understanding why this is so can help resin producers to further improve the stability. On the other hand, if the particles are not stable, then ways of stabilizing them must be found. Either way, the ultimate goal will be to improve the blend time of the resin.

## 1.2 OBJECTIVES

Originally, the objective of this research was to investigate the role that commercial stabilizers and other polymers play in forming a stable dispersion of PVC particles in n-butylchloride. This system was chosen to model PVC particles in vinylchloride monomer during suspension polymerization. N-butylchloride, a dangerous chemical in its own right, was substituted for vinylchloride because of its even greater potential health hazard. During the preparation of the PVC dispersion in n-butylchloride, it was observed that a very stable dispersion resulted without any stabilizers being added. The particle concentration in the prepared dispersion was significantly lower than in an aqueous dispersion of PVC particles. This interesting observation provided an opportunity to study the phenomena.

The objective of the research was therefore modified to determine the mechanism by which PVC particles made by aqueous emulsion polymerization were able to remain stable in n-butylchloride.

# CHAPTER 2

# LITERATURE REVIEW AND THEORY OF STABILIZATION IN NON-AQUEOUS MEDIA

This chapter describes the theory behind colloidal stability. An understanding of this phenomenon is necessary to determine the mechanism by which the PVC particles can remain in a stable dispersion. Consequently, the tests and measurements described in chapter 3 are based on this knowledge.

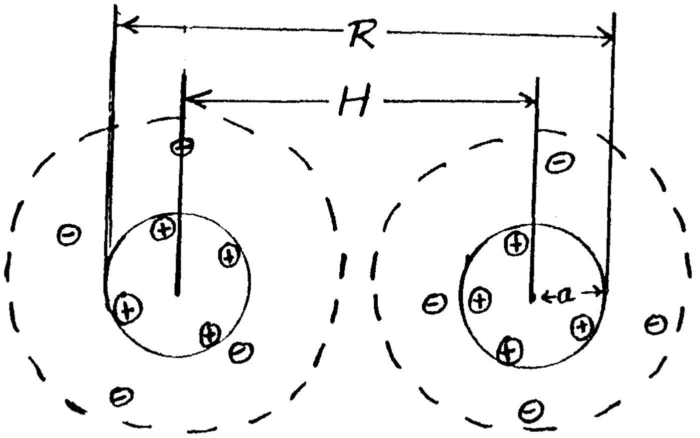
## 2.0 Colloidal Dispersions.

Colloidal dispersions are very important to mankind in many respects. They serve us in such things as paints, inks, glues, emulsions, polymer dispersions, detergents and lubricants. A colloidal dispersion consists of particles in the size range 1-1000 nm dispersed in a fluid. If the dispersed phase (particles) does not coagulate but remains as discrete, single particles for a long time (months), then the dispersion is said to be stable. This stability is achieved when a strong enough, long range repulsive force exists between the particles, preventing them from coming into the van der Waals attractive force field which usually extends about 5 - 10 nm from the particle surface [24].

In general, there are three ways of creating this repulsive force; by electrostatic repulsion, by steric repulsion, or by electrosteric repulsion. The latter is due to steric stabilizers that have charged groups attached to them. This has the effect of combining steric and electrostatic repulsive forces. Electrosteric repulsion will not be discussed further in this thesis. The objective of the next two sections is to review the literature on electrostatic and steric stabilization including a summary of the theory behind them.

## 2.1 ELECTROSTATIC STABILIZATION

Unless it can be proven otherwise, it should be assumed that all surfaces are charged [37]. The principle of electroneutrality demands that the net charge in the dispersion medium be of equal magnitude, but opposite sign to that of the particles. The counterions around the particles form the electric double layer which mutually repulse each other, thus preventing close approach of the particles which may lead to coagulation. This is illustrated in Figure 1. The further out the double layer extends, the further apart the particles are kept from each other and hence the stability will be increased.



$u = H/a$
$s = R/a = (H+2a)/a$

**Figure 1:** This figure illustrates the repulsion between the electric double layers that keep the particles stable.

As a result, if the ionic strength of the dispersion medium is low, one would expect the dispersion to be more stable. The spatial extension or thickness of the electric double layer is measured by the Debye length (1/K). This is the distance one must move from the particle surface out into the bulk diffuse layer such that the potential has dropped to 1/e times its value close to the surface of the particle.

In organic media, there are very few ionic entities in existence and as such, the Debye length is larger than 1 $\mu$m which is relatively large when compared to aqueous media [31]. As such, electrostatic stabilization can be very effective in organic media. This is usually impractical however, because it is very difficult for a charge to exist on a particle in an organic medium; apolar solids in apolar liquids should be uncharged according to the ionic mechanism. Parfitt and Peacock [25] contend that there is no reliable experimental method of establishing this. On the other hand, Fuoss and Kraus [12] and La Mer and Downes [17] have shown that ions do exist in hydrocarbon media. They contend that certain oil loving, or lipophilic substances can form micelles in hydrocarbon media in which the ions can exist. The formation of these micelles is likely to be very dependent on the presence of trace amounts of water. When charge occurs, it is usually due to either the dissociation of surface groups or the adsorption of ionic surfactants [19].

Non-aqueous dispersions are not as well understood as their aqueous counterpart. One interesting complication, for example, is the effect of moisture on the stability of organic dispersions.

The rest of this section will discuss the DLVO theory which mathematically models electrostatic stabilization. The literature on the effects of moisture on the stability of the dispersions will also be reviewed.

### 2.1.1 DLVO Theory

A quantitative theory of electrostatic stabilization was independently formulated by Deryaguin and Landau [8], and Verwey and Overbeek [34] around the same time. This theory, now known as the DLVO theory, has become generally accepted because it is theoretically sound and appears to be in sufficient agreement with many experimental facts [19]. The DLVO theory says that the interaction between two particles is a superposition of the electrostatic repulsive energy and the van der Waals attractive energy. A compilation of expressions for these energies under different circumstances is given by Woods [37].

The electrostatic repulsive component of the interaction energy between two spheres of equal size approaching each other is shown in equation (1) [22]. This equation is valid for organic media where Ka << 1.

$$V_R = \frac{4\pi\epsilon_r\epsilon_o a^2}{H + 2a} Y_o^2 \beta e^{-KH} \tag{1}$$

$$\beta = \left(\frac{s^9 + s^6 + 5s^4 + s}{s^9 + s^8 + 2s^6 + s^5 + 6s^4 + 5s^3 + 3s + 1}\right), \tag{2}$$

for Ka << 1

$$K = \left(\frac{e^2 \Sigma(n_i z_i^2)}{\epsilon_r\epsilon_o kT}\right)^{\frac{1}{2}} \tag{3}$$

$$n_i = N(i)N_A \tag{4}$$

$$s = (H + 2a)/a \tag{5}$$

where: $a$ = particle radius [m]

$H$ = shortest distance between the particle surfaces [m]

$V_R$= electrostatic repulsion [J]

$\epsilon_r$= relative permittivity

$\epsilon_o$= Permittivity of free space $[C^2/(Jm)]$

$Y_o$= surface potential of particle [V]

$K$ = inverse thickness of the electric double layer or the inverse debye length $[m^{-1}]$

$e$ = charge on the electron [C]

$n_i$= number of ions per $m^3$

$N(i)$= molar concentration of ions $[mols/m^3]$

$N_A$ = Avogadro's constant $[mol^{-1}]$

$k$ = Boltzman constant

$T$ = absolute temperature [K]

$\beta$ = accounts for the deformation of the two double layers when they overlap and is a function of H.

As the particles approach, their double layers overlap and two types of possible encounters can occur. In the first case, the surface potential remains constant. Lyklema pointed out that the surface charge will decrease to maintain this constant potential. This is possible through the rapid desorption of ions from the surface. In the second case, the surface potential increases to maintain a constant surface charge. It is not known which of the two best represents what occurs in organic media, although the constant charge encounter is more likely because rapid desorption of ions as required by the constant potential encounter is not consistent with organic media. The actual mechanism is also dependent on the source of the charge. If the source of the charge is end groups embedded in the surface, then constant charge is the more likely mechanism. In equation (2), $\beta$ accounts for the overlap of the electric double layers. The overlap involves only the outermost parts of the double layers and the stability calculations are not sensitive to whether the constant charge or the constant potential approach is used [25].

In organic media, the double layer extends out a large distance from the surface of the particle relative to the size of the particle. It is therefore assumed that KH <<1 and therefore $e^{-KH} \approx 1$. Values of the surface potential, $Y_o$, are needed to solve Equation 1. Because of the large debye length (> 1 $\mu$m), the decay of the potential as one goes out into the diffuse layer is small. Hence for all practical purposes, the surface potential is equal to the experimentally measured zeta potential [19]. Equation (1) becomes:

$$V_R = \left(\frac{4\pi\epsilon_r\epsilon_o a^2}{H + 2a}\right) Z^2\beta \qquad (6)$$

where Z = Zeta potential

At very low levels of surface charge, the use of a continuous double layer model is open to doubt [19]. This problem occurs because so few ions make up the surface charge and double layer.

The van der Waals attraction component for uniform spherical particles are given in equation (7) [6].

$$V_A = - \frac{A}{6} \left\{ \frac{2a^2}{4Ha+H^2} - \frac{2a^2}{(2a+H^2)} + \ln \left( \frac{4Ha+H^2}{(2a+H^2)} \right) \right\}$$

where,

A = effective Hamaker constant [J] corrected to allow for particle-particle and dispersion medium-particle interactions.

The effective Hamaker constant of the particle P in the liquid medium M is calculated from the Hamaker constants of the pure materials in vacuum V. Thus,

$$A_{PM} = \{ \sqrt{A_{PV}} - \sqrt{A_{MV}} \}^2 \qquad (8)$$

The Hamaker constant can be estimated experimentally or it can be estimated by pairwise summation of the molecular energies between the two bodies. The attractive energy is affected by the medium. This is so because propagation of electromagnetic waves is influenced by the dielectric properties of the medium and account must be taken for the medium displaced by the particles. Electromagnetic waves take a finite time to propagate through the medium. At large particle separations, the propagation time becomes significant. However, this effect can be ignored since at large separations, the attractive energy becomes negligible compared to the repulsive energy.

Cooper [6] gives equations for calculating $V_R$ and $V_A$ when the particles differ in terms of size and surface potential. These equations are valid for surface potentials less than 25 mV and Ka > 10 only.

Adding $V_R$ and $V_A$ together gives the total energy interaction between two spherical particles of equal size. To get a practical theoretical measure of how stable a particular dispersion is, McGown and Parfitt [22] defined the stability ratio W. This compares the actual rate of coagulation of the particles to the rate of rapid coagulation when there is no repulsive forces. The expression is shown in equation (9).

$$W = \frac{\int_2^\infty 2(\exp((V_A+V_R)/kT)/s^2)\,ds}{\int_2^\infty 2(\exp(V_A/kT)/s^2)\,ds} \tag{9}$$

Coagulation is instantaneous when W = 1. As W increases, the stability increases.

Any change in conditions such as the valence or concentration of ionic entities present, that increases the repulsion, will increase stability. On the other hand, the van der Waals attraction is fixed for a particular dispersion and cannot be manipulated.

### 2.1.2 Factors affecting electrostatic stabilization

From the Equations given in section 2.1.1, it can be shown that the electrostatic stabilization is dependent on several parameters. As a result, increasing the dielectric constant, particle radius, surface charge and surface potential will increase the particle stability while increasing the particle concentration, ionic strength of medium, temperature and the Hamaker constant will decrease the particle stability. These effects are described in detail by Woods [37].

There are other factors which affect the particle stability that are not obvious from the DLVO theory. One that is particularly important to stability in organic media is moisture. This will be discussed here in some detail.

#### 2.1.2.1 Effect of moisture on electrostatic stabilization.

Water is insoluble in many organic solvents, and will adsorb to the particle surface in an organic dispersion. This affects the electrokinetic properties. These effects are documented in Table 1.

Table 1: The effect of moisture on organic dispersions.

| | |
|---|---|
| Lyklema [19] | Water adsorbs on the particle surface making it more basic than the solvent. The particle becomes more positive. |
| Parfitt & Peacock [25], Vincent [35], McGown & Parfitt [22], Micale, Lui & Zettlemoyer [23] | The presence of moisture at the solid-liquid interface and possibly in the bulk liquid phase has a dramatic effect on the charge of the particle, usually making it more positive. |
| McGown, Parfitt & Willis [21] | Rutile dispersed in Aerosol-OT and p-xylene mixtures with traces of moisture was positively charged. |
| McGown & Parfitt [22] | Rutile dispersed in Aerosol-OT and p-xylene mixtures under strictly dry conditions was negatively charged. |
| McGown & Parfitt [22] | Trace water has been shown to actually reverse the sign of the charge on a particle. |

Table 1 cont'd: The effect of moisture on organic dispersions.

| | |
|---|---|
| Vincent [35] | Trace impurities of any polar materials, not only water, can affect the magnitude and sign of the surface charge. |
| Micale, Lui & Zettlemoyer [23] | Used trace water to vary the zeta potential of rutile in heptanol.<br>Found that the zeta potential will decrease with time to a constant value after about 200 minutes.<br>Plotted zeta potential versus fractional water coverage of the particle surface and found that a peak occurred at a fractional water coverage of 0.08. At 0.08 fractional water coverage, the interaction of the heptanol with the rutile surface was determined to be a maximum from infra-red analysis of OH bending band at 1535 $cm^{-1}$.<br>Size of aggregates were found to be a minimum at the fractional water coverage of 0.08. |
| Labib & Williams [15] | Trace water on the surface of $SiO_2$, $TiO_2$ and $Al_2O_3$ increased the zeta potential. |
| McGown & Parfitt | Used trace amounts of water to vary the |

Table 1 cont'd: The effect of moisture on organic dispersions.

| | |
|---|---|
| [22] | potential of rutile in Aerosol-OT and p-xylene mixtures. |
| Lyklema [19] | Water occupies the particle surface and therefore competes with the adsorption of other molecules. It also influences surface dissociation and conductance thereby influencing surface potential and electrokinetic properties. |
| Lewis & Parfitt [18] | Removed molecular water from the surface of rutile by heating above 200 C. |
| Micale, Lui & Zettlemoyer [23] | The amount of energy necessary to disperse a system is a function of the amount of moisture adsorbed on the particle surface. |

While the evidence seems consistent, the phenomenon is not well understood. Lyklema [19] considered four possible explanations for the phenomenon:

(1) Water adsorbs onto the particle surface making it more positive.

(2) Water is solubilized in the liquid phase by surfactants which redistributes the surfactant between adsorbate and solvent.

(3) Thick adsorbed water layers coalesce when two particles meet causing aggregation.

and (4) Water molecules may change the nature of the particle surface thus increasing or decreasing the sites available for adsorbing polymers or surfactants.

Any one or more of the above may be the mechanism by which water influences the stability of non-aqueous dispersions. Labib and Williams [15] tried to explain the mechanism by considering that the donicity of the solid changes with respect to the liquid when water is present. This affects the surface charge and ultimately the stability of the dispersion.

There is probably no single explanation for the behaviour of organic dispersions in the presence of trace amounts of water. However, it is important in conducting research to be aware of the effects that moisture could have on an organic dispersion as described above. One challenge is that it is extremely difficult to control or remove trace amounts of moisture in an organic dispersion.

#### 2.1.2.2 Effect of Polydispersity.

Cooper examined the effects of polydispersity on the stability of a colloidal dispersion. He applied the DLVO theory to two particles having size i and j coming into contact using equations for $V_A$ and $V_R$ which considers two particles of different sizes interacting. The stability ratio of particles of two different sizes interacting is calculated in the same manner as with monodisperse particles described earlier. A simulation was done to compare the stability ratio of dispersions having varying average particle size and particle size distribution.

The particle size distribution was assumed to be Gaussian. The probability that two particles will come into contact is a function of their concentration and size. The probability of occurrence of particle i, $P_i$, is given by:

$$P_i = \frac{1}{\sqrt{(2\pi\sigma)}} \exp\left(- \frac{(X_i - \hat{X})^2}{2\sigma^2}\right) \tag{10}$$

where, $X_i$ = radius
$\hat{X}$ = number average radius
$\sigma$ = standard deviation about the number average radius.

The probability that particle i and j will interact, $P_{ij}$, is given by the product of the individual occurrence probabilities corrected for the particle sizes. It is known that smaller particles disappear more rapidly than larger ones. Hence,

$$P_{ij} = P_i P_j \, (a_i + a_j)^2/(4a_i a_j) \tag{11}$$

such that,

$$\Sigma_{i,j} \, P_{ij} = 1.0 \tag{12}$$

The overall stability ratio, $W_T$, is found by summing the $W_{ij}$'s over the whole range of i's and j's.

$$1/W_T = \Sigma (P_{ij} / W_{ij}) \tag{13}$$

The result of Cooper's [6] simulation clearly shows that as the standard deviation increases, the stability ratio decreases. Also, the rate of decrease of $W_T$ increases as the average particle size increases. One problem with the simulation is that it is valid only for the initial stage of coagulation since the particle size distribution is changing with time. A Monte-Carlo simulation would be more relevant here although the level of complexity of the simulation will increase tremendously.

