FILM FORMATION FROM LATEXES

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ABSTRACT

The use of the ultracentrifuge to determine the minimum pressure required for coalescence of latex particles is described. The extent of coalescence is found to reach an equilibrium value after a short centrifugation time and this equilibrium provides the basis for calculating the required pressure. Displacements of the emulsifier from the coalescing latex particles affect the equilibrium but can be taken into account.

The centrifugation method provides a measure of the forces opposing coalescence of the latex particles and can be used to follow the influence of pH, emulsifier content and electrolyte on the stability of the latex system. The results are accounted for by the DLVO theory for colloidal stability. The stability of this latex system is primarily determined by electrostatic repulsion.

Examination of the films produced by centrifugation, and following the aging of these films in air and in water, confirmed that the coalescence is initiated under the influence of the centrifugation force, and that the filming process is then slowly completed under the influence of the surface tension of the polymer.

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by

Mohamed S.I. El-Aasser, B. Sc., M. Sc., (Alexandria, Egypt)

A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfilment of
the requirements for the degree of
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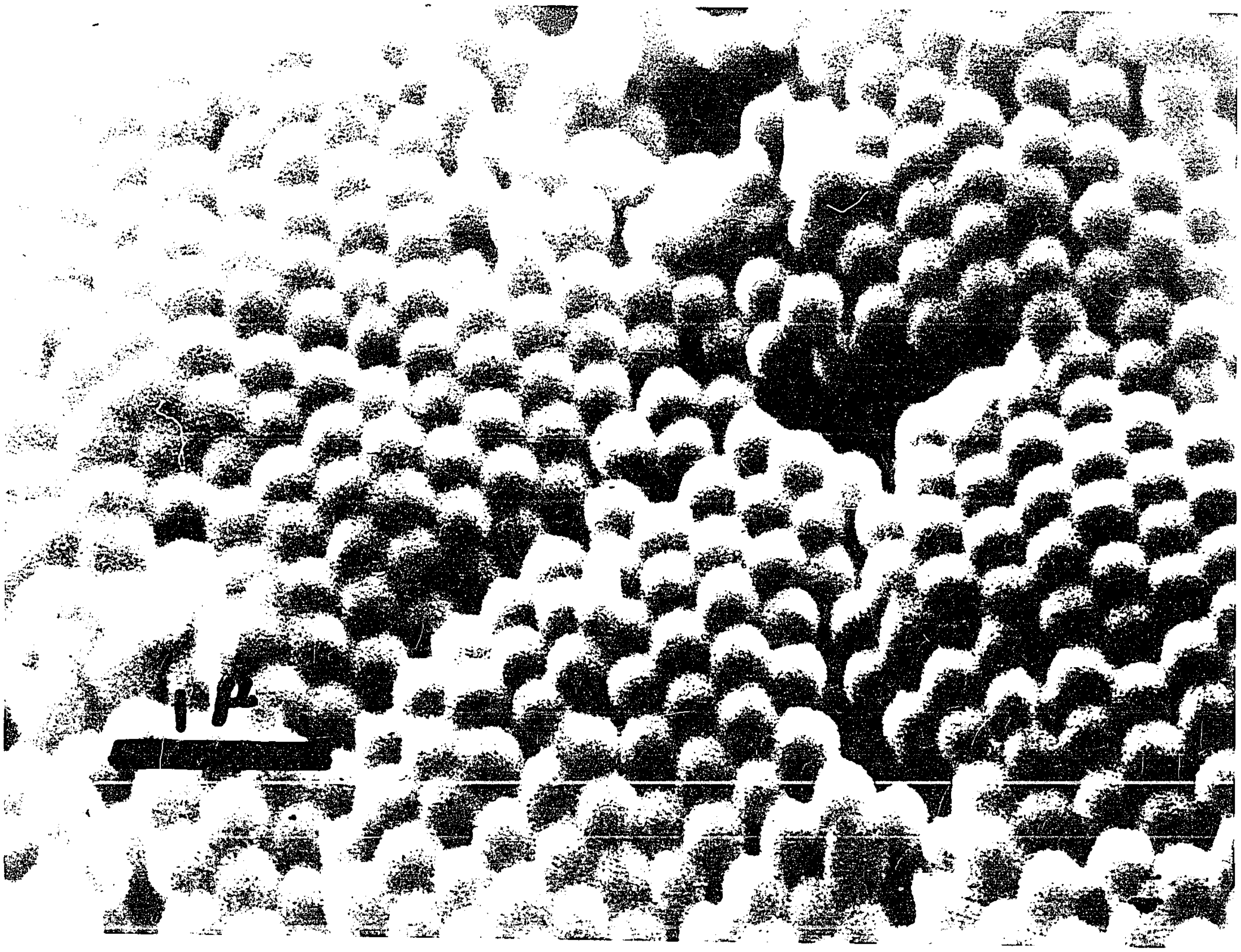
A Scanning Electron Micrograph

of

Incipient Film Formed

from

Styrene-Butadiene Latex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ABSTRACT

The use of the ultracentrifuge to determine the minimum pressure required for coalescence of latex particles is described. The extent of coalescence is found to reach an equilibrium value after a short centrifugation time and this equilibrium provides the basis for calculating the required pressure. Displacements of the emulsifier from the coalescing latex particles affect the equilibrium but can be taken into account.

The influence of pH, emulsifier content and electrolyte on the pressure required for coalescence of styrene-butadiene latex was studied using this technique. The maximum stability of the latex occurs between pH 8.8 and 10.7 but decreases outside these limits and the latexes are unstable below pH 2 and above pH 12. The minimum pressures required for coalescence were found to increase with the increase of the particle's surface coverage, at least till 25%, with ionizable emulsifier molecules. Particles covered with un-ionized emulsifier required a very low pressure for coalescence. The increase of the electrolyte content of the latex at constant pH and surface coverage led first to an increase in the pressure required for coalescence, and then to a decrease. The electrolyte effect was found to be dependent on the surface coverage of the particles.

The centrifugation method provides a measure of the forces opposing coalescence of the latex particles and can be used to follow the

influence of any of the above factors. The results are accounted for by the DLVO theory for colloidal stability, where the influence of the above factors on the theoretically calculated forces are found to correlate qualitatively with the experimentally measured values. The stability of this latex system is primarily determined by electrostatic repulsion.

Examination of the films produced by centrifugation, and following the aging of these films in air and in water, confirmed that the coalescence is initiated under the influence of the centrifugation force, and that the filming process is then slowly completed under the influence of the surface tension of the polymer.

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FOREWORD

Latexes find wide applications in the paper, textile, rubber and paint industries. All these applications require the formation of films from the latexes. Consequently, the investigation of the mechanism and the forces involved in the film formation has both theoretical and practical importance. This thesis represents one approach to the quantitative determination of the forces involved in initiating the coalescence of latex particles. The thesis is presented in the following format :-

Part I, the general introduction, includes a general review of the importance of latexes, the mechanism of film formation and the stability. The aim of this work and the scope of the investigation are also included.