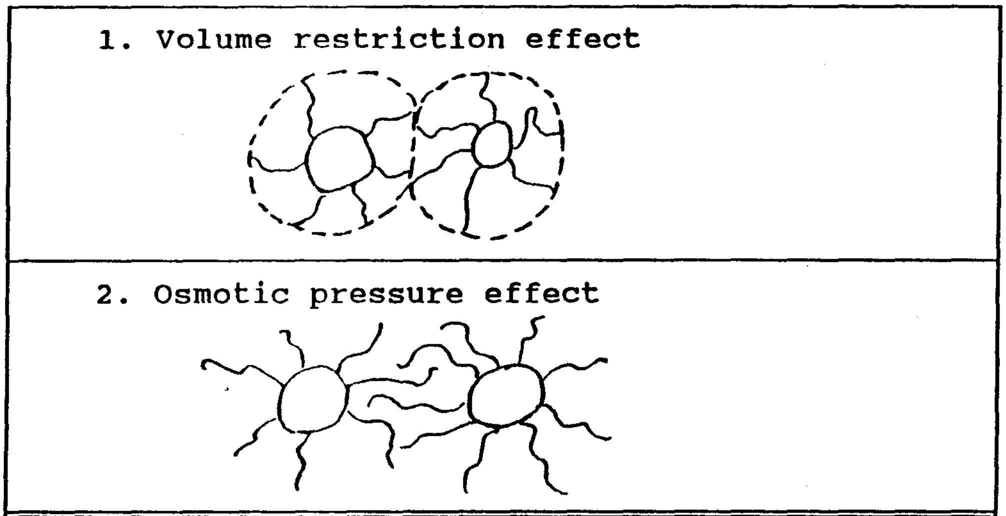
## 2.2 STERIC STABILIZATION

Steric stabilization is achieved by attaching macromolecules to the surface of the particles. A good stabilizer must be well anchored to the particles and must also extend out into the dispersion medium. This is achieved by grafting or physical adsorption. The best steric stabilizer is a block or graft co-polymer. The components of the co-polymer must be such that one is nominally insoluble in the dispersion medium so as to reside on the particle surface and act as an anchor for the other which is soluble and will extend out into the dispersion medium to act as the stabilizing moiety. Homopolymers are therefore generally poor stabilizers because of the conflicting requirements that the dispersion medium be a poor solvent to ensure strong adsorption of the stabilizer onto the particle and also be a good solvent to impart effective stabilization [14].

Figure 2 illustrates two ways in which steric stabilizers can impart stability to particles. In the first case which is known as the volume restriction effect, the stabilizing moieties are mutually repulsive. The polymer diffuse layers do not intermingle but become compressed as the particles approach. This causes a loss in configurational entropy which results in a repulsion. In the second case, polymer loops and chains interpenetrate. This causes less solvent-polymer interactions and more polymer-polymer interactions. Either a repulsion or an attraction may result depending on the specific interactions. This is called the osmotic pressure effect and does not always result in a stable dispersion.

When particles collide, the stabilizing moiety may try to move from the stress zone and coagulation may result. This is prevented by the anchor polymer and a full surface coverage which ensures that desorption and lateral movement of polymer does not occur respectively.

Suitable polymeric stabilizers can be chosen with the help of solubility parameters. These are governed solely by the heat of mixing of liquids or amorphous polymers and make no assumptions about polarity, solvation, or association. The



1. Volume restriction effect

2. Osmotic pressure effect

Figure 2: This figure illustrates two ways in which adsorbed polymers may impart steric stability to particles.

solubility parameter, $\delta$ is given by the expression:

$$\delta = (\Delta E / V)^{1/2} \tag{14}$$

where $\Delta E$ = energy of vaporization to a gas at zero pressure

$V$ = molar volume

A non-crystalline polymer will dissolve in a solvent of similar $\delta$ [4]. If the difference in solubility parameters between solvent and polymer is greater than about 3.5 to 4.0 $(J/cm^3)^{1/2}$, the polymer will not dissolve [2]. Burrell [4] lists several methods of estimating $\delta$ as well as a long list of $\delta$'s for various solvents and polymers.

### 2.2.1 Factors affecting steric stabilization

If steric stabilization is to be of practical use, it must be known under what conditions incipient flocculation will take place. Croucher and Hair [7] noted that it is now well established that the critical flocculation point for dilute dispersions correlates strongly with the theta-point of the stabilizing polymeric moiety in free solution, providing that desorption of the stabilizer is not a complicating factor. Theta conditions therefore represent the practical limit for the stability of such dispersions, assuming that multipoint anchoring is not significant. Napper [24] has conducted a comprehensive review of the literature and his conclusions are as follows:

Sterically stabilized dispersions may be flocculated by:

(1) changing the temperature

(2) changing the pressure

(3) adding a miscible non-solvent for the stabilizing moieties to the dispersion medium.

The transition from long-term stability to catastrophic flocculation occurs abruptly at the critical flocculation point (cfp). If the colloidal particles are:

(1) small in size ( $< 500$ nm )

(2) fully coated by well-anchored, high molecular weight polymer ($MW > 10^3$),

then the observed cfp is essentially independent of:

(1) the volume fraction of particles

(2) the chemical nature of the particles

(3) the chemical nature of the anchor polymer

(4) the particle size

(5) the molecular weight of the stabilizing moieties.

This is irrespective of whether the dispersion is aqueous or non-aqueous.

Flocculation at the cfp is reversible suggesting that the van der Waals attraction between the core particles is not responsible for flocculation. The cfp is dependent upon the surface coverage by the stabilizing chains. It becomes progressively easier to flocculate the dispersion as the surface coverage decreases. This may be due to the surface migration of the stabilizing chains away from the interaction zone during a Brownian collision. Coagulation can occur when the surface coverage is small in dispersion media that are very good solvents for the stabilizing moieties. The polymers will migrate easily from the interaction zones causing instability. Instability also appears to be induced by van der Waals attraction between the core particles, although bridging might also be implicated in some systems.

For low molecular weight stabilizing moieties and relatively large particle size, stability appears to be controlled by the relatively weak London dispersion attraction between the core particles. Consequently, the cfp in these systems depends on particle size and volume fraction. Dilute dispersions are more stable than concentrated dispersions.

Lambe, Tadros and Vincent [16] observed that stability and flocculation behaviour of dispersions stabilized by polymers adsorbed from solution in which free polymer remains, is more complex than for those systems in which the stabilizing polymer chains are terminally anchored to the surface and there is no free polymer in the continuous phase. For the former class of systems, the conditions (eg. temperature) under which flocculation is achieved may depend not only on the particle volume fraction, but also on the polymer concentration (for a given molecular weight). They feel that this may be partly due to multilayer adsorption of polymer for which evidence was found by van den Boomgaard, et. al. [28].

As the polymer concentration increases, an increase in stability is expected as more polymer is available to adsorb onto the particle surfaces, thus strengthening the steric barrier. However, after the particle surface becomes saturated and excess polymer reside freely in the solvent, a different phenomenon is observed. The actual behaviour is dependent on a volume restriction effect.

Hirtzel and Rajagopalan [14] noted that free polymer at low concentrations can add stability to or destabilize dispersions. Flocculation is favored thermodynamically when the polymer molecules are excluded from the interparticulate region. In such cases, mixing of almost pure solvent (from the interparticulate region) with the bulk solution decreases the free energy of the system and promotes contacts between the particles. The polymer molecules promote "phase" separation under these conditions. That is, a particle-rich phase (floc) and a particle-poor phase are formed. This phenomenon is known as depletion flocculation. The opposite effect, when rejection of polymer molecules from the interparticulate region is not favored thermodynamically, as in the case of good solvents, is known as depletion stabilization.

The conflicting actions of steric and depletion effects can mean that flocculation is possible in a restricted range of polymer concentrations; that is, at very low polymer concentrations, steric effects will dominate while at higher concentrations where free polymer exist in solution, depletion effects will take over.

Croucher and Hair [7] established that the stability of a non-aqueous dispersion is independent of molecular weight of the polymeric stabilizer. However, Napper [24] estimated a significant van der Waals force for low molecular weight stabilizers (MW less than $10^4$) when the particles are relatively large (greater than 1 $\mu$m). In these cases, stability will decrease with particle concentration since coagulation will occur due to a significant van der Waals force (10 kT).

There is disagreement about the dependence of the stability of the dispersion on the particle concentration. Some report no dependence, while others report a weak dependence [24], [14]. There is probably some dependence when the molecular weight of the stabilizer is low enough for the London - van der Waals forces to be effective. Then the particle size and concentration are important.

As the temperature of the dispersion is changed, the stability will vary. An upper and lower temperature boundary exists beyond which the dispersion will flocculate. It has been verified experimentally that a strong correlation occurs between these critical flocculation temperatures and the corresponding theta temperatures [24]. Croucher and Hair [7] found the upper and lower critical flocculation temperatures to be -19°C and 130°C respectively for polyacrylonitrile particles dispersed in n-butlychloride and stabilized with poly(alpha-methylstyrene).

### 2.2.2 Polymer Solution Thermodynamics.

The role that polymers play in steric stabilization is explained by polymer solution thermodynamics. Flory and Huggins formulated the most popular theory that predicts the Gibbs free energy of mixing of pure polymer with pure solvent [2].

Thus, $\Delta G^M = \Delta H^M - T \Delta S^M$ (15)

In this so called "lattice approach," the polymer segments and solvent molecules are placed on a grid in three dimensional space. The lattice sites are all assumed to be of the same size, which is taken to be of the same size as the solvent molecules. The polymer chains are assumed to be monodispersed, and each chain occupies x contiguous sites. It should be noted that x and the degree of polymerization are not the same in general.

Thus, the number of lattice sites is given by:

$$n_0 = n_1 + x\, n_2 \tag{16}$$

where 1 refers to solvent molecules,
2 refers to polymer molecules.
x is approximately $V_2/V_1$
V is molar volume

The configurational entropy is calculated from the number of different ways by which this placement can be accomplished. If pure crystal-like, well ordered polymer is mixed with pure solvent, the entropy change is given by the Boltzman equation.

$$\Delta S = k\, (\ln \Omega_1)\, /\, \Omega_2 \tag{17}$$

where $\Omega$ is the total number of ways in which the polymer molecules could be mixed with the solvent.

If only combinatorial effects are considered and any specific interactions between the polymer and solvent are ignored, it can be shown that: [24]

$$\Delta S^M = -k \{ n_1 \ln v_1 + n_2 \ln v_2 \} \tag{18}$$

where $v_1 = n_1 / (n_1 + xn_2)$ (19)

= solvent volume fraction

$v_2 = n_2 / (n_1 + xn_2)$ (20)

= polymer volume fraction

It is also assumed that the solvent and polymer possess identical free volume fractions and that the total free volume is conserved on mixing.

The enthalpy of mixing is determined by the van Laar approach.

$$\Delta H^M = n_1 v_2 X_1 kT \tag{21}$$

where $X_1$ = interaction parameter

The Flory-Huggins expression for free energy of mixing is therefore written as

$$\Delta G^M = kT \{ n_1 \ln v_1 + n_2 \ln v_2 + n_1 v_2 X_1 \} \tag{22}$$

Since mixing is usually endothermic, $X_1$ is normally positive and therefore opposes mixing. The combinatorial terms are negative due to the log terms and therefore promote mixing. The volume fraction of solvent is large, and hence $n_1 \ln v_1$ is the dominant term. This means that the mixing of the polymer and solvent occurs because of the additional space available to the solvent when the domains of the polymer molecules become accessible to the solvent.

According to the Flory-Huggins theory, the detailed structure of the polymer is irrelevant. This is in contrast to some claims that polymer molecules dissolve as a result of their increase in configurational entropy in solution.

Solubility occurs when the free energy of mixing is negative. The enthalpy of mixing can be written as [2]:

$$\Delta H^M = v_1 v_2 (\delta_1 - \delta_2)^2 \qquad \text{.....(23)}$$

where $v$ : volume fraction

$\delta^2$: cohesive energy density or, for small molecules, the energy of vaporization per unit volume.

1 : solvent

2 : polymer

As a first approximation, and in the absence of strong interactions such as hydrogen bonding, solubility can be expected if $(\delta_1 - \delta_2)$ is less than 3.5 to 4.0 $(J/cm^3)^{1/2}$, but not appreciably larger [2]. Thus, $\delta$ can be used as a criterion to determine if a polymer is expected to dissolve in a solvent. As such, $\delta$ is called the solubility parameter. Burrell and Immergut [4] gave several equations for estimating solubility parameters.

Flory defined enthalpy ($K_1$) and entropy ($Y_1$) of dilution parameters [2]:

$$\Delta H_1 = RTK_1v_2^2 \tag{24}$$

$$\Delta S_1 = RY_1v_2^2 \tag{25}$$

where $\Delta H_1$ and $\Delta S_1$ are the negative partial molar heats of dilution such that

$$\Delta G_1 = \Delta H_1 - T\Delta S_1 = (\mu - \mu^o)^E \tag{26}$$

But the excess chemical potential involved in 2-body interactions is:

$$(\mu_1 - \mu_1^o)^E = -\pi V_1^E \approx -(½ - X_1)v_2^2RT \tag{27}$$

Hence $(½ - X_1) = Y_1 - K_1$ (28)

The osmotic pressure is given by:

$$\pi/C_2 = RT(1/M_2 + v_2^2/V_1(1/2 - X_1)c_2 + \ldots..) \tag{29}$$

where $c_2$ = polymer concentration

$M_2$ = molecular weight of polymer

$v_2$ = partial specific volume = $V_2/M_2$

The second virial coefficient,

$$\beta_2 = v_2^2/V_1(1/2 - X_1), \tag{30}$$

becomes zero when $X_1 = ½$. It should be noted that under these conditions, the higher coefficient does not necessarily vanish although they are usually negligible.

Flory and Huggins defined the theta point as that condition when the second virial coefficient is zero, that is, when $X_1 = \frac{1}{2}$. This condition occurs at a particular temperature, called the theta temperature. From the Flory-Huggins theory,

$$\tfrac{1}{2} - X_1 = Y_1 - K_1 = Y_1(1 - \theta/T) \tag{31}$$

where $\theta = (K_1/Y_1)T$. (32)

Hence if $X_1 = \frac{1}{2}$, $T = \theta$.

When $X_1 < \frac{1}{2}$, the solvent is a better than theta-solvent and when $X_1 > \frac{1}{2}$, it is a worse than theta-solvent.

At the theta-point, the polymer molecules obey the ideal van't Hoff equation of state, that is, the second virial coefficient is zero. This ideal behaviour does not hold beyond polymer concentrations of several percent. This is because the higher virial coefficients involving the higher order, many-body interactions are then no longer negligible.

Napper [24] states that the theta point represents the theoretical limit of solubility of a polymer of infinite molecular weight. He said that it is important because:

(1) the polymer chains are able to telescope one another with impunity insofar as free energy changes are concerned at the theta-point.

(2) the theta-point identifies the region wherein the segmental interactions switch over from being mutually repulsive to

being mutually attractive.

(3) the polymer molecules adopt their unperturbed dimensions at the theta-point since the polymer segments behave as if they were volumeless lines in space.

Although the Flory-Huggins theory is widely accepted, it fails in several respects. First of all, $X_1$ is a function of the polymer concentration and is therefore not a constant as was assumed. Secondly, $X_1$ was introduced as an enthalpic term, yet for many systems, the interaction free energies embodied in $X_1$ are predominantly entropic in origin. Even at room temperature, there is a strong decrease in entropy on mixing, which is not properly accounted for by the Flory-Huggins theory. Finally, it is observed that phase separation occurs not only on cooling, but also on heating which is in direct contradiction of the Flory-Huggins theory. According to the theory, the mixing of a polymer with a solvent is governed by the combinatorial entropy ($\Delta S^{comb}$), which is positive. As a result, its contribution to the mixing free energy ($-T\Delta S^{comb}$) increases in absolute value with temperature. Thus, polymer solution should become more stable on heating while only cooling should result in phase separation.

# CHAPTER 3

# EXPERIMENTAL PROCEDURE, RESULTS AND DISCUSSION

As mentioned in Chapter 1, the objective of this thesis is to determine the mechanism by which PVC particles made by aqueous emulsion polymerization were able to remain in a stable dispersion in n-butylchloride. This chapter will explain how the aqueous dispersion was cleaned and redispersed in n-butylchloride and the tests and measurements that were carried out on the resulting dispersion to determine the nature of the dispersion's stability. Three models were hypothesized to explain the dispersion's behaviour, and the results of the tests and measurements was shown to be consistent with one of these models.

The chemicals used in this research are potentially hazardous. Appendix 1 outlines the safety precautions that were taken.

## 3.1 Preparation of Dispersion

The latex was obtained from B. F. Goodrich and was made by aqueous emulsion polymerization. The particle size distribution was expected to be monodisperse. The dispersion may contain emulsifier, buffer, residual initiator and its decomposition products. The polymer particle surface may contain both physically adsorbed emulsifier molecules and chemically bound emulsifier and initiator groups. When the emulsifier and inorganic salts are removed from the aqueous phase and particle surface, the result would be a system of particles stabilized only by chemically bound emulsifier and initiator groups. The surface should therefore have a constant charge.

The procedure for cleaning latex is given by Vanderhoff, Van Den Hul, Tausk and Overbeek [30]. They concluded that ion exchange is a better method for cleaning the latex than dialysis. Van Den Hul and Vanderhoff [29] pointed out that rigorous purification of the ion exchange resin is necessary to avoid contamination with leached polyelectrolytes. The method used to clean the latex was recommended by these sources.

The ion exchange procedure used two resins simultaneously for cleaning the latex; a 20-50 mesh Dowex 50W-x8 sulfonic acid resin and a 20-50 mesh Dowex 1-x4 benzyltrimethylammonium resin (from DOW Chemicals). The resins were conditioned before they were used by eluting several times with distilled water, methanol, 3N sodium hydroxide solution and 3N Hydrochloric acid. The procedure is described in detail in Appendix 2.

The latex was agitated several times with newly conditioned ion-exchange resins until the conductivity of a 0.004 volume % clean latex in distilled water was constant at 7 ± 3 μS. At this point, it was assumed that the latex was clean. A detailed description of these procedures is given in Appendix 2.

The latex was redispersed in n-butylchloride by two different methods to control moisture. The first involved oven-drying and redispersing the particles with sonic waves in a nitrogen blanketed glove box. The second involved dialyzing the aqueous latex with methanol and n-butylchloride using Spectapor cellulose dialysis tubing. Details of these procedures are contained in Appendix 2.