Part II is a review of the emulsion polymerization technique for the preparation of the monodisperse latex. The method, materials and equipment, used for the preparation of monodisperse styrene-butadiene (60:40) latex system are described. The use of the electron-microscope for the determination of the size and uniformity of the latex particles is also described.

Part III relates to the characterization of the latex system, and reports the properties of the latex system which are relevant to this work. This includes the effect of dilution and centrifugation on the emulsifier distribution in the system, and the effect of aging on the aqueous latex system and also on the morphological changes of the film.

Part IV* describes the ultracentrifugation technique for the determination of the minimum pressure required for initiation of coalescence of latex particles and the studies on the effects of the different factors influencing equilibrium in this technique.

Part V reports the application of the ultracentrifuge technique to the study of the interparticle forces in the latex system during coalescence. The effects of pH, emulsifier and electrolyte contents on the stability of the latex system are reported. The stability data are analysed in terms of the existing theories of colloidal stability.

Appendices I, II, III, and IV describe the different auxiliary experimental techniques used in this work.

The thesis is ended by suggestions for further works, and claims for original research.

(*) Part IV has been published in "J. Colloid and Interface Sci. 36, 86 (1971)".

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GLOSSARY OF SYMBOLS

A	Hamaker constant, erg.
Å	Ang strom unit, 10^{-8} cm.
a	Radius of the particle, Å, cm.
$\acute{a}$	Acceleration, cm/sec^2.
C	Numerical factor varies between 1/4 and 1/6.
D_i	Diameter of the individual particle, Å, cm.
D_n	Number average diameter, Å, cm.
D_w	Weight average diameter, Å, cm.
d	Density of solution, gm/cm^3; thickness of platinum plate, cm.
d_1	Density of medium, gm/cm^3.
d_2	Density of the polymer, gm/cm^3.
e	Electronic charge, 4.8×10^{-10} esu.
F	Force, dyne.
F_A	Force of attraction, dyne.
F_R	Force of repulsion, dyne.
g	Gravitational constant, 980 cm/sec^2.
gm	Gram.
H	Distance between the particles surfaces, Å.
H_o	Distance between the particles surfaces at the maximum in the potential energy curve, Å.
hp	Horsepower.
KV	Kilovolt.
k	Boltzmann constant, 1.38×10^{-16} erg/degree.
kT	Thermal energy, 4.1×10^{-14} erg.
L	Width of plate, cm.

M	Molar.
ml	Milliliter.
MFT	Minimum filming temperature, °C.
mV	Millivolt.
mm	Millimeter.
meq	Milliequivalent.
min	Minute.
m	Mass of uncoalesced latex particles, gm.
N	Normal solution.
n	Number of ions/cm^3.
n_i	Number of particles
oz	Ounce.
p.s.i.	Pounds per square inch, (1 p.s.i. = 68,947 dynes/cm^2).
R	Radius of rotation, cm; circumference of the platinum plate, cm.
rpm	Revolutions per minute.
T	Absolute temperature, °K; total parts of ingredients charged for polymerization.
t	Time, min.
U	Mobility, cm/sec./volt/cm.
V_A	Potential energy of attraction, erg.
V_R	Potential energy of repulsion, erg.
V_{RS}	Steric repulsive energy.
V_T	Total potential energy of interaction, erg.
v	Valency of the counter-ion.
W	Additional pull on the platinum plate, i.e. the force, gm.

ε	Dielectric constant.
η	Viscosity, centipoise.
μ	Micron unit, 10^{-4} cm.
$1/\kappa$	Thickness of the diffuse double layer, cm.
ψ_δ	Stern potential.
ζ	Zeta-potential, -mV.
γ	Surface tension, dyne/cm.
ω	Angular velocity, (radians/sec).
Φ	Volume fraction of polymer.

PART I

GENERAL INTRODUCTION

INTRODUCTION

"Latex" originally a Latin word which meant a liquid or a fluid, has been used by botanists to denote the milky juices obtained from several plants. Of these, the most important are those obtained from the rubber tree, and are aqueous colloidal suspensions of rubber particles stabilized by protein. More recently, the application of the term latex has been extended to include colloidal suspensions of spherical synthetic polymer particles as prepared by emulsion polymerization, and it will be used with this meaning throughout the thesis.

Latexes have a wide industrial use1) in surface coatings, adhesives and impregnating agents. They have rather diverse applications in each one of these fields.

In surface coatings, latexes are widely used as film binders in latex-based paints. Latexes are also used for coating the surface of paper to produce a product of high quality, by enhancing its appearance, increasing its rigidity and improving its "printability". In the textile industry, latexes are used for covering one surface of the textile with a coherent, impervious film of polymer in a process called "latex spreading". The intention of such treatment is to produce protective-clothings, such as rain-proof fabrics.

Latex adhesives are used in a wide range of different industries, the most important of which are their use as bonding in the manufacture of paper and leather products. Another important use of latex adhesives is their use as bonding agents to promote rubber-to-textile adhesion which has greatest importance in the production of tires and belts. Latexes are also used as polymeric adhesives in the textile industry, e.g. in combining and doubling processes in order to bond two or more textile layers together, and in producing non-woven fabrics.

Latexes are used in a variety of processes for impregnating textiles in order to enhance such properties as crease-resistance, resilience, wet strength etc. In the paper industry, latexes are used for impregnating the paper so that improvements are obtained in such properties as resistance to tear initiation and tear propagation, and resistance to delamination.

Another important application of latexes is in connection with carpet manufacture. Latex compounds are being used increasingly as carpet-back sizing in which they serve at the same time as coating, adhesive and impregnating agents.

All these applications exploit the advantages which are offered by polymer latexes as compared with polymer solutions. Some of these advantages are reduced cost and ease of application, non-flammability, the absence of toxic solvents, the possibility of a wide range of high solid contents at low viscosities, the possibility of depositing higher-molecular-weight material of superior aging resistance, and the ease with which the penetration and wetting tendencies can be varied. Another advantage of latexes, especially in its application as adhesive, is their ability to wet surfaces already wet with water.

The major disadvantage of latexes, as compared to polymer solutions, is their possible lack of stability resulting in coagulation during storage or application.

From the foregoing considerations, it is clear that the use of latex in any of the above applications requires that a film be formed, i.e. the polymer particles must coalesce and lose their identity. Film formation is usually accomplished by drying with the development of capillary tension pulling the particles together. An exception is latex-dipping in which the film is formed by electodeposition$^{2)}$.

The films produced from latexes for most applications must be coherent and tough and must adhere well to the surface to which latex is applied. The character of the film depends upon, among other factors, the polymer composition of the latex particles.

The most common latexes are based on various diene polymers and copolymers, such as polybutadiene, styrene-butadiene, and acrylonitrile-butadiene, or on vinyl polymers and copolymers such as polyvinylacetate and its copolymers with higher fatty esters and with alkyl acrylates.