The sonication method resulted in a stable dispersion in 48 hours starting with the oven dried particles. The particle concentration in the dispersion was 0.26 g/L. The dialysis method was more time consuming. It took 5 successive 24 hour batch processes to replace the aqueous dispersant with methanol and a further 4 successive 24 hour batch processes to replace the methanol with n-butylchloride. The measured particle concentration in the resulting stable dispersion was 0.38 g/L.

The dispersion made by sonication was adopted for this research because it had several advantages over that made by the dialysis procedure. First of all, the dialysis process was time consuming and rather tedious. Also, the dispersion made by dialysis was apt to be contaminated with water and methanol and the methanol had possibly removed some species from the latex surface which may play a role in the particle stability. Finally, the particle size of the dispersion made by dialysis was greater than 1000 nm which meant that the particles had formed clusters.

## 3.2 Characterizing the Dispersions

In this section, the moisture content, particle size distribution and surface charge of the cleaned latex are discussed. The particle size distribution of the PVC particles redispersed in n-butylchloride with sonic waves and by dialysis were also measured. Whenever "dispersion" is referred to without qualifying the medium, it should be assumed that the medium is n-butylchloride.

### 3.2.1 Test for Moisture

In section 2.1.1. the ability of moisture to change the surface charge of particles dispersed in organic media was discussed. With this in mind, it was attempted to conduct the experiments under dry conditions by redistilling the n-butylchloride, keeping the particles and glassware in an oven at elevated temperatures and making the dispersions in a glove box flushed with nitrogen.

To test the success of the precautions taken to make a moisture free dispersion, four samples were analyzed for moisture content with a NETTLER DL-18 Carl Fisher apparatus using hydronal reagent. Sample #1 was the n-butylchloride that was used in the preparation of the dispersion. A small volume of n-butylchloride was shaken up with an equal volume of distilled water in a test tube and then allowed to stand for one day. The n-butylchloride was decanted off and assumed to be saturated with water. This was sample #2. Sample #3 was the dispersion prepared by sonication. Another sample of the dispersion prepared by sonication was centrifuged to remove the particles. Sample #4 was the n-butylchloride left behind after the particles were removed.

The results of the moisture analysis is shown in Table 6. By subtracting the % water in the dispersion from the % water in the n-butylchloride left after the particles were centrifuged out, it can be seen that 0.02 % of the water in the dispersion was adsorbed onto the surface of the particles. The particle concentration in the dispersion was found to be 0.00026 g/cm$^3$ (section 3.3.2.2.2). Therefore the moisture analysis is telling us that 0.0002 cm$^3$ of water is adsorbed to 0.00026 g of particles in 1 cm$^3$ of dispersion. This translates to 0.77 cm$^3$ of water adsorbed onto 1 g particles. This is not very likely. The discrepancy occurred because of the method of separation of the particles from the dispersion. Some water that was in the n-butylchloride but not adsorbed to the particles must have been centrifuged out along with the particles.

It can be concluded that:

(1) The n-butylchloride used to prepare the dispersion was not bone dry even though the n-butylchloride was redistilled.

(2) The PVC dispersion in n-butylchloride was saturated with water in spite of the precautions taken to prepare the dispersion under dry conditions.

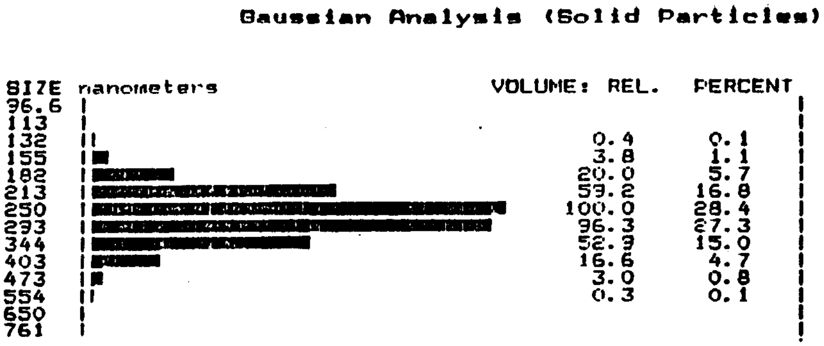
| SAMPLE | VOLUME PERCENT OF MOISTURE |
|---|---|
| n-bc* | 0.175 ± 0.005 % |
| n-bc saturated with $H_2O$ | 0.191 ± 0.005% |
| n-bc dispersion | 0.192 ± 0.005% |
| n-bc from dispersion with particles centrifuged out | 0.172 ± 0.005% |
| * n-bc = n-butylchloride | |

Table 6: Carl Fisher moisture analysis.

### 3.2.2 Particle Size Distribution

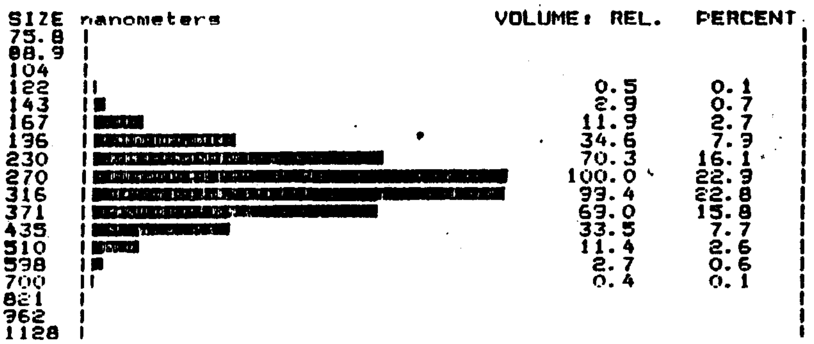
The particle size distribution (PSD) of the PVC dispersions were analyzed by a dynamic light scattering method using a Nicomp 370/autodilute submicron particle sizer by Pacific Scientific. Figure 3 shows the PSD's obtained for the original aqueous latex received from B.F. Goodrich, the latex after it was cleaned by ion exchange, and the cleaned latex after it was dried and redispersed in n-butylchloride with sonic waves. The arithmetic volume average particle diameter of cleaned latex after it was dialyzed with methanol and n-butylchloride was larger than 1 $\mu$m.

1. Original aqueous latex



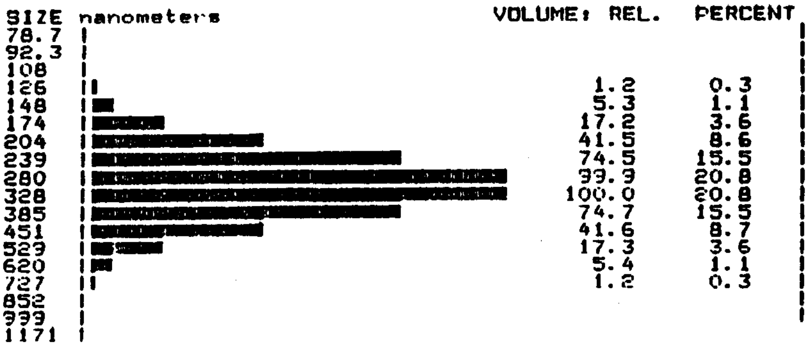
```
                    Gaussian Analysis (Solid Particles)

SIZE nanometers                        VOLUME: REL.   PERCENT
96.6  |                                                      |
113   |                                                      |
132   ||                                      0.4      0.1   |
155   |                                       3.8      1.1   |
182   |                                      20.0      5.7   |
213   |                                      59.2     16.8   |
250   |                                     100.0     28.4   |
293   |                                      96.3     27.3   |
344   |                                      52.9     15.0   |
403   |                                      16.6      4.7   |
473   |                                       3.0      0.8   |
554   ||                                      0.3      0.1   |
650   |                                                      |
761   |                                                      |
```

2. Cleaned aqueous latex



```
SIZE nanometers                        VOLUME: REL.   PERCENT
75.8  |                                                      |
88.9  |                                                      |
104   |                                                      |
122   ||                                      0.5      0.1   |
143   |                                       2.9      0.7   |
167   |                                      11.9      2.7   |
196   |                                      34.6      7.9   |
230   |                                      70.3     16.1   |
270   |                                     100.0     22.9   |
316   |                                      99.4     22.8   |
371   |                                      69.0     15.8   |
435   |                                      33.5      7.7   |
510   |                                      11.4      2.6   |
598   |                                       2.7      0.6   |
700   ||                                      0.4      0.1   |
821   |                                                      |
962   |                                                      |
1128  |                                                      |
```

3. PVC dispersed in n-butylchloride with sonic waves



```
SIZE nanometers                        VOLUME: REL.   PERCENT
78.7  |                                                      |
92.3  |                                                      |
108   |                                                      |
126   ||                                      1.2      0.3   |
148   |                                       5.3      1.1   |
174   |                                      17.2      3.6   |
204   |                                      41.5      8.6   |
239   |                                      74.5     15.5   |
280   |                                      99.9     20.8   |
328   |                                     100.0     20.8   |
385   |                                      74.7     15.5   |
451   |                                      41.6      8.7   |
529   |                                      17.3      3.6   |
620   |                                       5.4      1.1   |
727   ||                                      1.2      0.3   |
852   |                                                      |
999   |                                                      |
1171  |
```

Figure 3: This figure illustrates the particle size distribution of the dispersions measured by a dynamic light scattering method.

This is outside the range of the particle sizer. The arithmetic volume average diameters and the standard deviations are compared in Table 2.

The arithmetic volume average diameters of the particles in various dispersions are shown in Table 2. A dispersion is usually considered monodisperse if its standard deviation is less than 15%. Using this criteria, the original latex with an arithmetic volume average diameter of 274.6 nm and a standard deviation of 21.2% was not monodisperse.

After the latex was cleaned by ion exchange, its arithmetic volume average diameter rose to 302.2 nm with a standard deviation of 26.5%. This was evidence that coagulation took place during the cleaning process. This was physically observable during cleaning because the filter paper was frequently clogged with coagulated particles when the ion exchange resins were being filtered from the dispersion. This was expected since most if not all of the surfactant that was used, polyvinyl alcohol, was removed by the cleaning process.

The method of cleaning, drying and redispersing the PVC particles in n-butylchloride with sonic waves broadened the PSD. The arithmetic volume average diameter became 317.2 nm with a 29.4% standard deviation. Note that the average diameter is still within one standard deviation of the original latex. However, transferring the particles into n-butylchloride via dialysis has a significant broadening effect on the PSD. The

| SAMPLE | Volume Average Diameter [nm] | Standard Deviation [nm] | Standard Deviation % |
|---|---|---|---|
| Original aqueous latex | 274.6 | 58.1 | 21.2 |
| Aqueous latex after cleaned by ion exchange | 302.2 | 80.2 | 26.5 |
| Cleaned latex dried and redispersed in n-butylchloride with sonic waves | 317.2 | 93.1 | 29.4 |
| PVC particles transferred from aqueous media into n-butylchloride by dialysis | >1000 | very | large |

Table 2: The particle size distribution of various dispersions of PVC.

arithmetic volume average diameter rose to greater than 1 $\mu$m which was the largest diameter that the particle sizer could measure with any confidence. The standard deviation became very large also. Drying and redispersing with sonic waves was the easier and faster method of preparing the PVC dispersion in n-butylchloride from an aqueous dispersion. It also produced a narrower particle size distribution when compared to the dialysis method. Also, the dispersion produced by the dialysis method would contain trace amounts of water and methanol which was not desirable. The particle concentration of the dispersion prepared by dialysis was higher (0.38 kg/m$^3$) than that prepared with sonic waves (0.26 kg/m$^3$).

### 3.2.3 Surface Charge

The surface charge of the cleaned aqueous PVC latex was estimated by performing a conductometric titration with 0.01M NaOH solution. Details of the titration is given in Appendix 3.

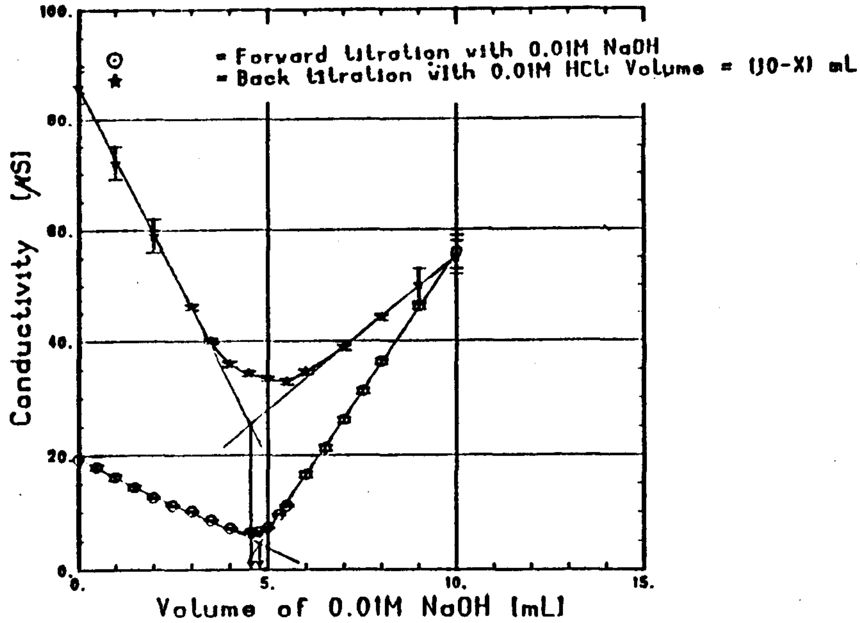


Figure 4: Conductometric titration curve obtained when 0.05 L of the cleaned PVC latex diluted with 0.2 L distilled water was titrated with 0.01M NaOH and then backtitrated with 0.01M HCl.

Figure 4 shows the titration curve.

It was assumed that the titrant added neutralized charge on the particles only. This was verified by obtaining the same neutralization point of 0.047 ± 0.005 equivalents within experimental error for the backtitration with acid as for the forward titration with base.

The surface charge was calculated by dividing the charge on the particles estimated from the titration by the surface area of the particles estimated from the PSD. The calculations are shown in Appendix 3. The surface charge was estimated to be 0.068 ± 0.005 $C/m^2$. Woods [37] gave values of surface charge for polystyrene latices which ranged from 0.016 to 0.081 $C/m^2$ which is of the same order of magnitude as obtained here for the PVC latex.

## 3.3 Investigating the Observed Stability

The PVC particles were stable in n-butylchloride after drying and redispersing with sonic waves as well as after they were transferred from aqueous media to n-butylchloride by dialysis. However, the concentration of particles that remained dispersed in n-butylchloride was much smaller than in the aqueous dispersion. It is the purpose of this section to investigate the cause of these observations. Before the investigation is described, some plausible explanations for the observed stability are hypothesized.

The stability of PVC particles in n-butylchloride must be due to the presence of one or more molecular species in the dispersion. These species must have been present on the cleaned PVC particles in a limited quantity. This was so because only about one hundredth of the particles stable in the aqueous latex was stable in n-butylchloride. This was quite dramatic in the dialysis procedure where about 99.6% of the particles in the original aqueous latex settled out leaving about 0.4% in dispersed in n-butyl-chloride. Also, the particle size of the dispersion in n-butylchloride from the dialysis procedure is much larger than the aqueous dispersion.

### 3.3.1 Models of the Particle Surface

Figure 5 illustrates three models that were postulated to explain the observed particle stability in n-butylchloride. It was assumed that the species causing the stability had come from the particles and was present in the original aqueous latex. The ion exchange cleaning procedure failed to remove all of the species from the particles.

Model 1 postulated that the particles were sterically stabilized by a polymer. The polymer may be adsorbed or chemically bonded to the particle surface. The polyvinylalcohol molecule which was used as a stabilizer in the polymerization of the particles is a candidate to be such a species.

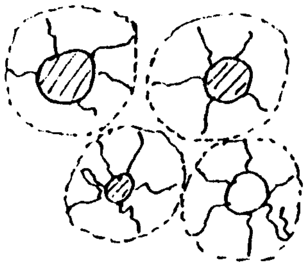
Model 2 hypothesized that the stability was electrostatic in nature. The existence of electrically charged PVC particles is based on the work of Davidson and Witenhafer [8]. They concluded that in suspension polymerization of vinylchloride with a polyvinyl alcohol dispersant, a pericellular membrane or skin surrounds each particle. This skin traps water soluble chloride ions in the particle which were postulated to be formed by a hydrodehalogenation reaction during polymerization. This results in a negative charge on the particles.

Davidson and Witenhafer [8] explained the skin formation as a special case for vinylchloride polymerization which is a result of the slight solubility (about 1%) of the monomer in water. Below 1 to 2 % conversion, submicroscopic particles precipitate in the monomer droplets which agglomerates to microscopic size. Simultaneously, polymerization takes place in the water phase which result in the droplet being covered with a layer of 0.2 $\mu m$ water phase polymer particles. These particles are a mixture of PVC and graft co-polymer of PVC/PVA. Due to the limited amount of monomer in the water phase (solubility is 1%), these polymers must be essentially oligomeric in nature. These form the skin which is further thickened by polymerization in both the water and monomer phase.

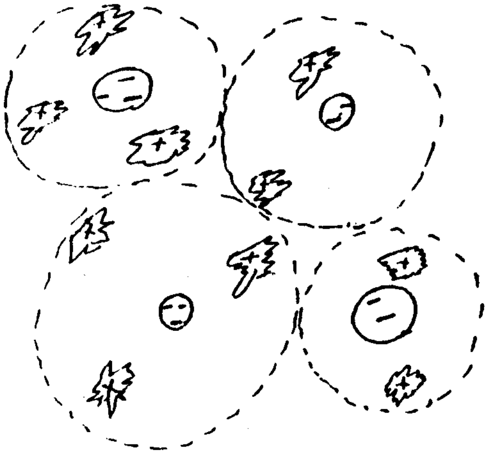
Based on the above information, this model postulates that there was an electron rich environment in the n-butylchloride such as some dissolved vinylchloride molecules, polyvinylchloride oligomers and polyvinylchloride-polyvinylalcohol oligomers which came from the particles. Such molecules can form electron-rich micelles that would allow a simple positive charge to exist within it. This allowed charge separation to occur, possibly $Cl^{-}$- $H^{+}$ facilitating a surface charge on the particles.