CURRENT VIEWS ON THE MECHANISM OF FILM FORMATION

Upon drying at room temperature, the latex particles are transformed either into a tough, transparent, continuous film, or a friable, opaque powder. Whether latex systems are film forming or non-film forming depends primarily upon the chemical composition of the polymeric particles, and the conditions of drying. For each chemical composition of latex, a minimum filming temperature (M F T) may be determined below which only an opaque powder is produced. Raising the temperature during or after drying results in the formation of a continuous film.

Even though the production of synthetic latex started about half a century ago, investigations of the transformation of particles into continuous film did not start until about thirty years later. Most of the early investigations were limited to devising hypotheses to explain the macroscopic observations during the film formation. Later on, electron-microscopy was applied to investigate the submicroscopic phenomena in the film formation, which helped to refine the theory. Today, twenty years after the beginning of the investigations, although a qualitative picture of the mechanism of film formation has been given, a complete understanding of the mechanism in quantitative terms is far from complete.

The latest qualitative picture of the mechanism of film formation is due to Vanderhoff3) and is summarized as follows.

> "As the water evaporates, the particles are brought together, so that their stabilizing layers are in contact and their further approach is hindered. The

> pressures forcing the particles together is increased by the further evaporation of the water (that is by the force arising from water-air interfacial tension or in other words the capillary pressure), until the stabilizing layers are ruptured and a polymer-polymer contact is formed. Once this occurs, the pressures exerted upon the particles are increased further by the forces arising from the polymer-water and polymer-air interfacial tension until the film formation is completed."

Brown[4)] was the first to note that film formation and water evaporation are concurrent events, and he proposed that the capillary force provides the major contribution to the forces required to bring the particles into contact. The capillary forces result from the surface tension of the water when evaporation has caused the formation of menisci with very small radii of curvature between the particles. He stated that the capillary force must exceed the resistance of the spherical particle to deformation for film formation to occur. If the particles have sufficient rigidity to resist deformation for the duration of the capillary pressure, water will evaporate without particle coalescence. He calculated the pressures exerted upon the particles according to his hypothesis and found that pressures as great as 1100 p.s.i. for small particles (1000 Å in diameter) could develop and that they vary inversely with the particle size.

Vanderhoff et al[5)] examined the first stage of drying latex particles under the optical microscope. They followed the drying of a drop of 1% solid content of monodisperse latex particles with large diameters of 12,000 Å. Among other interesting phenomena they observed the packing of the latex particles into a regular pattern at the edge of the drying drop, and the spontaneous arrangement of the latex particles into close-packed hexagonal arrays. They reported that the arrangement is complete before the water evaporates completely. The first stage of film formation was investigated further by examining[6)] replicas of the surface of the film formed from styrene-butadiene (60:40) latex under the electron microscope. The particles were found to be coalesced, but their surface contours were still visible, though the film was transparent tough and continuous.

These observations showed that in the first stage of film formation from latexes, the particles are brought together by water evaporation, arrange themselves in a uniform pattern (in the case of monodisperse particles), then under the effect of capillary pressure the stabilizing layers are ruptured and polymer-polymer contacts are established.

The effect of polymer-water interfacial tension in film formation was first introduced by Dillon et al[7)], which was considered, at that time, as the major driving force for latex coalescence; under its effect the particles fuse together. They considered a viscous flow mechanism and the model developed by Frenkel[8)] to describe the particle coalescence in the latex system, where the particle surface tension, the time of contact, the particle radius and viscosity, determine whether a continuous film will be formed when the latex is dried. For a given latex all the quantities, except the radius, were considered as constant, and on calculating the pressures exerted upon the particles they found that pressures as great as 1740 p.s.i. were predicted at small particle size (500 Å diameter), and these vary inversely with the particle size. Brown$^{4)}$, and Vanderhoff et al$^{3)}$, pointed out that this polymer-water interfacial force of Dillon is operative only after the particle-particle contact is established under the influence of the capillary force.

The effect of the polymer-water interfacial force in completing the filming process was proved experimentally by the aging experiment of Vanderhoff et al$^{9)}$. The aging effect, at room temperature, on the morphology of the films formed from styrene-butadiene (67:33) latex was followed in the air, using the replication-electron microscope technique. This showed that the contours of the individual particles were still well-defined in the transparent, continuous film, but disappeared gradually until they become invisible after 14 days of aging.

The effect of the viscosity of the polymer in the film formation was restated by Voyutskii$^{10)}$ who introduced the idea of applying the "autohesion" concept to explain the physical properties exhibited by latex cast films. According to this concept, introduced earlier by Josefowitz and Mark$^{11)}$, (but not applied to latex films), the free ends of the polymer chains diffuse across the particle-particle interface of the coalesced film, knitting the film into a single coherent mass.

Experimental support for the effect of autohesion was obtained by studying[9)] the effect of polymer structure on the rate of "further gradual coalescence" in the dried film from styrene-butadiene (65:35) latex, using the replication-electron microscope technique. Decreasing the polymer molecular weight of the latex particles, by the addition of modifying agents such as tert-dodecyl mercaptan during their preparation, results in acceleration to the "further gradual coalescence" process. On the other hand, increasing the cross-linking of the polymer, by adding divinylbenzene to the polymerization charge, results in retardation of the "further gradual coalescence" process. These results are consistent with Voyutskii's theory of autohesion, where the greater the viscosity of the particles (e.g. due to cross-linking) the slower the rate of autohesion.

These observations showed that the completion of film formation after polymer-polymer contacts is mainly due to the polymer interfacial tension, and is a time dependent process. In this stage the visible contours of the particles disappear gradually and the polymer chains diffuse from one particle to another resulting in the formation of film with a coherent structure. The rate of completing this stage depends a great deal on the viscosity of the polymer.

The effects of other factors such as temperature[12)] and plasticizer concentration[13)], were investigated using the replication-electron microscope technique. Increasing the temperature during the filming process from polyvinyl toluene latex[12)], and increasing the plasticizer concentration in vinyl chloride-vinylidene chloride (75:25) latex[13)], were found to increase the tendency of the given latex to form a continuous film, as indicated by the increase of the degree of particle coalescence in the electron micrographs. These behaviors were explained on the basis that raising the temperature and increasing the addition of plasticizer result in decreasing the viscosity of the latex particles i.e. decreasing the resistance of the latex particles to deformation. These observations correlate with the macroscopic appearance of the films where the opaque, friable films were transformed into transparent and continuous films on raising the temperature or increasing the concentration of plasticizer.

Vanderhoff et al3) in an attempt to refine the theory of film formation extended the hypothesis of Dillon et al7) and Brown4), and considered the effect of the stabilizing layers surrounding the latex particles as well as the very small curvature formed in the initial stages of coalescence, and how they affect the magnitude of the forces exerted on the particles. Calculations of the pressures exerted upon the particles according to their concept, showed that the pressures do not vary inversely with the particle size in a simple relationship, as proposed by Brown4) and Dillon et al7).