Model 3 considered an electrosteric stabilizer. This would consist of a charged polymer that was adsorbed or chemically

Model 1: Steric Stability



Model 2: Electrostatic Stability



Model 3: Electrosteric Stability

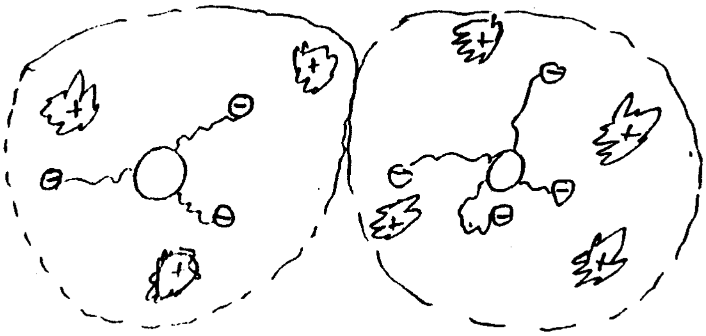


Figure 5: Illustrates of the three models postulated to explain the stability of the PVC particles in n-butylchloride that was observed.

bonded to the particles. As in model 2, an electron rich or electron poor environment was necessary in the medium for the existence of a double layer.

### 3.3.2 Testing the Models

This section describes several tests that were done to obtain sufficient evidence to reject two of the models and accept one as being the most likely explanation for the observed stability. Figure 6 illustrates a simple logic flow diagram that shows the experiments done and gives some brief conclusions to help the reader follow the logic of the tests performed.

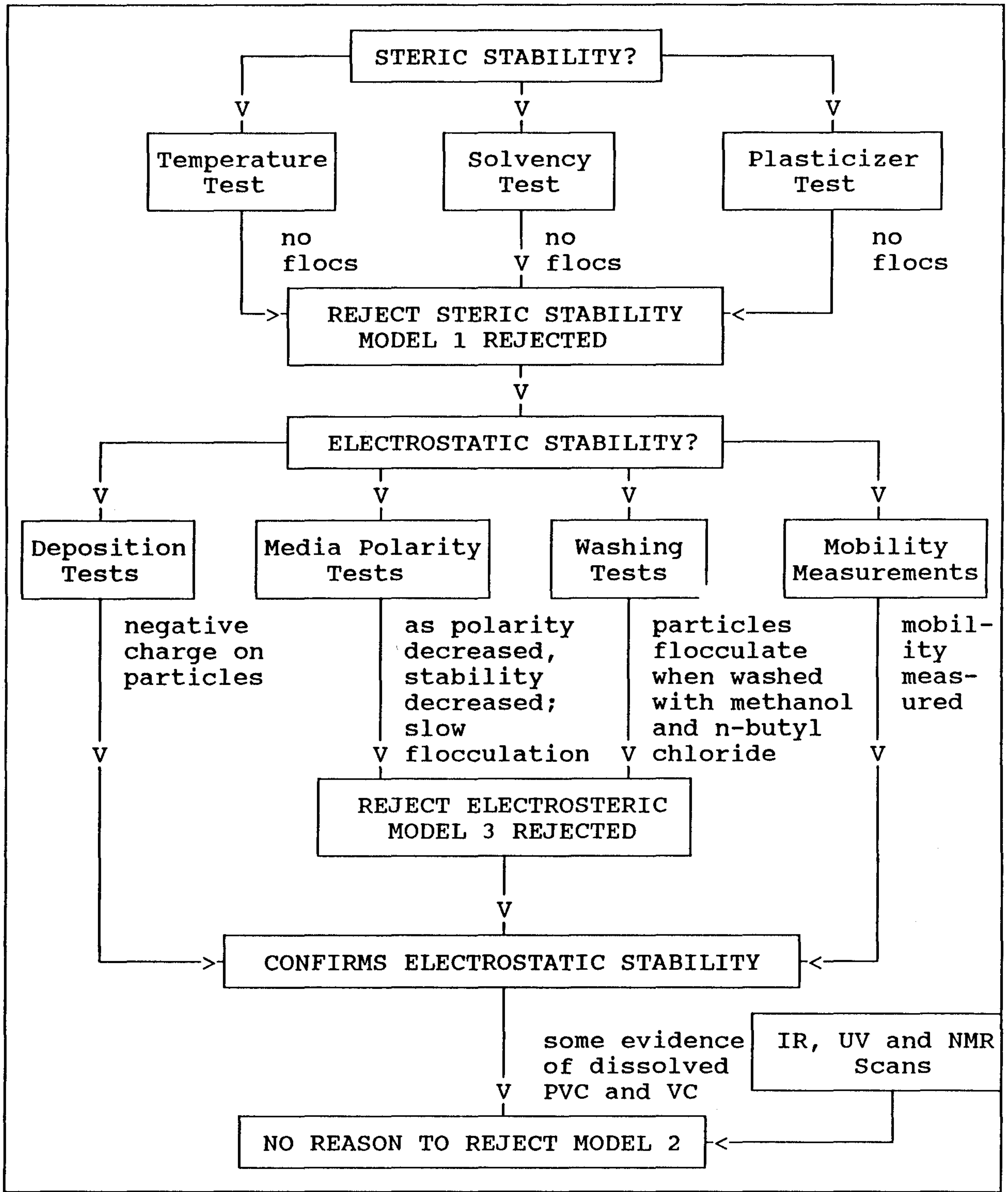


Figure 6: Flow diagram describing the experiments done and the conclusions drawn from the results.

### 3.3.2.1 Tests for Steric Stability

Since the medium was organic in nature, it was expected that no charge would exist on the particles and they would be sterically stabilized. The working hypothesis is given below:

**Hypothesis:** Model 1 is true; the particles are sterically stabilized by a polymeric species.

**Alternative:** Model 1 is false; the particles are either electrostatically stabilized or electrosterically stabilized.

This hypothesis was tested by observing the stability of the dispersion as the temperature and solvency was varied and a plasticizer was added.

#### 3.3.2.1.1 Temperature Test

Sterically Stabilized dispersions are usually critically flocculated by changing the temperature. The theory behind this was described in detail in chapter 2. A sample of the dispersion was slowly heated to boiling (78°C) and another sample was cooled to freezing (-123°C) with liquid N2. The samples were closely observed and there was no sign of flocculation. This observation provided some evidence to reject the null hypothesis that the particles were sterically stabilized.

#### 3.3.2.1.2 Solvency Test

To further strengthen the evidence that the particles were not sterically stabilized, a number of solvents with a range of solubility parameters were added to the dispersion. If the particles were stabilized by polymers, then it was expected that some of the solvents added would be non-solvents for these polymers and would therefore cause the polymers to collapse causing incipient flocculation. The solvent was added 0.25 $cm^3$ at a time with a burette into 5 $cm^3$ of the dispersion. The solution was stirred for 30 seconds and then observed for signs of flocculation. This was continued until 35 $cm^3$ of the solvent was added. Table 3 shows that the dispersions remained stable; there was no sign of flocculation.

The fact that changing the solvency did not cause incipient flocculation provided strong evidence that the particles were not sterically stabilized. However, after the dispersions were allowed to stand for several days, some small flocs were observed in the dispersions to which pentane, carbon-tetrachloride and heptane were added. These were all media with low polarity. This observation was compatible with electrostatic stabilization. It appeared as if adding solvents of low polarity had reduced the surface change on the particles and consequently the extent of the double layer. Flocs slowly formed due to

| Solvent added | Solubility Parameter | | Observation |
|---|---|---|---|
| | $(J/m3)^{\frac{1}{2}}$ | $\{cal/cm^3\}^{\frac{1}{2}}$ | |
| Pentane | 13,913 | {6.8} | Dispersion remained stable |
| Heptane | 15,346 | {7.5} | Dispersion remained stable |
| Carbon-Tetrachloride | 17,597 | {8.6} | Dispersion remained stable |
| Chloroform | 19,029 | {9.3} | Dispersion remained stable |
| Acetone | 20,257 | {9.9} | Dispersion remained stable |
| Cyclohexanol | 23,326 | {11.4} | Dispersion remained stable |
| Methanol | 29,669 | {14.5} | Dispersion remained stable |

Table 3: Effect of adding at least 35 $cm^3$ of various solvents to 5 $cm^3$ of the PVC dispersion in n-butylchloride. PVC = 16,573 {8.1}. Solubility parameter values taken from Burrell [4].

Brownian collisions. This was consistent with Model 2 which postulated electrostatic stabilization. Model 3 which postulated electrosteric stabilization was ruled out since the polymers should have kept the particles stable even though the double layers were compressed. This observation will be discussed later.

### 3.3.2.1.3 Plasticizer Test

Some plasticizer, di-iso-octyl phthalate, was added to the dispersion to soften the particles and observe if this would cause flocculation. The reasoning behind this was that if the particles were sterically stabilized, then softening the particles may affect the anchoring of the stabilizer and cause flocculation. This was by no means a conclusive test, but the observation that no flocculation occurred after the plasticizer was added is a weak indicator that steric stabilization was not playing a role in the particles' stability.

### 3.3.2.2 Test for Electrostatic Stability

From the results presented so far, there was good evidence to reject the hypothesis that polymers were stabilizing the particles. This was quite interesting because the alternative hypothesis which postulated electrostatic stabilization was quite unexpected since the continuous phase was organic. In this section, test results are presented that will confirm the electrostatic nature of the stabilization, and reject the electrosteric model.

### 3.3.2.2.1 Deposition Test

One way to determine if the particles were charged, and the sign of that charge, was to expose the dispersion to an electric field and observe if the particles would migrate to one of the electrodes and deposit there. A sample of the dispersion was placed in a small beaker. A potential difference of 1000 volts was applied across two steel electrodes that were kept 0.01 m apart in the beaker. Within 10 seconds, all of the particles in the dispersion deposited unto the positive electrode. This proved that the particles were negatively charged. Davidson and Witenhafer [8] had demonstrated that aqueous PVC latex made by suspension polymerization with PVA as the dispersant was negatively charged.

### 3.3.2.2.2 Stability in Media of Different Polarity

The results of the solvency tests had indicated that the stability of the particles were dependent upon the polarity of the media. This was compatible with the theory used to explain how charge separation may occur in Model's 2 and 3. If a species was dissolving out into the media from the particles and was forming micelles to provide an electron rich environment in which simple positive charges could exist, then the solubility of this species, which is expected to depend upon the polarity of the medium, will affect the stability.

Model 3 could be ruled out because the particles should have remained stable due to the polymers even though the electrostatic stabilization had failed. It could be argued that the solvency for the polymers was also changed which was causing the flocculation. This argument is incorrect though because in that case, incipient flocculation would be expected and not the rather slow flocculation that was observed. This slow flocculation was a result of coagulation caused by Brownian motion. In the medium of less polarity, the double layer was compressed because of the reduced solubility of the species that allowed separation of charge which in turn resulted in a lower surface charge.

The amount of this unknown species in the medium will not only determine the stability of the medium, but also the concentration of particles that can become charged and remain in the dispersion. For example, if enough species are dissolved in the medium to support 100 $H^+$ ions, then perhaps 50 particles may become charged with an average charge of +2 equivalents. On the other hand, if the solubility of the species decreased such that only 50 $H^+$ ions could be supported, then perhaps only 25 particles may become charged with an average of +2 equivalents. The first dispersion will therefore be more concentrated than the second. A decrease in solubility of the species would therefore explain why the concentration of particles may vary in different media. It also explains the low concentration of the stable dispersion in n-butylchloride in comparison to the dispersion in water and in methanol.

A more quantitative test was done to determine how the stability of the particles were affected by the polarity of the medium in which they were dispersed. The test involved determining how much PVC particles remained stable in liquids of different polarities. The particle concentration of the dispersions were measured.

Methanol was used as a medium of higher polarity than n-butylchloride and pentane as one of lower polarity. 1 g of dried PVC particles were placed in each of three beakers containing 15 mL of methanol, 15 mL of n-butylchloride and 15 mL of pentane respectively. The mixtures were exposed to sonic waves for 24 hours, then allowed to stand for a further 24 hours. The dispersion formed was decanted off and the particles that had settled out was discarded. The sonication procedure was the same as described in Appendix 2 for preparation of the n-butylchloride dispersion with sonic waves.

The dispersion in methanol appeared very turbid, the one in n-butylchloride appeared slightly turbid, and the one in pentane was clear. To quantify these observations, the particle concentrations were measured. The concentration measurements were done by evaporating off the liquid from a known volume of dispersion and weighing the particles that remained. The results of the measurements are given in table 4.

| PVC DISPERSION IN: | PARTICLE CONCENTRATION |
|---|---|
| Methanol | 66.1 ± 0.5 $kg/m^3$ |
| n-butylchloride | 0.26 ± 0.5 $kg/m^3$ |
| Pentane | not measurable |

Table 4: Particle concentration of PVC dispersed in various liquids of different polarity starting with 1g of particles in 15 mL of the liquid and subjecting them to equal amounts of sonic waves.

From these results, it was clear that the stability of the dispersion and the amount of particles that will remain in stable dispersion will increase with increasing polarity of the medium. The observation made in section 3.3.2.1.2 that the particles will slowly flocculate on addition of pentane was investigated further. Pentane was added to five samples of the dispersion so as to get mixtures containing 20%, 40%, 60%, 80%, and 90% of pentane. After forty-eight hours, flocs were observed in the mixtures having 60%, 80% and 90% pentane. However, some of the particles still remained dispersed in the liquid mixtures. Control experiments were done in which an equivalent amount of pure n-butylchloride was added to the dispersion instead of pentane. No flocculation was observed in any of the control samples. This verified that as the polarity of the medium decreased, the stability of the particles also decreased.

#### 3.3.2.2.3 Washing the Particles

If the theory that a molecular species from the particles was dissolving into the medium to provide a favorable environment for charge dissociation, then it should be possible to wash out this species. The species could not be soluble in water since it was not removed by the ion exchange cleaning procedure. The dispersion was washed by centrifuging the dispersion and decanting off the n-butylchloride. New n-butylchloride was added and the particles were redispersed by stirring. This was accomplished quite easily and the dispersion remained stable. The washing procedure was repeated five times. At this point, some larger flocs of approximately 2 μm were observed under an optical microscope. The dispersion was left to stand for twelve hours and about half of the particles settled. The washing was repeated four more times after which some particles still remained in stable dispersion. By this time, some larger flocs could be seen by the naked eye. The dispersion was exposed to a potential difference of 1000 V and the particles deposited on the positive electrode. Some charge was therefore still left on the particles after rigorous washing with n-butylchloride.

The washing procedure was redone, but this time the particles were washed with methanol instead of n-butylchloride. After the first wash almost all of the particles flocculated, and it was difficult to redisperse them by stirring. After the second wash, larger flocs formed which quickly settled and could not be redispersed by stirring.

The species that was allowing the charge dissociation was readily soluble in methanol and was therefore washed out quite easily by methanol. This removed the ability for the charges to dissociate causing the particles to quickly flocculate and they could not be redispersed. Another possibility is that the methanol could possibly dissolve away the PVC/PVA co-polymer skin. If this occurs, then the trapped chloride ions will escape and the particles will completely lose their charge. This could not have occurred though because some fines remained dispersed after the majority of the particles flocculated. These deposited out onto the positive electrode when exposed to a potential difference of 1000 V. Also it will be showed later that no significant amount of polymer was detected when the methanol washings were analyzed. This suggested that the skin did not dissolve.

The observations of the dialysis procedure could be explained by Model 2. The particles formed a stable dispersion in methanol because the species forming the electron rich environment were readily soluble in methanol. When the methanol was displaced by n-butylchloride however, the solubility of the species were significantly reduced, and so only a limited amount of particles could have charge separation. This resulted in most of the particles flocculating out. Some of the species may also have dialyzed out of the dispersion which reduced the stability even more causing the larger particle sizes and standard deviations relative to the dispersions made by sonic waves.

### 3.3.2.2.4 Mobility Measurements

The mobility of the particles were measured by special electrophoretic equipment adapted for mobility measurements in organic media. This was done by Dr. Ian Morrison, courtesy of Xerox Laboratories in Webster, New York state. The dispersion was placed in a rectangular cell specially coated with silicone to prevent the electric field from passing through the cell walls. This is a concern whenever electrophoretic measurements are made on liquids with a conductivity that is lower than the walls of the cell. A voltage was applied across two electrodes in the cell. The electrodes were facing each other 1 mm apart. If the particles are charged, they will migrate towards the electrode of opposite polarity. The velocity of the particles was measured utilizing two laser beams whose frequency shift was varied until an interference pattern was produced such that the particles moving in the electric field appeared stationary. The frequency shift was recorded graphically from which the particle velocity and hence mobility can be deduced. The data, frequency shift records and mobility calculations are given in Appendix 4.