One important problem in film formation from latexes is the fate of the emulsifier surrounding the particles. Many speculations are offered by different investigators. Voyutskii and Starkh14) stated that the emulsifier could remain in the film either as an independent network or dissolved in the polymer. Wheeler et al15) proposed three possibilities: the emulsifier remains in the particle-particle interface, it is forced into small islands within the film or it diffuses into the particles. Lately Vanderhoff9) offered an example in which the emulsifier is exuded to the film surface as it ages. Until now, direct experimental evidence of the fate of emulsifier during film formation is lacking.

From the above considerations it could be summarized that the experimental investigation of the film formation from latex particles has not gone beyond the characterization of the latex particles and the following-up of the effects of different factors on the morphological changes (macroscopic and microscopic) during the filming process. No effort has been given to the actual experimental determination of the forces involved in the coalescence of the latex particles which are required for their transformation into film. As a matter of fact, it seems to be implied[3)] that the maximum force exerted upon the particles during the water evaporation, i.e. the capillary force, was taken to be the force required for initiation of coalescence.

CURRENT VIEWS ON THE STABILITY OF LATEXES

The stability of latexes is important since flocculation or coagulation must be prevented during preparation and storage and during industrial applications especially if the latexes are to be subjected to stirring, blending, shaking or other modes of agitation.

In classical latex preparations, stability was achieved by the physical adsorption of emulsifier on the particle surface. Emulsifiers fall into four main classes, anionic, cationic, non-ionic and amphoteric. The most commonly used emulsifiers for stabilizing latexes are **anionic**, especially the carboxylates (fatty acid soaps) and sulfonates. Other means of stabilizing the latex are known and are becoming more common e.g. the introduction of carboxyl groups into the polymer composition of the particle, producing carboxylated latexes which are more water resistant because of diminished surfactant16). Another stabilizing agent for latexes is a polymerized emulsifier such as sodium acrylamidostearate polymerized *in situ*17), and which is chemically bound to the surface of the particle.

As a hydrophobic colloidal system, a latex should conform to current theories of colloidal stability18-22). The stability of latexes, in common with other colloidal systems, has been interpreted generally from two view points: either from the electrostatic theory of stability, which specifies the presence of an electrical double layer on the surface of the particles resulting in electrostatic repulsion; or from the presence, around the particles, of a coating of emulsifier possessing structural and mechanical properties which result in an entropic repulsion or other steric barrier. Both concepts start from the premise that a layer of emulsifier is adsorbed or bound, physically or chemically, on the surface of the particles.

The theoretical treatment of the electrical double layer and its relation to the stability of colloidal systems have been established by Derjaguin and Landau23), and Verwey and Overbeek18) and is designated as DLVO theory. According to the theory, a combination of the van der Waals attractive energy with the double layer repulsive energy leads to potential energy of interaction that involves an energy barrier. The magnitude of the potential energy barrier depends upon, among other factors, the nature and concentration of the adsorbed ionic emulsifier, the ionic strength of the medium, and determines whether or not the colloidal system is stable to coagulation, flocculation or coalescence.

A more detailed presentation of the theory may be found elsewhere in this thesis24). Originally the theory was developed for two simple cases of interaction, namely that between two flat plates and that between two spheres of equal size. Valid experimental testing of the theory required the use of systems conforming closely to the theoretical models. A cross-linked monodisperse polystyrene latex system has been chosen by many investigators25-28) as a "model suspension" to test the DLVO theory for the "sphere" case. This choice is due to the highly spherical shapeand uniform size of the particles and the possibility of characterizing the surface of the particles.

The theoretical treatment of the mechanical29), or steric30-35) effect of the adsorbed emulsifier layer on the colloidal stability is still in a rather primitive state compared to the electrostatic effect.

Mackor and van der Waals[30)] introduced the term "entropic repulsion" to describe the loss of translational freedom of the "tails" of the adsorbed molecules during particle interactions, which leads to a loss of entropy and thus to repulsion. Other workers[31,32)] attempted to formulate the entropic repulsion quantitatively. Other attempts[33-35)] were made to introduce a term to account for the solvation of the adsorbed layers and its effect on the colloidal stability. Another attempt[29)] was also made to account for the mechanical effect of the stabilizing layer in preventing the contact of the polymer particles, through the use of the elasticity modulus of this layer. All these attempts help in clarifying some of the principles which govern the steric stabilization, but a concrete quantitative theory which describes this mechanism is still lacking.

Information on the stability of any disperse system is usually obtained by kinetic methods[25,26,36)], in which the effect of electrolyte on the rate of coagulation is followed. Some systems are known[37-41)], in which a direct determination of the forces developed between surfaces can be carried out under equilibrium conditions.

Most of the experiments on the stability of latexes have been based on kinetic methods[25-28,35)]. The rate of flocculation or coagulation was followed, by visual or microscopic methods[28)], by light scattering methods[25, 26)], or by following the optical density with time[35)]. Some experiments have been designed to test the mechanical stability of the latexes by determining[42)] the time required to produce complete flocculation by high speed stirring of the latex system, or by determining[43)] the weight of the coagulum produced from the latex system subjected to a constant shearing stress for a desired length of time.

Recently, Ottewill et al[41)] applied the equilibrium method to measure the pressure developed in a montmorillonite system as a function of the distance of separation of the plates. No publication has appeared on the use of this equilibrium method in studying the stability of latexes, though Ottewill reported in his paper[41)] that monodisperse polystyrene latex particles had been used for similar studies.

Most of these investigations, kinetic or equilibrium, proved the importance of the DLVO theory in any quantitative description of the electrostatic role in the stability. But they also pointed out the shortcomings of the theory in dealing with cases where repulsive forces, other than electrostatic, are involved.

APPROACH TO THE PROBLEM

The use of latexes in such applications as paints, paper coatings, or textile sizings requires that the latex particles form a continuous film on drying. Therefore, an understanding of the mechanism and forces involved in the coalescence of latex particles is not only desirable from a theoretical point of view, but also has obvious practical importance.

The existing theories of the mechanism of film formation from latex particles identifies two forces as being essential for the filming process. First, there is a force which acts to bring the particles together into contact and initiates the coalescence between them. This was taken to be the capillary force developed between the particles due to water evaporation. Second, the polymer-water interfacial tension acts (with or without the aid of the first force) to complete the filming process.

The present study represents the first attempt to determine, experimentally, the force required for initiation of latex particle coalescence, and the quantitative investigation of the effect of different factors on this force.

MATERIALS

Commercially produced latexes usually contain several additives which complicate the system and which are rarely identified. In addition, the particles are often non-uniform. Consequently, these commercially produced latexes are unsuitable for carrying out any meaningful systematic investigation. The latex system used throughout this work is a monodisperse styrene-butadiene (60:40) latex which is typical of the compositions used in paper coatings. The latex was prepared by an emulsion polymerization technique44) using lithium stearate as emulsifier and potassium persulfate as initiator at 60°C. The particle diameters are between 3,100 Å to 3,700 Å ; and the ratio of weight average diameter to number average diameter is between 1.02 to 1.05, which indicates the uniformity of the particles.

SCOPE OF INVESTIGATION

The emulsion polymerization technique is used for the preparation of the styrene-butadiene (60:40) latex system. A general characterization of the latex is undertaken to determine its basic properties and behavior. Included are specific investigations of the properties of the latex system which are relevant to the work in-hand. Electron microscopy, conductometric titration and surface tension measurements are used in this characterization. The filming process is followed by the use of the scanning electron microscope.

The ultracentrifuge is employed in developing a method for the determination of the force required to produce coalescence of the latex particles, under equilibrium conditions. Since the fate of the emulsifier during the filming process influences the establishment of equilibrium in the system, a study of this effect is undertaken.

The ultracentrifuge technique is used to investigate the effect of pH, emulsifier and electrolyte contents on the stability of the latex system. These stability data are analysed in terms of the existing theories of colloidal stability in order to define the important factors in the stability of the latex system.

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PART II

EMULSION POLYMERIZATION

INTRODUCTION

Systematic research into the mechanism of film formation in latex systems requires development of model systems in which the significant variables can be modified independantly through (1) the control of particle size distributions, (2) control of polymer properties, and (3) control of the emulsifiers and other chemicals in the surrounding medium.

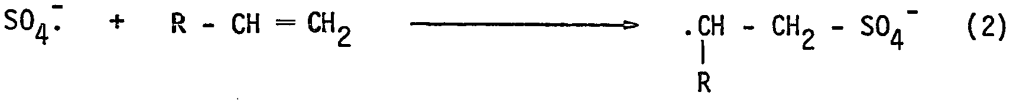
Commercially produced latexes contain many undisclosed chemical additives that influence the behavior of the latex system. Consequently the monodisperse styrene-butadiene (60:40) latex required for this work was prepared in our laboratory using the emulsion polymerization technique. The general technique to be followed can be found in the text books, but a great amount of trial and practice was required before attaining monodispersity and mastering its reproducibility. This part gives a summarized account of the mechanism of preparation of monodisperse latex and describes the procedure as used in our preparations.

MECHANISM

Some understanding of the mechanism of emulsion polymerization is necessary before dealing with the preparation of monodisperse latex particles. Due to the multiplicity of reactants, additives and the interacting phenomena involved in the emulsion polymerization, the details of the polymerization are not completely understood. The mechanism of emulsion polymerization as given by Harkins$^{1)}$ for an "ideal" system which containsthe essential ingredients, i.e. water, a water-insoluble monomer, an emulsifier and a free-radical initiator, can be summarized in the following three stages; a more detailed and general account can be found elsewhere$^{2)}$.

1. Initiation Stage:- On adding emulsifier to water in a concentration above the critical micelle concentration (cmc), micelles are generated in the medium. Each micelle is composed of about a hundred soap molecules with their hydrophobic portions directed toward the centre of the micelle. It is this structure of the micelle which gives it the power of solibilization of the water-insoluble monomer such as styrene. Only about 1% of the monomer charge is actually solubilized by the micelles which swell to twice their original dimensions. The bulk of the monomer is dispersed in large droplets. On using persulfate as initiator, free-radicals are generated in the aqueous phase and enter the monomer-swollen micelles in which polymerization starts as given in the following equations,

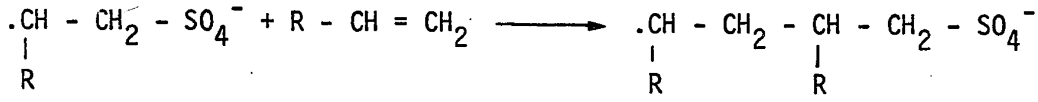
$$S_2O_8^{-2} \longrightarrow 2\ SO_4^{\overset{-}{\cdot}} \qquad (1)$$



$$SO_4^{\overset{-}{\cdot}} + R - CH = CH_2 \longrightarrow \underset{\displaystyle R}{\cdot\underset{|}{C}H} - CH_2 - SO_4^{-} \qquad (2)$$

2. Propagation (or Growth) Stage:- After initiation, the

radical continues to grow inside the micelles, by the addition of monomer molecules in the following manner,

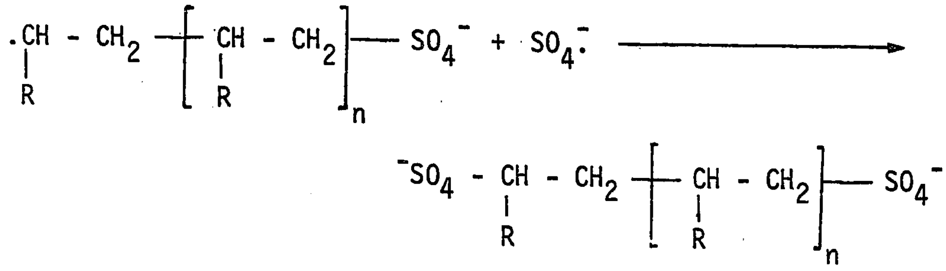


$$\underset{\substack{|\\ R}}{.CH} - CH_2 - SO_4^- + R - CH = CH_2 \longrightarrow \underset{\substack{|\\ R}}{.CH} - CH_2 - \underset{\substack{|\\ R}}{CH} - CH_2 - SO_4^- \qquad (3)$$

The growing particles are prevented from flocculation during polymerization by the adsorption of emulsifier molecules which are provided from the aqueous phase. A point is reached at a conversion of 10 - 20% of the monomer to polymer, where the emulsifier concentration has been reduced below the cmc, and no micelles are left. The disappearance of the micelles separates the particle initiation stage from the particle growth stage, after which no new latex particles can be formed, since initiation can take place only in a monomer swollen micelle. Consequently the number of the particles is constant during the growth stage, in which polymerization continues with the monomer being supplied from the monomer droplets by diffusion through the aqueous phase.

3. <u>Termination Stage</u>:- The process of growth in the polymer particles continues as described above, until the monomer droplets vanish from the water phase; this is reached at about 60% conversion From this point on the monomer in the particles is gradually used up, until the end of the polymerization.

The termination of polymerization in any growing particle can also occur, once another free-radical enters the particle due to combination with the growing polymer radical, as given in the following equation,



$$\cdot\underset{R}{CH} - CH_2 \left[\underset{R}{CH} - CH_2 \right]_n - SO_4^- + SO_4^{\overset{-}{\cdot}} \longrightarrow {}^-SO_4 - \underset{R}{CH} - CH_2 \left[\underset{R}{CH} - CH_2 \right]_n - SO_4^- \qquad (4)$$

Thus in case of termination by combination, two sulfate endgroups should exist for each polymer molecule which, if present on the surface of the particles, will add to its stability.