The surface potential was assumed to be equal to the zeta potential which was approximated by the Huckel equation [15].

$$Z = 3\ v\ U_E\ /\ 2\ \epsilon_0\ \epsilon_r \qquad (33)$$

where: $Z$ = zeta potential [V]

$v$ = viscosity of medium [Kg/m.s]

$\epsilon_0$ = permittivity of vacuum

= $8.85*10^{-1}2$ [$C^2$/Jm]

$\epsilon_r$ = relative permittivity

$U_E$ = electrophoretic mobility [$m^2$/V.s]

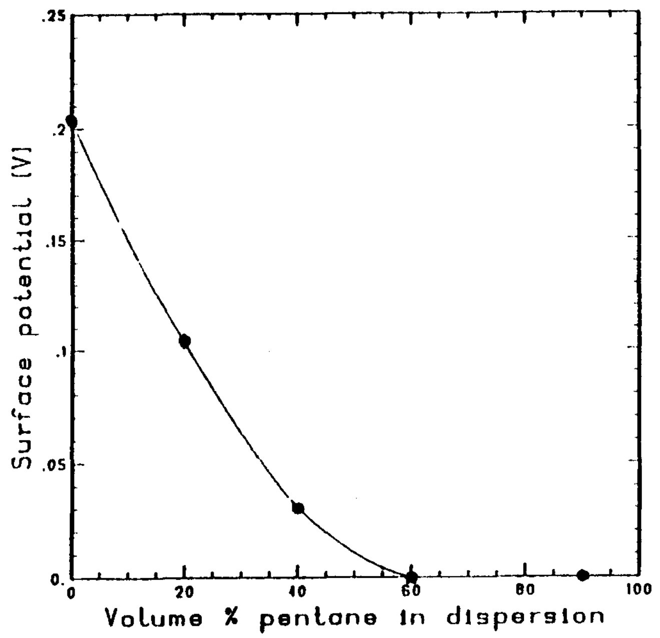


Figure 7: Surface potentials calculated from the mobility measurements as a function of the volume percent of pentane in the dispersion.

Five samples were provided containing mixtures of pentane and the dispersion with 0%, 20%, 40%, 60% and 90% pentane.

Figure 7 shows that the addition of pentane to the dispersion reduced the surface potential of the particles to zero. The calculated surface potential of the pure dispersion and that containing 20% pentane was quite large, 0.203 V and 0.104 V respectively. On the other hand, no mobilities were observed for the dispersions having 60% or more pentane. This was consistent with the observations that dispersions with 60% or more pentane would flocculate after they were left to stand for forty-eight hours.

Lyklema had observed that in organic dispersions, a small surface charge can lead to a much larger surface potential than would be expected for aqueous media. To determine if a surface charge still existed on the particles with more than 60% pentane, the deposition tests were done on these samples. No deposits were observed at 1000 V after one minute, but the particles did deposit on the positive electrode when 2300 V were administered. Thus, although the surface charge on the particles became much smaller as the amount of pentane increases, there was still a small charge existing which kept the particles stable in the short run.

A computer program was written to calculate the stability ratio and the peak potential energy of the dispersions using DLVO theory. This was done to verify that the DLVO theory will predict the stability behaviour observed. The calculations were done for the dispersion in pure n-butylchloride, in 20% pentane and in 40 % pentane. Appendix 5 describes the calculations and their limitations in detail. Table (5) shows the results.

Note how the stability ratio and the peak potential energy decreases with % pentane in the dispersion. As the % pentane in the dispersion goes beyond 40%, the stability ratio approaches 1.0 and the peak potential energy is significantly lower than 5 kT which indicates the onset of instability. The calculations are based on monodispersed particles. As pointed out by Cooper [6], polydispersity can have a significant effect on the stability. This is shown in the table by the change in stability ratio caused by varying the particle radius. One can conclude here that the observed stability/instability of the dispersion in n-butylchloride/pentane mixtures are consistent with the DLVO theory. However, the absolute numbers obtained must be used with caution bearing in mind the limitations of the equations and the estimated parameters used in the calculations.

| % Pentane in Dispersion | Estimated Dielectric Constant | Measured Surf. pot [V] | Avg. Radius [nm] | Calc. Stability Ratio | Calc. Peak Pot. Energy |
|---|---|---|---|---|---|
| 0 | 7.06 | 0.203 | 159 | $5.8*10^{11}$ | 29.2 kT |
|  | 6.02 | 0.104 | 100 | 20.6 | 3.9 kT |
| 20 | 6.02 | 0.104 | 159 | 174.6 | 6.3 kT |
|  | 6.02 | 0.104 | 200 | 825.4 | 8.0 kT |
| 40 | 4.97 | 0.03 | 159 | 1.32 | 0.38 kT |

Table 5: Computed stability ratio and peak potential energy for the dispersion with varying amounts of pentane added to it. The particle radii was varied in the dispersion with 20% pentane to show the effect on stability ratio and peak potential energy.

### 3.3.2.3 IR, UV, NMR Spectra of Materials Washed from the Particles.

At this point, there is evidence to support the hypothesis that the particles were electrostatically stabilized and that there was one or more unidentified species dissolved in the media which allowed the charges on the particles to dissociate. An attempt was made to identify the species by washing it off the particles and doing infra-red (IR), ultra-violet (UV), and nuclear magnetic resonance (NMR) scans on the wash media.

About 1 g of the dried particles were agitated in methanol for twelve hours. The particles were centrifuged out and the methanol was used for the analysis. Another sample was prepared in a similar manner, except that the wash liquid was carbon-tetrachloride.

The carbon-tetrachloride and methanol that were used to wash the particles were scanned in the ultra-violet region. For all practical purposes, nothing was visible in the scans. The peaks are very small and indistinguishable. This indicated that the species dissolved from the particles were present in very minute quantities.

Figure 8 shows the infra-red scan which was done on the methanol extract. The peaks are very broad and it was difficult to draw conclusions with much confidence. Comparing the approximate wavenumber where the peaks occur to standard infra-red spectra [10], some general conclusions could be made. The peak occurring near wavenumber 3600 $mm^{-1}$ was possibly due to OH stretching vibrations. This may be from PVA, methanol or from any water present. The one at 1650 $mm^{-1}$ was possibly due to an alkene monosubstituted (vinyl) group. This could come from residual vinylchloride monomer from the polymerization process. Around 800 $mm^{-1}$, peaks are due to C-Cl or $C-Cl_2$ vibrations. Again, vinylchloride monomer seems to be present and also some polyvinylchloride, most likely of very low molecular weight.

Figure 9 shows the NMR scan on the carbon-tetrachloride extract. Figure 10 shows the NMR scan for benzoyl peroxide. This chemical was present in the polymerization reaction and may be dissolved from the particles. Comparing figures 9 with 10, there was no reason to believe that benzoyl peroxide was present in the extract in a significant quantity. The largest peak in figure 9 between 3 to 4 ppm was due to the carbon-tetrachloride. The peaks to the right are typical of aliphatic compounds while those to the far left are typical of aromatic compounds. The broad peaks are usually due to polymeric molecules and may also be due to micellization of smaller molecules. The broad peaks between 4 to 5 ppm could be due to a C-Cl group. The peaks between 2-3 ppm were due to -CH groups in a chain while the one between 1 to 2 ppm was due to an end $-CH_3$ group. From the ratio of the areas, the chain length of the polymers is about 2 to 3 carbon units long.

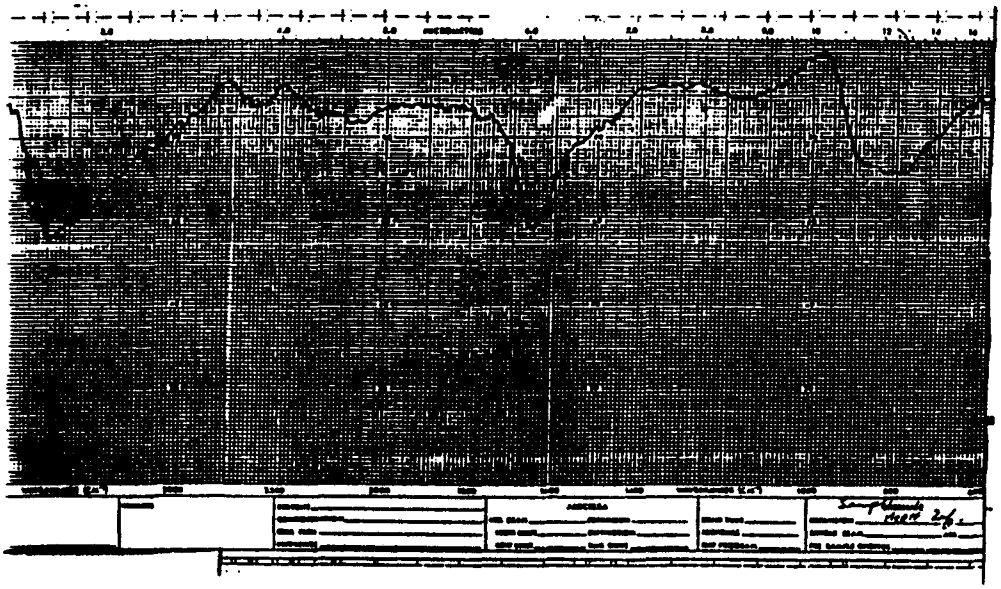


Figure 8: This figure illustrates the IR spectra of methanol after it was used to wash the PVC particles.

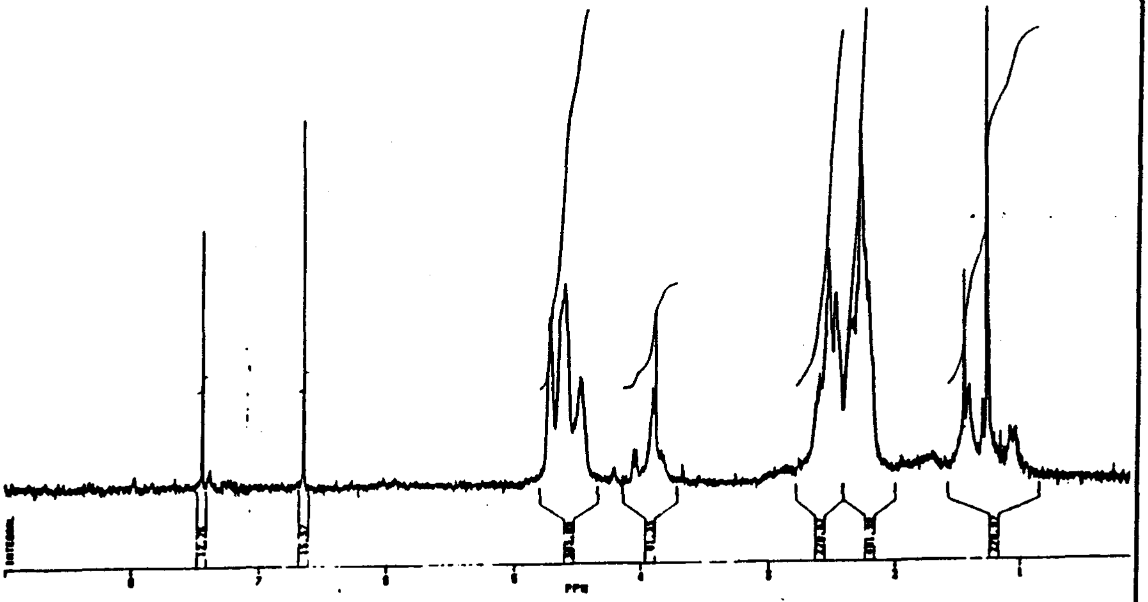


Figure 9: This figure illustrates the NMR spectra obtained from carbon-tetrachloride that was used to wash the PVC particles.

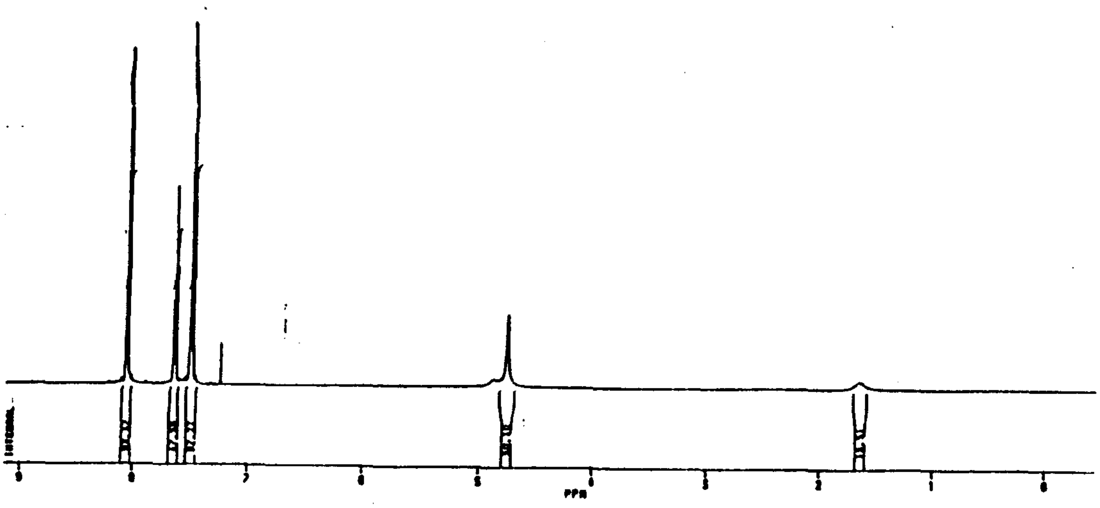


Figure 10: This figure illustrates the NMR spectra of benzoyl peroxide.

The information obtained from the spectra are not precise. Concentrations were too small and it was impossible to correlate the peaks to decide which belongs together. Another NMR spectra was obtained using deuterated methanol. That is methanol in which the hydrogens were replaced with deuterium. However, this did not result in any new information. A $C^{13}$ scan was also done, but the concentration of the dissolved molecules were too small and nothing showed up.

These scans suggest that some species is dissolving out from the particles. However, they are present in too small quantities to be positively identified. There was some evidence that the species may be vinyl-chloride and PVC/PVA oligomers which are possibly forming micelles. These molecules fit the characteristics of the species that came out from the investigation; they would be insoluble in water, they would be present in a limited quantity, the double bond of the vinylchloride molecule and the electronegativity of the chlorine atom would form micelles that are electron rich.

### 3.4 Model 2 Explains the Behaviour of the Dispersion.

The above discussion shows that model 2 is compatible with the observed phenomena. In summary, the particles have chloride ions trapped in a pericellular membrane or skin made up of PVC and PVC/PVA polymers, with a significant quantity having low molecular weights. Separation of charge is allowed in n-butylchloride due to the desorption of oligomers of PVC and/or PVC/PVA from the skin. These oligomers form micelles in which simple hydrogen ions can reside due to the electronegative nature of the OH and Cl groups. As a result, charge separation occurs and the particles attain a small negative charge. This is responsible for the observed stability of the dispersion.

An interesting phenomena was observed when equal volumes of water and the dispersion were vigorously shaken and then allowed to settle. Tiny droplets were observed to settle to the bottom of the test tube. Above these droplets, the liquid was clear. There was no interface between the water and n-butlychloride as one would expect. Instead, the water were all in stable droplets which had settled to the bottom. This gave the bottom portion of the fluid a gel like appearance. If the test-tube was tilted and rotated, the droplets would roll over each other without coalescing.

This phenomenon could be explained by the model that the particles are surrounded by a PVC/PVA skin. Such a skin would have hydrophobic areas (hydrocarbon portion) and hydrophillic areas (alcohol and chloride group). It would therefore act as a surfactant which explains the stable droplet formation. The particles therefore reside on the surface of the water droplets.

In a test tube, 1 $cm^3$ of water was added to 10 $cm^3$ of dispersion and shaken vigorously. Again, stable droplets of water settled to the bottom. However, because of the smaller amount of water present, the particles could be clearly observed on the surface of the droplets. All of the particles were at the interface and the n-butylchloride layer was observed to be clear.

In another test-tube, 3 $cm^3$ of dispersion was shaken with 10 $cm^3$ of water. In this case, the liquids separate into two distinct layers with the particles residing at the interface. This occurred because there was not enough particles present in the 3 $cm^3$ of dispersion to stabilize the n-butylchloride droplets in water. Instead the particles went to the interface.

These observations confirm the existence of a hydrophobic/hydrophillic skin made up of PVC-PVA co-polymer. This skin traps chloride ions which will dissociate if countercharges are available in the dispersion medium. For methanol, such countercharges can readily exist and the interface and the n-butylchloride layer was observed to be clear.

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These observations confirm the existence of a hydrophobic/hydrophillic skin made up of PVC-PVA co-polymer. This skin traps chloride ions which will dissociate if countercharges are available in the dispersion medium. For methanol, such countercharges can readily exist and the dispersion is very stable. In pentane however, no countercharge can exist and therefore no dispersion will form. Butylchloride is in-between. With the formation of micelles made up of dissolved vinylchloride monomer, PVC oligomers and PVC-PVA oligomers, a limited amount of simple counterions can exist which will give a limited stability to a small concentration of particles. Washing the dispersion with methanol which readily dissolves these molecules will quickly remove all oligomers from the particles and the dispersion will quickly flocculate. However, these molecules are only slightly soluble in n-butylchloride and therefore it takes many washings with n-butylchloride to eventually flocculate all of the particles.

# CHAPTER 4

## SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The objective of this thesis was to determine the mechanism by which PVC particles made by aqueous emulsion polymerization were able to remain stable in n-butylchloride. Understanding this mechanism is important to PVC resin producers because they want to control the stability of particles formed during suspension polymerization which will control the particle size distribution and ultimately the polymer blend time.

The PVC particles were cleaned by the method of Vanderhoff, Van Den Hul, Tausk and Overbeek. The surface charge of the cleaned aqueous latex was estimated to be 0.068 ± 0.005 $C/m^2$ by conductometric titration with 0.01 M NaOH and backtitration with 0.01M HCl. The particles were dispersed in n-butylchloride by two methods to control moisture. In the first method, the particles were dried in an oven and then redispersed in n-butylchloride by exposing the mixture to sonic waves. The second method involved dialyzing the cleaned aqueous latex with methanol and then with n-butylchloride.