On using more than one monomer, the mechanism of polymerization is basically the same as given above. The composition of the copolymer formed, as compared to the monomer mixture from which it is derived, depends on the "monomer reactivity ratios"[3) r_1 $(= k_{11}/k_{12})$ and r_2 $(= k_{22}/k_{21})$, where k's are the rate constants for the reaction of monomer M_1 or M_2, with the polymer radical which has an end derived from either M_1 or M_2. These quantities, (r_1 and r_2), measure the relative tendencies of the two monomers to add to a radical ending in one of the other monomer unit. When $r_1 = r_2^{-1} = 1$, the polymerization is considered to be "ideal copolymerization", in which the copolymer formed from any mixture of the two monomers at any instant during the polymerization will have the same composition as the monomer feed. Few monomer pairs are known of ideal behavior; in most instances the product $r_1 r_2$ is less than unity, which result in the "alternating copolymers", on polymerization. The closest example to "ideal copolymerization" is found in the case of the styrene-butadiene monomer pair, whose $r_1r_2 = 1.08$4), produces a random copolymer with final composition very close to that of the monomer feed.

Mercaptans are usually added to the polymerization to function as modifying agents5), i.e. to regulate the molecular weight of the growing polymer chain by ending the long chains and initiating a new radical as given in the following equations:-

$$\underset{\text{(mercaptan)}}{RSH} + \underset{\substack{\text{(growing polymer)}\\ \text{radical}}}{M_n^{\bullet}} \longrightarrow M_n H + R S^{\bullet} \tag{5}$$

$$R S^{\bullet} + \underset{\text{(monomer)}}{M} \longrightarrow R S M^{\bullet} \tag{6}$$

In the specific cases of the persulfate-initiated polymerization of styrene-butadiene, and butadiene, the mercaptan has another function, that is, as a promotor6). In this specific case, very small quantity of n-dodecyl mercaptan is necessary for the acceleration of the polymerization. The exact explanation for this behavior is not known, but it is frequently stated7) that the mercaptan reduces the persulfate, and consequently the mercaptan and the persulfate form a redox couple.

Monodisperse latex particles

Most commercial latexes prepared from conventional soap recipes are very heterogeneous in particle size. Theoretical considerations predict that any procedure which aimsat controlling the particle size distribution of a latex must provide a mean of separating the particle initiation period from the particle growth stage. It has been reported[8,9] that the synthesis of uniform latexes may be accomplished if the number of particles formed during the nucleation stage is kept small and if this period is relatively short compared to the growth stage of the process.

In general, the approach for producing uniform latexes by emulsion polymerization involves the use of emulsifier-starved recipes in which the last two stages in the polymerization are extended. In this way, while the particles are still small, competitive growth[8] favors the smaller particles and the latex particles in the dispersion become more uniform. Decreasing the quantity of emulsifier favors development of uniform particles because the number of latex particles is reduced and the nucleation period is shortened relative to the succeeding stages. The disadvantage of the use of this emulsifier-starved technique is the destabilization of the latexes produced.

Bobalek et al[9] reported that the use of certain lithium soaps, in the ordinary recipe quantity, permitted very uniform latexes to be prepared with fewer problems in reproducing results or in maintaining stability of the latex. Specifically, lithium stearate was found[10] to have a unique solubility property, in that its critical micelle concentration is quite close to its solubility in water. Consequently the micelles which are formed, and which can function as nucleation sites for polymerization, are limited in number; even though the soap remains available in some form for adsorption as a stabilizer of the latex particles. Accordingly this behavior of the lithium stearate soap fulfils the requirements previously reported 8) for preparing monodisperse latex. A method was presented 9) for controlling the particle size of synthetic latexes by using this soap as the emulsifier in emulsion polymerization. By the use of the common-ion effect, e.g. addition of lithium carbonate 9), it was possible to vary the particle size of a latex without impairing its uniformity.

It has to be mentioned here that this approach to the control of uniformity and size of latex particles is applicable only to systems in which micelles are the main sites for particle initiation.

TECHNIQUE

The techniques of emulsion polymerization are well known and have been extensively reported in the literature 11).

Equipment

Since emulsion polymerization is a diffusion controlled process, it is necessary that both the temperature and agitation be under full control in order to assure the uniformity of the latex particles.

The polymerizations were carried out in a bottle polymerizer. The reactor bottles were placed in safety baskets which were in turn placed on a rotor and rotated end-over-end in a water bath, see Fig. 1,

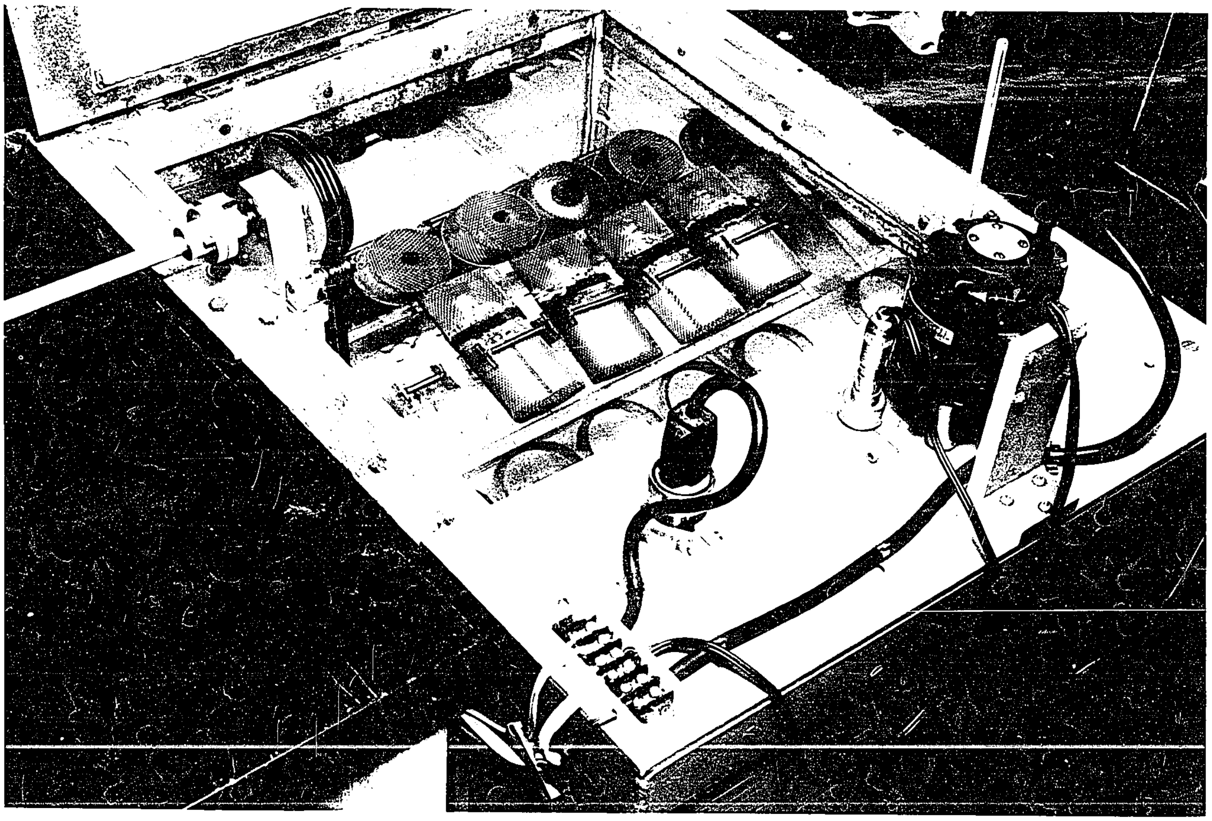


Figure I. General view of the water bath used in emulsion polymerization for the preparation of styrene-butadiene (60:40) latex. The reactor bottles were placed in safety baskets which are mounted on a rotor.