Both methods produced a dispersion that was very stable, but with a relatively small particle concentration. Only 0.4 % of the particles in the original aqueous latex was redispersed in the n-butylchloride medium. The arithmetic volume averaged particle diameter of the dispersion produced by dialysis was greater than 1000 nm compared to 317.2 ± 29.4 nm for the dispersion produced with sonic waves. Redispersing the particles by the dialysis method was definitely inferior to drying and dispersing with sonic waves; the dialysis procedure took a much longer time, caused the dispersion to be contaminated with water and methanol, possibly removed surface species and produced a dispersion with large particle size and particle size distribution. As a result, the dispersion prepared by sonication was used for the research.

It was postulated that a species present in the original aqueous latex was causing the observed stability. This species must be present in a very limited quantity since only a very small concentration of particles remained in stable dispersion. The species must also be insoluble in water since it was not removed by the cleaning procedure.

Three mechanisms were hypothesized to explain the particle stability in n-butylchloride, each assuming the presence of a molecular species. The first mechanism was that the particles were sterically stabilized by the species present. The second model was based on Davidson and Witenhafer conclusion that during polymerization of vinyl chloride using PVA surfactant, a PVC/PVA skin forms around the particles which traps chloride ions. This cause the particles to be negatively charged in aqueous media.

In n-butylchloride, model 2 postulated that the species have electronegative groups and form micelles. Simple positive ions such as $H^+$ can exist within these micelles causing the particles to be electrostatically charged. The third model was that the species caused the particles to be electrosterically stabilized.

To determine which model best represented the observed behaviour of the particles, several tests were conducted. These tests are based on known behaviour of particles stabilized by electrostatic, electrosteric and steric stabilizers.

Three tests were performed to confirm or reject steric stability. The temperature of the dispersion was varied from the freezing point of the n-butylchloride dispersant to its boiling point. If the particles were sterically stabilized, they would undergo incipient flocculation. No flocculation was observed. Changing the solvency of a sterically stabilized dispersion would cause incipient flocculation. Again, this did not occur when the solvency of the dispersion was changed by adding various solvents with solubility parameters ranging from 13,913 to 29,669 $(J/m^3)^{\frac{1}{2}}$. Finally, the plasticizer di-isooctyl phthalate was added to soften the particles, and affect the anchoring of any steric stabilizer or the extent to which tails extend into the continuous phase. Any of these would cause coagulation. Nothing was observed. Based on these results, the steric stabilization model was rejected.

The electrostatic model was confirmed by showing that the particles were electrostatically charged. This was done by placing two steel electrodes, 1 cm apart in a sample of the dispersion and applying a potential difference of 1000 V across the electrodes. The particles migrated to the positive electrode which proved that the particles were negatively charged.

Trace quantities of moisture affect the surface charge of particles dispersed in organic media. In the preparation and tests done, great care was taken to exclude moisture: redistilling the n-butylchloride, keeping the particles and glassware in an oven at elevated temperatures and working in a glove box with a dry nitrogen atmosphere. However, a Carl Fisher analysis showed that all the dispersions prepared were saturated with 0.19 volume % water. The effect of this is not known. However, all tests were carried out with the dispersion in n-butylchloride being saturated with water.

This poses the question as to what constituted the counter charge in the organic dispersant. The more polar the dispersant, the more ions can be supported in solution through local molecular orientation and the formation of micelles by species with polar groups that leach into the dispersant from the particle surface. The solvency test that was done had shown that while incipient flocculation did not occur, dispersions that were mixed with pentane, carbon-tetrachloride and heptane were observed to slowly form some flocs after the dispersions were left standing for several days. It was postulated that these non-polar solvents reduced the solubility of the species which model 2 assumed to be forming micelles and carrying the countercharge. As a result, the surface charge decreased which caused some flocculation. This observation also ruled out model 3 since an electrosteric stabilizer should have kept the particles stable even though the double layer decreased.

To investigate the above mentioned observation further, it was attempted to prepare dispersions of PVC particles in methanol, n-butylchloride, and pentane using sonic waves and the exact same conditions in each case. Methanol is more polar than n-butylchloride while pentane is less polar. The results were clear. As the polarity of the medium increased, the particle concentration in the dispersion increased. This reinforced the theory that a species is dissolving out of the particles and are forming micelles in which positive charges can reside thus allowing a negative surface charge on the particles to exist.

It should be possible to wash out the species from the dispersion which will cause the particles to flocculate. The n-butylchloride dispersion was washed with methanol. The procedure was simple; a sample of the dispersion was centrifuged and the n-butylchloride decanted off. The particles readily redispersed in methanol. This was then centrifuged and the methanol decanted off. When new methanol was added, almost all of the particles flocculated. When the particles was washed with n-butylchloride instead of methanol using the same procedure, it took five washings to get flocculation to the same extent as with methanol. This verified that a polar species that is much more soluble in methanol than n-butylchloride was responsible for the observed stability as described above.

The mobility of dispersions of PVC in mixtures of n-butylchloride and pentane were measured and the surface potential was calculated using the Huckel equation. The surface potential decreased from 0.203 V in pure n-butylchloride to 0 V in 40 % n-butylchloride and 60 % pentane. Again, this is consistent with the polar species explanation of model 2. A calculation of the stability ratio based on estimated parameters and the DLVO theory showed that the stability ratio approached 1 with 40 % pentane in the dispersion. This predicts instability of the dispersion in 40 % pentane. Flocculation was observed in dispersions containing 60 % pentane, but the calculations are limited by the estimated parameters and the fact that the particle size distribution is not monodispersed as the equations assume.

An attempt was made to identify the species that was dissolving out from the particles using infra red, ultra violet and nuclear magnetic resonance spectra. The major problem was that the amounts of material dissolving out was very small which made any positive identification impossible. There was evidence of C-Cl, C-$Cl_2$, -CH, -$CH_3$, and O-H groups, oligomers with carbon chain lengths of 2 to 3 and micelles. Although the evidence was not conclusive, there is reason to believe that the species were oligomers of PVC and PVC-PVA.

When water was added to the dispersion of particles in n-butylchloride, the particles move to the water - n-butylchloride interface. This supports the PVC-PVA surface "skin" on the particles which is hydrophobic/hydrophilic. The PVC-PVA skin traps chloride ions inside the particle; surface oligomers dissolve in the organic liquid to form micelles that provide a safe haven for hydrogen ions. Hence charge separation occurs and the particles are electrostatically stabilized.

Future work in this field should involve experiments which positively identify the species and determine the characteristics of the micelles formed. A method must be devised to extract enough of the species from the particles to be able to identify them. Examination of the micelles may be done by electron micrographs. A preparation technique would have to be developed so that the micrographs will develop properly. Finally, the role that trace moisture is playing in this mechanism must be determined. A method must be developed to carry out the preparations and tests in a moisture free environment.

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# APPENDIX 1

## Safety

All of the chemicals used in this project are potentially dangerous. As a result, all preparation and experiments were carried out in a fume hood. Laboratory coat, rubber gloves, and safety glasses were always worn. In addition, an organic gas mask was worn when handling n-butylchloride and carbontetrachloride.

The solvent n-butylchloride was used with caution. It is flammable with a very low flash point of -8.3°C and can be ignited under all normal temperature conditions. Water is ineffective to quench the flames and a foam, carbon-dioxide or dry chemical fire extinguisher must be used. During a fire, a full-faced mask with a self-contained breathing apparatus and eye protection must be worn. N-butylchloride emits dangerous phosgene gas when heated to decompose. During use, lab coat, rubber gloves, respirator and safety glasses were worn. Although the solvent is normally stable in terms of reactivity, it will react violently with aluminum, liquid oxygen, oxidizing agents, potassium, and sodium [26].

The PVC latex can cause skin or eye irritation. Residual vinylchloride monomer present is carcinogenic and the latex was used with adequate ventilation. Safety glasses and gloves were worn when using the latex. In case of contact, eyes must be flushed with plenty of water for at least five minutes and skin washed with soap and water.

# APPENDIX 2

## CLEANING AND PREPARING THE DISPERSION

### CONDITIONING THE ION-EXCHANGE RESIN

The apparatus used for conditioning the resin is illustrated in figure A2-1.

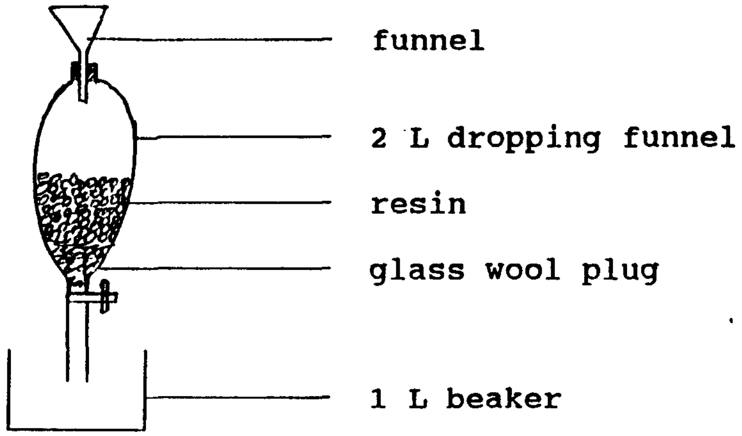

Figure A2-1: The apparatus used for conditioning the resin.

1. The resins (1 L of each) were washed separately with 1 L 85°C distilled water and 0.5 L methanol until no more colored material could be removed.
2. Each resin was then eluted consecutively with 0.5 L (approximately a fivefold excess) of 3N NaOH, 1 L 85°C distilled water, 0.5 L methanol, 1 L cold distilled water, 0.5 L (approximately a fivefold excess) of 3N HCl, 1 L hot distilled water, 0.5 L methanol and 1 L cold distilled water.
3. Procedure 2 above was repeated four times.
4. The Dowex 50W was slowly eluted with 0.5 L of 3N HCl to convert to the $H^+$ form.
5. The Dowex 1 was stored in the $Cl^-$ form. When ready to use, it was converted to the $OH^-$ form by slowly eluting with 0.5 L of 3N NaOH. (It was then used immediately because when left standing, an odour of amines was detected.)

## ION EXCHANGE PROCEDURE

1. 0.5 mL of the concentrated latex was added to 125 mL of distilled water and the conductivity was found to be 55 ± 2 μS with a radiometer CDM2 conductivity meter. Thus the conductivity of 0.004 volume fraction of concentrated latex in water was 55 ± 2 μS.
2. 0.2 kg of Dowex 1 was converted to the $OH^-$ form by slowly

eluting with 0.5 L of 3 N NaOH solution. It was then rinsed copiously with distilled water.

3. 0.2 kg of Dowex 50W was rinsed copiously with distilled water and mixed with the Dowex 1 in a 2 L pyrex beaker under stirring.
4. Before use, the mixed resin was washed under agitation, decanted and filtered.
5. The mixed resin was then added to 0.2 L of the concentrated latex in an open pyrex container and agitated slowly for two hours.
6. The mixture was vacuum filtered through a sintered glass Buchner funnel with Watman #41 ashless filter paper to remove the resin beads. The filter paper became clogged frequently and had to be changed. This was due to some coagulation that took place during cleaning. Care was taken to ensure that water from the tap did not suck back into the flask because tap water contains ions which would contaminate the cleaned latex.
7. During the filtering process, it was necessary to rinse the resin and container used for agitation with distilled water to get back as much of the particles as possible which had a tendency to adhere to the resin beads and to the glass walls. As a result, 0.825 L of distilled water was added to the latex.
8. A sample of the diluted latex was taken and more distilled water added to make the concentration 0.004 volume fraction

of concentrated latex to distilled water and the conductivity was found to be 7.5 ± 0.3 $\mu$S.

9. The process was then repeated using clean resin. The new conductivity of a 0.004 volume fraction of the concentrated latex was found to be 7.1 ± 0.3 $\mu$S.
10. The process was again repeated and the conductivity was found to be 7.0 ± 0.3 $\mu$S. At this point, it was felt that no more ions could be removed, and the latex was clean. During the cleaning process, 1.425 L of distilled water was added to the 0.2 L of concentrated latex.

Table A2-1 summarizes the conductivity of the latex after each cleaning. Note that during the cleaning, distilled water was used to wash the latex off the resin. To ensure that the concentration of the original latex in distilled water was constant for all the conductivity measurements, samples were diluted to 0.004 volume percent of the original latex before their conductances were measured.

| Number of times latex cleaned | Conductivity of diluted latex ($\mu$S) |
|---|---|
| 0 | 55 ± 2 |
| 1 | 7.5 ± 0.3 |
| 2 | 7.1 ± 0.3 |
| 3 | 7.0 ± 0.3 |

Table A2-1: Conductivity of the latex after being cleaned by ion exchange. Conductivity of the distilled water used was 0.725 ± 0.015 $\mu$S

## REDISPERSING WITH SONIC WAVES

Barrett [3] noted that the displacement of water by the organic solvents have generally proved less satisfactory than techniques which involved the redispersion of vacuum-dried emulsion polymer into organic media. The dried polymer powder is added to the organic liquid and is agitated to break up agglomerated particles to yield discrete and partially swollen polymer particles. However, the control of particle size required is frequently difficult to achieve.

In this project, the cleaned aqueous latex was placed in an oven at 40°C for two weeks. A glove box was set up which contained an electronic balance, a Fisher model 300 sonic dismembrator, a 2 L beaker, a 1 L flask, a 0.1 L flask and a funnel. All of the glassware used in this experiment were kept in an oven at 200°C for at least one week. Dry nitrogen was continuously blown into the glove box for eight hours prior to the experiment and was maintained throughout the experiment to displace air and moisture. The n-butylchloride used was BDH standard and was distilled before use. The distilled n-butylchloride was placed in a 2 L stoppered flask which was placed in the glove box.

About 0.01 kg of the PVC particles were removed from the oven and placed in the 2 L beaker in the glove box. About 1.5 L of n-butylchloride was transferred into the beaker and the probe of the sonic dismembrator was lowered into the liquid. It was exposed to sonic waves for 48 hours. The probe was then removed and the dispersion was allowed to stand for a further 48 hours. The dispersion was decanted off into the 1 L flask without disturbing the settled agglomerates. 0.1 L of the dispersion was carefully measured off with the 0.1 L flask. The measured dispersion was placed into a flat dish and weighed. The n-butylchloride was allowed to evaporate completely. The dish and particles remaining was weighed and the particle concentration was calculated to be 0.26 kg/m$^3$. The remaining dispersion was kept in the stoppered 1 L flask.

## REDISPERSING BY DIALYSIS

The particles were redispersed in n-butylchloride from the aqueous dispersion by dialyzing the aqueous latex first with methanol and then with n-butylchloride. Methanol was used as an intermediate dispersant because water and n-butylchloride are immiscible.

A 0.25 m length of a standard 0.025 m Spectrapor cellulose dialysis tubing was boiled in distilled water for one hour. This procedure was repeated twice with clean distilled water. About 0.04 L of cleaned aqueous PVC dispersion was put into the tubing and the ends were tightly knotted. The tubing was then placed in a bottle filled with clean methanol, and the bottle was corked. The methanol was agitated with a magnetic stirrer for twenty-four hours, after which the methanol was replaced with clean methanol and the density of the methanol-water mixture taken from the bottle was measured with a picometer. This was repeated until the density of the methanol-water mixture taken from the bottle was constant. This indicated that no more water was dialyzing out of the tubing. The results of the density measurements are given in Table A2-2.

| CHANGE # | DENSITY OF MeOH-$H_2O$ [kg/$m^3$] |
|---|---|
| 1 | 810 |
| 2 | 802 |
| 3 | 794 |
| 4 | 792 |
| 5 | 792 |

Table A2-2: The density of the methanol-water mixture taken from the bottle in which the dialysis tube containing the original aqueous latex was placed before pure methanol was added again each time.

N-butylchloride was then placed in the bottle to displace the methanol in the dialysis tubing. However, after eight hours, it was observed that almost all of the methanol had dialyzed out of the tubing, but no n-butylchloride had replaced the methanol, and all of the particles had coagulated. It was concluded that either n-butylchloride could not pass through the membrane or the rate at which it passed through was very slow relative to methanol's rate.

To overcome this problem, a new strategy was used. The dialysis of the aqueous dispersion with methanol was done as before. The dialysis tubing was then opened and the PVC dispersion in methanol was placed in a beaker. The dispersion appeared to be quite stable and no flocs were apparent to the naked eye. An equal volume of n-butylchloride was added to the methanol dispersion. A new piece of dialysis tubing was boiled in methanol for one hour. The methanol was changed twice. About 0.04 L of the PVC dispersion in the methanol-butylchloride mixture was placed in the tubing and its ends were tightly knotted. The tubing was then placed in the bottle which was filled with n-butylchloride, and corked. The n-butylchloride was stirred continuously, and after allowing twelve hours for the methanol to dialyze out of the tubing, the old n-butylchloride in the bottle was replaced with clean n-butylchloride. The density of the n-butylchloride-methanol mixture taken from the bottle was measured. This was repeated until the density of the n-butylchloride-methanol taken from the bottle was constant. Table A2-3 gives the measured densities.

| CHANGE # | DENSITY OF N-BUTYLCHLORIDE-METHANOL MIXTURE [kg/m$^3$] |
|---|---|
| 1 | 879 |
| 2 | 881 |
| 3 | 884 |
| 4 | 884 |

Table A2-3: The density of the n-butylchloride-methanol mixture taken from the bottle in which the dialysis tube containing the dispersion in the mixture of n-butylchloride and methanol was placed before pure n-butylchloride was added again each time.

The dispersion in n-butylchloride was removed from the dialysis tubing. It was observed that a large quantity of the particles had settled out of the dispersion. However, a stable dispersion was still evident although it was much less concentrated than the aqueous dispersion. The dispersion remained stable for as long as it was observed (greater than two months). The particle concentration of the original cleaned aqueous latex that was dialyzed was 87.1 kg/m$^3$ while the particle concentration of the stable dispersion obtained in n-butylchloride was 0.38 kg/m$^3$.

# APPENDIX 3

## DETAILS OF TITRATION OF LATEX AND SURFACE CHARGE CALCULATION

Figure A3-1 shows the apparatus that was used. 50 ml of the cleaned aqueous latex was placed in a 300 ml double walled pyrex container. The latex was diluted by adding 200 ml of distilled water. Constant temperature water from a Neslab TEV-45 water bath set at 25 C was circulated through the double walls of the

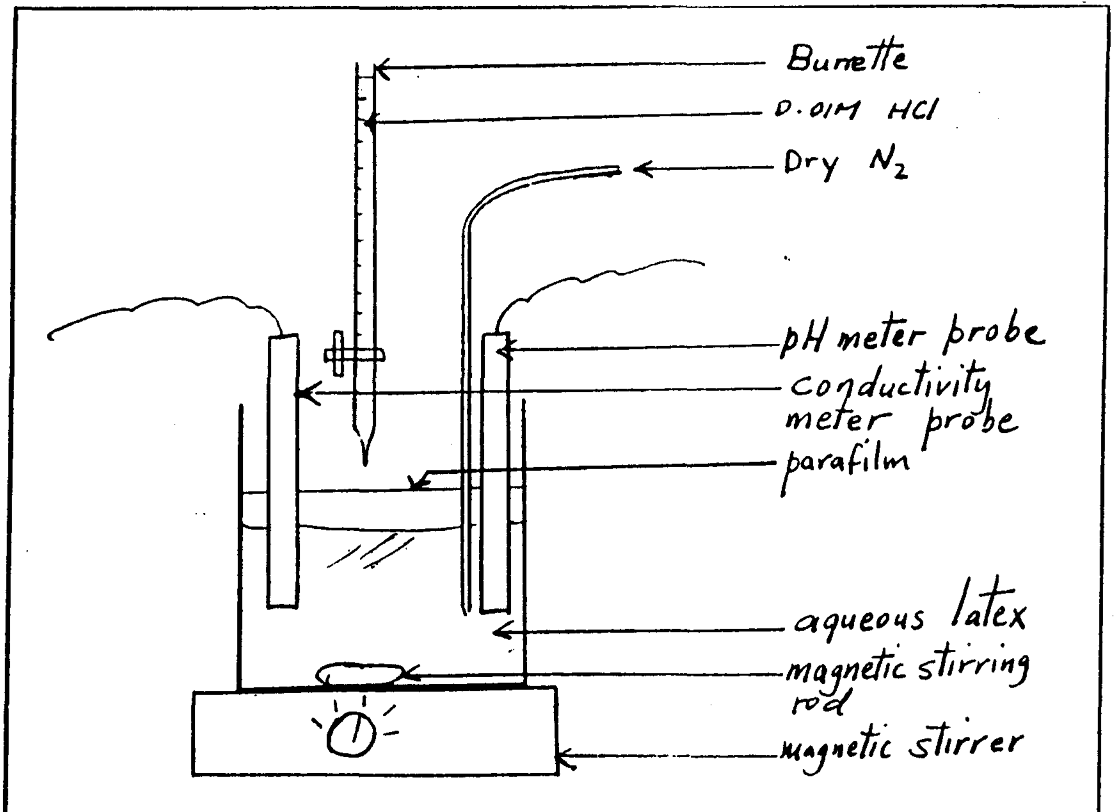

Fig. A3-1; Apparatus used for titration of the latex.

container. The electrodes from a Fisher Accumet 810 pH meter and a conductivity meter were placed in the diluted latex. The temperature of the latex was monitored by a mercury thermometer and the titrant was added from a burette. The container was covered with parafilm and $N_2$ was bubbled in to displace air. This was done to remove $CO_2$ which would maintain the

$$H_2O + CO_2 = H^+ + HCO_3^-$$

equilibrium and therefore affect the NaOH titration. Throughout the titration, an atmosphere of $N_2$ was maintained above the solution.

The titration with NaOH was carried out well past the endpoint. This was done because the identification of the endpoint is often wrong and misleading. A practical identification of the endpoint is obtained by extrapolating the upward and downward slopes of the conductivity versus equivalents of base to the point of intersection. To get a more accurate endpoint, the slope of the conductivity curve was steepened by adding a neutral electrolyte, 0.01M KCl, before titrating. However, this did not give a significantly better estimate because the measurement error of the conductivity meter in the higher conductivity ranges is large. As a check, the solutions were then backtitrated with 0.01M HCl solution. Obtaining the same endpoint ascertains that the charge neutralized were due only from the particles.

The titration data obtained when the latex was titrated with 0.01M NaOH and then backtitrated with 0.01M HCl is given in Table

| Volume of 0.01M NaOH added to latex [mL] | Conductivity [$\mu$S] | Volume of 0.01M NaOH added to latex [mL] | Conductivity [$\mu$S] |
|---|---|---|---|
| 0.0 | 19.3 ± 0.5 | 0.25 | 18.7 ± 0.5 |
| 0.50 | 17.9 ± 0.5 | 0.75 | 16.9 ± 0.5 |
| 1.0 | 16.1 ± 0.5 | 1.25 | 15.1 ± 0.5 |
| 1.50 | 14.3 ± 0.5 | 1.75 | 13.3 ± 0.2 |
| 2.00 | 12.5 ± 0.2 | 2.25 | 11.8 ± 0.2 |
| 2.50 | 11.1 ± 0.2 | 2.75 | 10.6 ± 0.2 |
| 3.00 | 10.1 ± 0.2 | 3.25 | 9.2 ± 0.2 |
| 3.50 | 8.6 ± 0.2 | 3.75 | 7.9 ± 0.2 |
| 4.00 | 7.2 ± 0.2 | 4.25 | 6.6 ± 0.2 |
| 4.50 | 6.4 ± 0.2 | 4.60 | 6.4 ± 0.2 |
| 4.75 | 6.6 ± 0.2 | 5.00 | 7.3 ± 0.2 |
| 5.30 | 9.6 ± 0.2 | 5.50 | 11.1 ± 0.2 |
| 5.75 | 13.5 ± 0.2 | 6.00 | 16.6 ± 0.5 |
| 6.25 | 19.1 ± 0.5 | 6.50 | 21.3 ± 0.5 |
| 6.75 | 23.5 ± 0.5 | 7.00 | 26.2 ± 0.5 |
| 7.20 | 28.8 ± 0.5 | 7.50 | 31.2 ± 0.5 |
| 7.75 | 33.7 ± 0.5 | 8.00 | 36.4 ± 0.5 |
| 8.50 | 41.4 ± 0.5 | 9.00 | 46.1 ± 0.5 |
| 10.00 | 56. ± 3 | | |

Table A3-1: This table gives the conductivity of the latex as a function of the volume of 0.01M NaOH added. 50 mL of the latex was diluted with 200 mL of distilled water before the titration.

| Volume of 0.01M HCl added to latex [mL] | Conductivity [$\mu$S] | Volume of 0.01M HCl added to latex [mL] | Conductivity [$\mu$S] |
|---|---|---|---|
| 0.00 | 55 ± 3 | 1.00 | 50 ± 3 |
| 2.00 | 44.2 ± 0.5 | 3.00 | 38.8 ± 0.5 |
| 4.00 | 34.6 ± 0.5 | 4.50 | 32.9 ± 0.5 |
| 5.00 | 33.4 ± 0.5 | 5.50 | 34.3 ± 0.5 |
| 6.00 | 36.0 ± 0.5 | 6.50 | 40.0 ± 0.5 |
| 7.00 | 46.1 ± 0.5 | 8.00 | 59 ± 3 |
| 9.00 | 72 ± 3 | 10.00 | 86 ± 3 |

Table A3-2: This table gives the conductivity of the latex as a function of the volume of 0.01M HCl added. 50 mL of the latex was diluted with 200 mL of distilled water then titrated with 10 mL of 0.01M NaOH before this back-titration.

A3-1 and A3-2 respectively. The titration curves are shown in figure 4 (section 3.3.2).

The endpoint of the titration is 0.047 meq NaOH.

1 equivalent of NaOH has $6.023 * 10^{23}$ elementary charges. therefore, 0.047 meq NaOH has $2.8308 * 10^{19}$ elementary charges.

Total charge = $2.8303 * 10^{19} * 1.602 * 10^{-19}$ Coloumbs

= 4.5349 Coloumbs

50 ml of the latex was weighed before and after drying. The particles weighed 4.355625 g. Since the density of PVC is 1.41 g/cm$^3$, then the volume of the particles that were titrated is 3.089cm$^3$.

From the Gaussian analysis done on the cleaned latex (see figure 3), table A3-3 can be constructed. This estimates that the total surface area of the particles in the latex that was titrated is 65.93 m$^2$.

$$\text{Surface Charge} = \frac{\text{Total Charge}}{\text{Total Surface Area}} ,$$

assuming that all of the NaOH used went to neutralize charge on the particles only.

Surface charge = 4.53 Coloumbs / 65.93 m$^2$

= 0.068 C/m$^2$

| DIAMETER $*10^9$ [m] | % VOLUME from PSD | ABSOLUTE VOLUME $*10^{-9}$ [$m^3$] | SURFACE AREA [$m^2$] |
|---|---|---|---|
| 122 | 0.1 | 3.089 | 0.151918 |
| 143 | 0.7 | 31.623 | 0.907258 |
| 167 | 2.7 | 83.406 | 2.996622 |
| 196 | 7.9 | 244.039 | 7.470581 |
| 230 | 16.1 | 477.344 | 12.974191 |
| 270 | 22.9 | 707.403 | 15.720066 |
| 316 | 22.8 | 704.314 | 13.37305 |
| 371 | 15.8 | 488.077 | 7.893428 |
| 435 | 7.7 | 237.860 | 3.280827 |
| 510 | 2.6 | 80.316 | 0.944894 |
| 598 | 0.6 | 18.535 | 0.185969 |
| 700 | 0.1 | 3.089 | 0.026477 |
|  |  | 3089.096 | 65.925281 |

**Table A3-3: This table summarizes the calculations for the surface area of the PVC particles dispersed in n-butylchloride with sonic waves.**

# APPENDIX 4

## MOBILITY CALCULATIONS

An example of the mobility calculation is given below. The frequency shift graphs are displayed in figure A4-1 to A4-. Table A4-1 gives the calculated mobility of the different dispersions.

Fringe spacing = $8.4*10^{-6}$ m
Gap Width = $1*10^{-3}$ m
Dielectric, D = 1.844
Perm. of free space, $E_0$ = $8.85*10^{-12}$
Viscosity, N = 0.00024 Kg/ms

### <u>100 % N-BUTYLCHLORIDE DISPERSION</u>

Applied PD = 100 V

Frequency Shift from graph = 109.5 $s^{-1}$

$$U^E = \frac{8.4*10^{-6}\ \mathrm{m} * 109.5 \quad * \quad 1*10^{-3}\ \mathrm{m}}{\mathrm{s} \qquad 100\ \mathrm{V}}$$

$$= 9.198*10^{-9}\ \mathrm{m^2/V.s}$$

From equation (33)

$$Y_0 = Z = \frac{3 * 0.00024\ \mathrm{kg} * 9.198*10^{-9}\ \mathrm{m^2} * \qquad \mathrm{J.m}* \quad 1}{2 \qquad \mathrm{m.s} \qquad \mathrm{V.s} \quad 8.85*10^{-12}\ \mathrm{C^2} \quad 1.844}$$

$$= \frac{0.203\ \mathrm{kg.m * m * J}}{\mathrm{s^2} \qquad \mathrm{C^2.V}}$$

$$= \frac{0.203\ \mathrm{J^2}}{\mathrm{C^2.V}} \qquad = 0.203\ \mathrm{V^2/V} \quad = 0.203\ \mathrm{V}$$

| % PENTANE IN SAMPLE | POTENTIAL DIFFERENCE APPLIED [V] | MOBILITY $m^2/V.s$ | CALCULATED SURFACE POTENTIAL [V] |
|---|---|---|---|
| 0 | 100 | $9.198*10^{-9}$ | 0.203 |
| 20 | 500 | $4.729*10^{-9}$ | 0.104 |
| 40 | 500 | $1.4*10^{-9}$ | 0.030 |
| 60 | 1000 | 0.0 | 0.0 |
| 90 | 1000 | 0.0 | 0.0 |

**Table 7: Measured mobilities and calculated surface potentials using the Huckel equation for the PVC dispersion in mixtures of pentane and n-butylchloride.**

# APPENDIX 5

## COMPUTER SIMULATION OF DLVO MODEL.

A computer simulation of the attractive and repulsive energies acting on the particles dispersed in n-butylchloride was done. The energies were added up in accordance with the DLVO theory to give the total potential energy. As a rule of thumb, a total energy of greater than 5 kT was used to be the minimum requirement for a stable dispersion.

The purpose of this simulation was to:

(1) Predict the stability ratio for the dispersion.

(2) Relate the stability ratio to the peak potential energy experienced by the particles and thus determine the minimum stability ratio necessary for stability in this dispersion.

(3) Predict the effects of radius, Hamaker constant and dielectric constant on the stability ratio.

Two computer programs were written. The first computed the stability ratio, W. It was calculated by integrating the total potential energy from the surface of the particle to an infinite distance away and dividing it by the integral of the attractive energy from the surface of the particle to an infinite distance away. This gave the ratio of the total attractive and repulsive force acting on the particle to the attractive force alone acting on the particle. The second program simply calculated the attractive, repulsive and total potential energy as a function of distance from the particle surface and wrote the data into output files. By examining or plotting the total potential energy versus distance data, the maximum or peak potential energy was determined.

## Model Equations and Constants.

The DLVO theory and associated equations were described in section 2.1.1. The repulsive force, attractive force and the stability ratio, were modelled as done by McGown and Parfitt [22]. The equations are summarized below [22] and they assumed that the particles were monodispersed spheres, and Ka << 1.

$$V_R = \left(\frac{4\pi\epsilon_r\epsilon_o a^2}{H + 2a}\right) Z^2\beta$$

$$V_A = - Aa\left(\frac{2.45L}{120\pi H^2} - \frac{2.17L^2}{720\pi^2 H^3} + \frac{0.59L^3}{3360\pi^3 H^4}\right) \quad \text{for } H > 150 \text{ Å}$$

$$V_A = - \frac{Aa}{12H}\left(\frac{L}{L+11.12H}\right) \quad \text{for } H < 150 \text{ Å}$$

$$W = \frac{\int_2^\infty 2(\exp((V_A+V_R)/kT)/s^2)\, ds}{\int_2^\infty 2(\exp(V_A/kT)/s^2)\, ds}$$

$$s = (H+2a)/a$$

$$\beta = \left(\frac{s^9 + s^6 + 5s^4 + s}{s^9 + s^8 + 2s^6 + s^5 + 6s^4 + 5s^3 + 3s + 1}\right),$$

for Ka << 1

where:

A = effective Hamaker constant [J] corrected to allow for particle-particle and dispersion medium-particle interactions.

a = particle radius [m]

H = shortest distance between the particle surfaces [m]

k = Boltzman constant

L = Wavelength of the intrinsic electrons oscillations,

T = absolute temperature [K]

$V_R$= electrostatic repulsion [J]

$V_A$= Van Der Waals Attraction [J]

Z = Zeta potential [V]

$\beta$ = accounts for the deformation of the two double layers when they overlap and is a function of H.

$\epsilon_r$= relative permittivity

$\epsilon_o$= Permittivity of free space [$C^2/(Jm)$]

The required property constants were estimated as explained below.

The Hamaker constant, A, of PVC in n-butylchloride was estimated using equation (8) and the following estimates:

$A_{PVC/n\text{-}bc/PVC} = A_{PVC/C5/PVC}$

$A_{C5/W/C5} = 3.36*10^{-21}$ J [37]

$A_W = 43.8*10^{-21}$ J [37]

where n-bc = n-butylchloride

C5 = hydrocarbon of chain length 5, eg., pentane

W = water

This gave an estimate of $7.2*10^{-21}$ J for the Hamaker constant of PVC particles in n-butylchloride. Except in cases where a specific parameter is varied to observe its effects on stability, the constants used in the computations involving the PVC dispersion in n-butylchloride were always as follows:

a = 159 nm

$\epsilon_r = 7.06$ for n-butylchloride [27]

T = 298 K

$L = 10^{-7}$ m [22]

$\epsilon_0 = 8.85*10^{-12}$ $C^2/Jm$

$k = 1.38054*10^{-23}$ J/K

## Computer Simulation.

The logic of the computer program to calculate the stability ratio was simple. The attractive and repulsive energies were computed at various distances, $s_i + \Delta s$, from the surface of the particle. These were added together to give the total potential energy as a function of distance, $s_i + \Delta s$. The data were stored and represented numerical functions of attractive energy versus distance, repulsive energy versus distance and total potential energy versus distance. To calculate the stability ratio, W, the total potential energy function and the attractive energy function are numerically integrated using the IMSL routine DCADRE and their ratio was calculated. The computer program computed W at several surface potentials varying from 0.01 to 0.1 V. A second program was written which computed the repulsive, attractive and total potential energies as functions of distance from the particle surface and put the data into files. A copy of the program codes is included below.

## Result of Simulation.

Calculation of the stability ratio was a means of comparing the relative stability of dispersions. However, the literature does not give a minimum value of W which is required for a stable dispersion. If W is unity, then rapid coagulation is expected and the stability would increase with increasing W.

Figure A5-1 shows a plot of W versus surface potential. Figure A5-2 shows a plot of log W versus the peak-potential energy from the particle interaction. Using the criteria that the peak must be greater than 5kT for stability, the minimum W for stability in this dispersion is approximately 50. Figure A5-3 therefore shows that a minimum surface potential of 90 mV is required for the dispersion to be stable.