held to constant temperature of 60 ± 0.1°C. The rotor was designed so that the bottle with its safety basket was held securely but it could be easily removed when desired. The rotor is made of plexiglas and designed to hold 24 8-oz bottles by means of spring clips. This rotor was driven by a V-belt from a 1/6 hp. electric motor. A speed of about 35 rpm provides sufficient agitation for the emulsion polymerization.

The bottles were standard 8-oz flint glass bottles fitted with screw metallic caps, in which 3 1/16-inch holes had been drilled. Sealing was effected with a rubber gasket consisting of circles of hard rubber and butyl-sealant soft rubber, designated as "W-9" and "W-7", respectively. The circles were cut so that the hard rubber fitted just inside the cap and the butyl-sealant fitted just inside the bottle opening. These were cemented together with GA-1 Adhesive and placed inside the cap so that the smaller circle faced and covered the holes drilled in the cap. After the caps had been screwed on the bottles a few drops of toluene were placed over the holes in the cap causing the butyl-sealant rubber to swell and effect a tight seal. This arrangement permitted additions of liquid ingredients or withdrawal of latex by puncturing the gasket closure with a hypodermic syringe.

Materials

The styrene, obtained from Borden Chemical Co., was prepared for use by distillation under vacuum using fractionating column, in order to remove the inhibitor. The inhibitor-free styrene was collected at 62°C and 40 mm Hg, purged with nitrogen to remove traces of oxygen and stored at 4°C prior to use. The butadiene, obtained from Philips Petroleum Co., was purified just before charging by passing its vapor over a desiccant (calcium sulfate) and then over finely divided sodium hydroxide (Ascarite). It is then condensed in the reactor bottle immersed in a dry ice-acetone mixture.

Chemically pure grades of the following compounds were used in this work: lithium hydroxide, stearic acid and lithium carbonate from Fisher Scientific Co., and potassium persulfate from Baker Chemical Co. Dodecyl mercaptan (D.D.M.) produced by Borden Chemical Co. was distilled under nitrogen and the fraction used was collected at 118°C and 3 mm Hg. Doubly distilled deionized water was rendered oxygen-free by boiling and subsequent nitrogen purging.

The rubber gasket material "W-9" and "W-7" was obtained from B.F. Goodrich Co.

Recipe and charging procedure

Several trials were carried out until experience was gained for the production of the uniform styrene-butadiene (60:40) latexes in a reproducible fashion.

A typical recipe, which was used in most of this work, is given below:

90 gm	water
30 gm	styrene
20 gm	butadiene
2.276 gm	stearic acid
0.336 gm	lithium hydroxide (Li OH, H_2O)
0.05 gm	D.D.M.
0.25 gm	$K_2S_2O_8$

The lithium stearate soap was prepared <u>in situ</u>, by using stearic acid-lithium hydroxide combination in the amounts of 0.008 moles of each per charged bottle. Special care was taken to reduce the air content of the reaction mixtures by purging all solutions and bottle charges with high-grade nitrogen. These precautions minimized oxygen inhibition problems. The materials were weighed into the bottles by adding the weight of each successive charge to the weight of the bottles plus ingredients. The new material was then added to make up the proper weight. A Mettler Balance P-1200 was very suitable for this charging process.

The following schedule for charging the polymerization ingredients was used. 1) The required amount of stearic acid was weighed separately on an analytical balance, and charged to the reactor bottle, dry; 2) the alkali was dissolved in the greater part of the water required for the recipe and charged to the bottle; 3) the bottle was capped and then purged with nitrogen using hypodermic needles; 4) the styrene containing the dodecyl mercaptan was charged to the bottle using a hypodermic needle after purging with nitrogen;

5) butadiene vapor was then condensed into the chilled bottle using a hypodermic needle. A slight excess of butadiene was added and allowed to boil off until the bottle and contents come to the desired weight, in order to sweep out the air in the gas space; 6) after the bottle was brought to the temperature, the potassium persulfate dissolved in the rest of the water was injected through the gasket.

Conversion percentage

Per cent conversions were determined by a direct method based on total solids, using the syringe sampling technique[12].

A small sample was withdrawn from the bottle, weighed, short stopped with a 0.3% hydroquinone solution in isopropyl alcohol and dried to constant weight at 130°C. From the **wet weight** (S), the weight of residue (R), and a suitable correction for non-volatile, non-polymeric solids (N), the per cent conversion could be calculated from the following equation:

$$\%\text{ of conversion} = [\,(R\,T)/S\,] - N \tag{7}$$

where T is the total parts of all ingredients charged (based on 100 parts of monomer).

Usually the polymerizations were carried out to 90% conversion; this required a polymerization time of about 5 days.

Stripping

The remaining monomers were removed from the latex medium by steam distillation under vacuum. A Fisher flash evaporator was used for this purpose. The pressure inside the apparatus was kept at 100 mm Hg, and the temperature of the water bath around the rotating flask containing the latex was kept at 50°C. The steam from the steam-generator, passed through a Teflon tube to the latex container. Usually steam distillations were carried out for about 3 hours.

PARTICLE SIZE DETERMINATION

Preparation of sample

The method of Maron et al13) served as a basis for the measurement of latex particles by transmission electron microscopy.

In this work, latex samples were first diluted by adding one drop of latex to 100 ml of 0.2% Aerosol-OT solution in water as a dispersing agent. The particles were then brominated14, 15) by addition of bromine water to the diluted latex, and the latex-bromine mixture was exposed to ultraviolet light. Bromination of the soft styrene-butadiene latexes is used to harden the particles by the addition of bromine to the double bond in the butadiene part of the copolymer. This prevents flattening and distortion of the latex particles and increases their opacity under the electron beam.

The brominated latex was further diluted with distilled water. The grids for the electron microscope were prepared as follows: carbon films were formed on glass slides by evaporation of carbon in the vacuum chamber; these films were then removed by floating them on the surface of water. Portions of these films were transferred to woven copper screens of 200 mesh; these served as mounts for the latex specimens. One or two drops of the diluted brominated latex were placed upon the grid and left to dry. Excess dispersing agent was washed off the carbon film with hot, freshly distilled water. This was done by placing one drop of hot water upon the prepared grid with a pipette, and removing it after few seconds of contact by means of a filter paper. This process was immediately repeated 3 or 4 times before drying.