The effect of radii on the stability was observed by plotting the stability ratio as a function of surface potential at three different radii's. This is shown in figure A5-4. Below a surface potential of 40 mV, the particle radius has a negligible effect on stability. As the surface potential increased, the repulsive component of the potential energy became more significant and particle radii became important. This was so because the repulsion is proportional to the square of the particle radius.

Figure A5-5 shows that the Hamaker constant had a negligible effect on the stability ratio. This was good because there was some uncertainty in the estimate of the effective Hamaker constant. The effect of the dielectric constant or relative permittivity on the stability ratio was much more significant. Figure A5-6 shows the effect on the stability ratio when the dielectric constant for pentane ($\epsilon_r$ = D = 1.844 [36]) was used instead of the dielectric constant for n-butylchloride ($\epsilon_r$ = D = 7.06 [36]).

In section 3.3.2.2.4, it was observed that particles with measured surface potential of 204 mV and 104 mV were stable while those with surface potential of 30 mV was unstable. Table (5) shows W's and peak potential energies computed for those three dispersions. The dielectric constant used was found by linear interpolation between the dielectric constants of pure pentane and pure n-butylchloride using the volume fraction as the weighing factor. Using either criteria that W > 50 or peak potential energy greater than 5 kT predicted that the dispersions with surface potentials of 204 mV and 104 mV to be stable and that with 30 mV to be unstable. This agreed with the actual observations.

| % Pentane in Dispersion | Relative Permit-tivity | Measured Sur. Pot. [V] | Radius [nm] | W, Stability Ratio | Peak Potential Energy |
|---|---|---|---|---|---|
| 0 | 7.06 | 0.203 | 159 | $5.8*10^{11}$ | 29.2 kT |
|  | 6.02 | 0.104 | 100 | 20.6 | 3.9 kT |
| 20 | 6.02 | 0.104 | 159 | 174.6 | 6.3 kT |
|  | 6.02 | 0.104 | 200 | 825.4 | 8.0 kT |
| 40 | 4.97 | 0.03 | 159 | 1.32 | 0.38 kT |

Table 5; Computed stability ratio and peak potential energy for the dispersion with varying amounts of pentane added to it. The radii and relative permittivity were varied in the dispersion with 20% pentane to show the effects on stability ratio and peak potential energy.

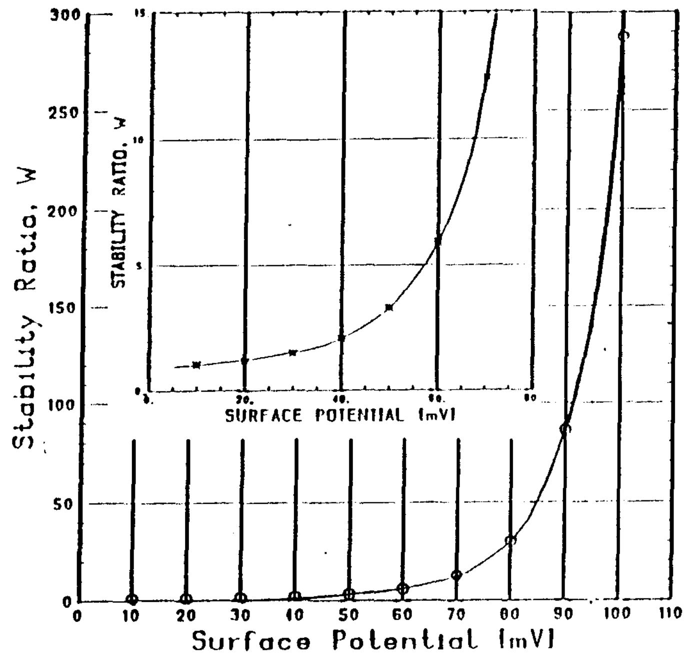

Fig. A5-1:Stability Ratio as a function of surface potential for PVC particles, radius 158.6 nm, dispersed in n-butylchloride.

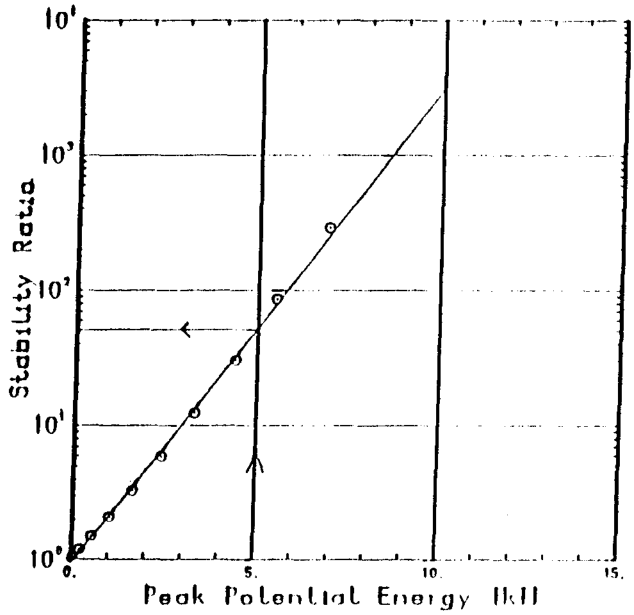

Fig. A5-2: Stability Ratio versus peak potential energy for PVC particles, radius 158.6 nm, dispersed in n-butylchloride.

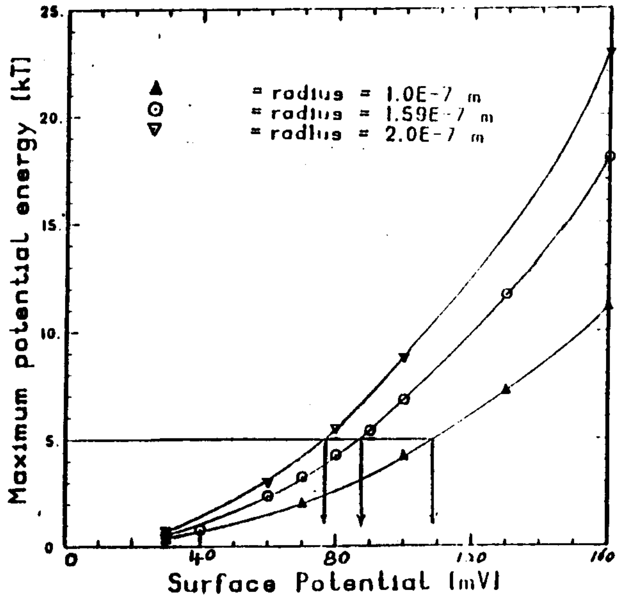

Fig. A5-3; Minimum surface potential for electrostatic stability.

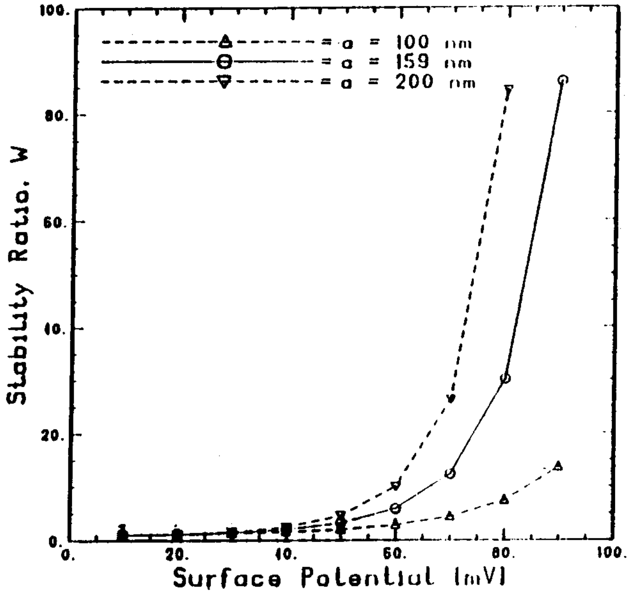

Fig. A5-4; Effect of particle radius on electrostatic stability,

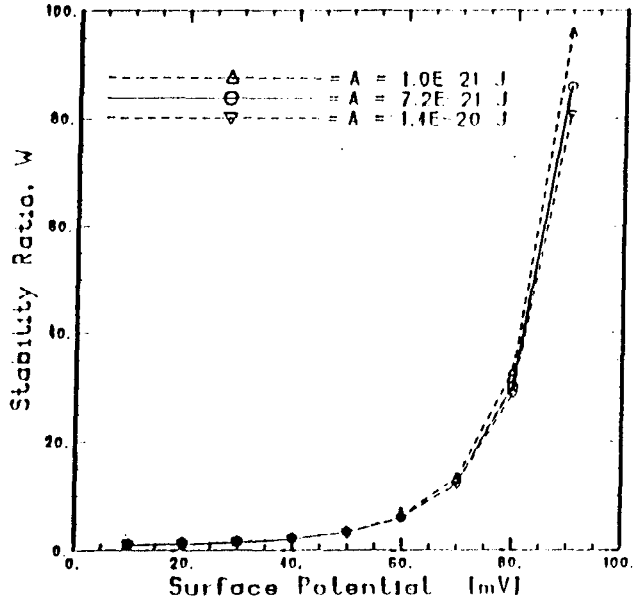

Fig. A5-5: Effect of Hamaker constant on electrostatic stability.

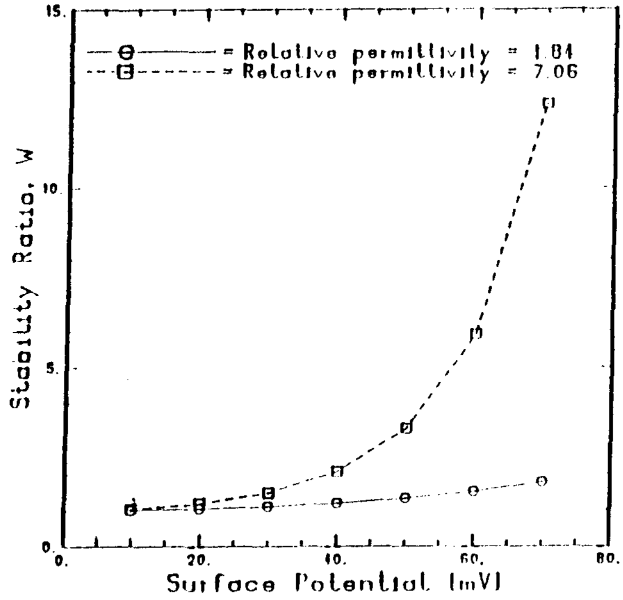

Fig A5-6: Effect of Relative Permittivity (Di-Electric constant) on electrostatic stability.

## PROGRAM LISTINGS

The two computer program listings are given below. The first calculates the stability ratio of the PVC particles dispersed in n-butylchloride as a function of the zeta potential using the DLVO theory. The second calculates the attractive, repulsive and total potential energies of the particles as a function of the distance from the particle surface.

```
      PROGRAM STAB

C     THIS PROGRAM CALCULATES THE STABILITY RATIO
C     AS A FUNCTION OF ZETA POTENTIAL FOR PARTICLES
C     OF EQUAL SIZES, PROVIDED THAT K*a <<1.  IT
C     USES IMSL ROUTINE TO EVALUATE THE INTEGRAL.
C     EVERYTHING IS IN SI. THE STABILITY RATIO AT
C     DIFFERENT POTENTIALS ARE WRITTEN TO FILE W.DAT.

      IMPLICIT REAL*8(A-H,O-Z)
      EXTERNAL F1,F2,F3,F4
      COMMON RLAMBDA,RAD,A1,B1,B2,B3,CT,Z
      OPEN (UNIT=1,FILE='W.DAT',STATUS='NEW')
C     READ DATA
      DATA RAD,HA/2.0E-7,7.2E-21/
      DATA PERM,T,RLAMBDA,C/6.248E-11,298.15,1.0E-7,1.38054E-23/

      DO 10 I=1,20
      ZETA=0.01+(I-1)*0.01

      PI=3.141592654
```

```
C     BOUNDARY CONDITIONS FOR WHICH FIRST
C     VERSION OF VDW'S EQUATION VALID
      A=2.001
      B=(1.5E-8+2*RAD)/RAD

      RERR=0
      AERR=1.0E-6

C     INTERMEDIATE CONSTANTS
      Z=ZETA**2*PERM*RAD
      A1=-HA/12.0
      B1=(2.45*RLAMBDA)/(10.0*PI*RAD)
      B2=(2.17*(RLAMBDA**2))/(60.0*(PI**2)*(RAD**2))
      B3=(0.59*(RLAMBDA**3))/(280.*(PI**3)*(RAD**3))
      CT=C*T

C     CALCULATE ENERGIES
      C1=DCADRE(F1,A,B,AERR,RERR,ERROR,IER)
      C2=DCADRE(F2,A,B,AERR,RERR,ERROR,IER)

C     BOUNDARY CONDITIONS FOR WHICH SECOND
C     VERSION OF VDW'S EQUATION VALID
      A=(1.5E-8+2*RAD)/RAD
      B=10000

C     CALCULATE ENERGIES
      C3=DCADRE(F3,A,B,AERR,RERR,ERROR,IER)
      C4=DCADRE(F4,A,B,AERR,RERR,ERROR,IER)

C     CALCULATE STABILITY RATIO
      W=(C1+C3)/(C2+C4)
      ZETA1=ZETA
      WRITE(1,100) ZETA1,W
 100  FORMAT(X,2(E10.4,X))

 10   CONTINUE
      END


      FUNCTION F1(X)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON RLAMBDA,RAD,A1,B1,B2,B3,CT,Z

      F1=DEXP(((Z*((X**8)+(X**5)+5*(X**3)+1))/
      +        ((X**9)+(X**8)+2*(X**6)+(X**5)+6*(X**4)+5*(X**3)+
      +     3*X+1)+(A1*RLAMBDA)/((X-2)*RLAMBDA+11.12*(X-2)**2*
      +     RAD))/CT)/X**2
      RETURN
      END
```

```
      FUNCTION F2(X)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON RLAMBDA,RAD,A1,B1,B2,B3,CT,Z

      F2=DEXP(((A1*RLAMBDA)/((X-2)*RLAMBDA+11.12*(X-2)**2*RAD))/
      +     CT)/X**2
      RETURN
      END

      FUNCTION F3(X)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON RLAMBDA,RAD,A1,B1,B2,B3,CT,Z

      F3=DEXP(((Z*((X**8)+(X**5)+5*(X**3)+1))/
      +        ((X**9)+(X**8)+2*(X**6)+(X**5)+6*(X**4)+5*(X**3)+
      +     3*X+1)+A1*((B1/(X-2)**2)-(B2/(X-2)**3)+(B3/
      +     (X-2)**4)))/CT)/X**2
      RETURN
      END


      FUNCTION F4(X)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON RLAMBDA,RAD,A1,B1,B2,B3,CT,Z

      F4=DEXP(A1*((B1/(X-2)**2)-(B2/(X-2)**3)+(B3/(X-2)
      +    **4))/CT)/X**2
      RETURN
      END



      PROGRAM ENERGY


C     THIS PROGRAM EVALUATES THE ATTRACTIVE,
C     REPULSIVE AND TOTAL ENERGY FOR TWO
C     EQUAL SIZED PARTICLES, AS A FUNCTION
C     OF THE DISTANCE FROM THE PARTICLE SURFACE,
C     S, PROVIDED THAT K*a << 1. DISTANCES ARE
C     IN ANGSTROM UNITS. EVERYTHING ELSE IS SI.
C     THE VDW ATTRACTIVE ENERGY IS WRITTEN TO
C     FILE VA.DAT, THE REPULSIVE ENERGY IS WRITTEN
C     TO FILE VR.DAT AND THE TOTAL ENERGY IS WRITTEN
C     TO FILE VAVR.DAT.

      IMPLICIT REAL*8(A-H,O-Z)
      OPEN (UNIT=1,FILE='VA.DAT',STATUS='NEW')
      OPEN (UNIT=2,FILE='VR.DAT',STATUS='NEW')
      OPEN (UNIT=3,FILE='VAVR.DAT',STATUS='NEW')
```

```
C     READ DATA
      DATA DELTAS,N/0.25,60/
      DATA ZETA,RAD,A/30.0E-3,1000,7.2E-21/
      DATA PERM,T,LAMBDA,C/6.248E-11,298.15,1000,1.38054E-23/

C     VARY DISTANCE FROM PARTICLE, S
      DO 10 I=1,N
         S=2+(I-1)*DELTAS+(DELTAS/2)

C     CALCULATE ENERGIES
         CALL FUNC(S,ZETA,RAD,A,PERM,T,LAMBDA,C,VA,VR)

C     MAKE ENERGIES DIMENSIONLESS
         VA=VA/C/T
         VR=VR/C/T
         VAVR=(VA+VR)

C     WRITE OUTPUT FILE
         WRITE(1,100) S,VA
         WRITE(2,100) S,VR
         WRITE(3,100) S,VAVR

 100     FORMAT(5X,2(E10.4,2X))
 10   CONTINUE

      END

      SUBROUTINE FUNC(S,ZETA,RAD,A,PERM,T,LAMBDA,C,VA,VR)

C     THIS SUBROUTINE CALCULATES THE REPULSIVE AND
C     ATTRACTIVE ENERGIES AS A FUNCTION OF S

      B1=S**8+S**5+5*S**3+1
      B2=S**9+S**8+2*S**6+S**5+6*S**4+5*S**3+3*S+1
      B=B1/B2

      VR=ZETA**2*PERM*RAD*1E-10*B

      H=RAD*(S-2)
      IF(H.GT.OR.EQ.150) THEN
      VA1=2.45*LAMBDA/(120*PI*H**2)
      VA2=2.17*LAMBDA**2/(720*PI**2*H**3)
      VA3=0.59*LAMBDA**3/(3360*PI**3*H**4)
      VA=-A*RAD*(VA1-VA2+VA3)
      ELSE
      VA=-A*RAD*(LAMBDA/(LAMBDA+11.12*H))/(12*H)
      ENDIF


      RETURN
      END
```