The specimens were shadowed by evaporating platinum in the vacuum chamber. This improves the sharpness of particle outline and made measurements of the diameter considerably easier.

Preparation of micrographs

Micrographs of latex specimens were made with a JEM 6A transmission electron microscope using the double condenser system and an accelerating voltage of 80 KV. Eastman Kodak contrast emulsion lantern slide plates were used. The magnification of an individual micrograph was determined from the lens current settings. These settings were calibrated previously by making an exposure of a diffraction grating replica at each magnification setting of the microscope. Typical positive prints of micrographs obtained in this work are shown in Fig. 2.

The diameters of the particles were measured directly from the electron micrographs with the help of a Beck-London travelling microscope.

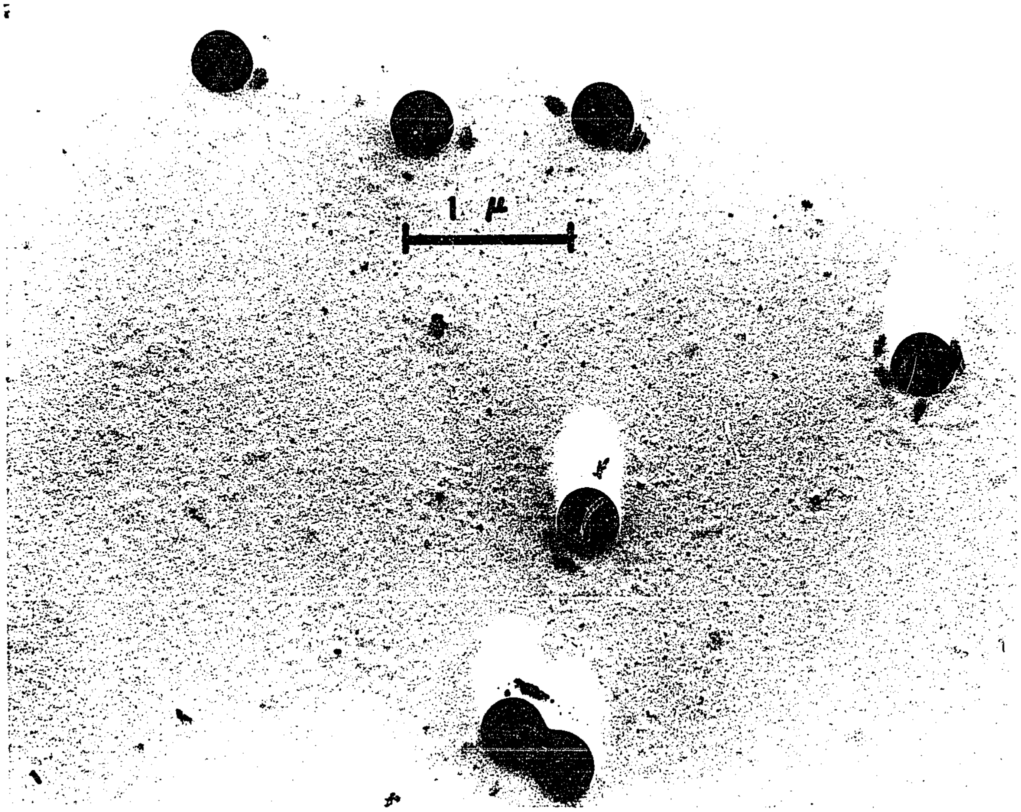


Figure 2. Electron micrograph of styrene-butadiene (60:40) latex. Number average diameter D_n = 3,115 Å , with (D_w / D_n) = 1.02.

The diameter of each particle was determined in two perpendicular positions and the average was taken. A correction was used to take into account the swelling due to bromination. The particle diameter increase on bromination for the styrene-butadiene (60:40) latex has been reported16) to be 13%.

Measurements were usually made for about 100 particles and the number average diameters D_n and the weight average diameters D_w were calculated using the following equations10, 13):

$$D_n = \frac{\Sigma\, n_i\, D_i}{\Sigma\, n_i} \qquad (8)$$

$$D_w = \left[\frac{\Sigma\, n_i\, D_i^6}{\Sigma\, n_i\, D_i^3}\right]^{1/3} \qquad (9)$$

The departure of D_w / D_n from unity gives a quantitative indication of the uniformity. Table I summarizes the results of the particle size measurements of some latex particles used in this work.

TABLE I

Particle Size and Uniformity of
Styrene-Butadiene (60:40) Latex System.

Number of particles	D_n (Å)	D_w / D_n
77	3,115	1.022
120	3,756	1.048
75	3,583	1.026

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PART III

DESCRIPTION OF PROPERTIES AND BEHAVIOR OF LATEXES

ABSTRACT

The properties of a styrene-butadiene latex system produced by emulsion polymerization using lithium stearate as emulsifier and potassium persulfate as initiator[1)] have been studied.

The particles are monodisperse and are stabilized by the adsorption of the stearate anions. Most of the emulsifier content of the latex system is adsorbed on the particle surfaces, in equilibrium with a small amount of the emulsifier dissolved in the bulk aqueous phase. This distribution of the emulsifier is very slightly affected by dilutions or by centrifugations (when no coalescence is involved) of the latex system.

The latex is film-forming. Initial coalescence is followed by a period of up to several days before the contours of the coalesced particles disappear. This process may be followed by scanning electron microscopy. Coalescence and filming of the latex particles displace about 50% of the stabilizer from their surfaces.

Ion-exchanging the latex removes the soap, but stability is maintained presumably by sulfate groups chemically bound to the polymer.

INTRODUCTION

A latex is essentially a two-phase system, comprising a disperse phase and a dispersion medium. The disperse phase consists of small particles, the constituent molecules of which are polymeric in nature. The aqueous dispersion medium of a latex is usually a dilute solution of various salts and emulsifiers. In appearance, latexes are usually white, free-flowing fluids. Upon drying some of them form coherent transparent films, while others form friable opaque powders, depending on the chemical composition of the particles and the conditions of drying. The latexes are hydrophobic colloidal suspensions usually prepared by emulsion polymerization and are stabilized by charges originating from chemically bound and/or physically adsorbed group.

The latex system produced by emulsion polymerization1) and used during the course of this work is styrene-butadiene (60:40), which is a composition typical of commercial latexes used in paper coating. The disperse phase consists of particles of uniform size. Their surfaces may contain both physically adsorbed stearate molecules and chemically bound sulfate groups as well as other groups such as carboxyls formed in side reaction. The aqueous phase of the latex system may contain lithium stearate, stearic acid, residual initiator and its decomposition products e.g. potassium sulfate.

In order to interpret our experimental results, it was necessary to characterize the latex components responsible for the behavior of the system. The properties of the latex described in this part are not intended to cover all the properties of the latex system, but rather only those related to the stability, centrifugation, and film formation.

This part describes the particle size and structure, density, film forming properties, aging properties of the emulsifier and its distribution between the particle surface and the medium, effect of dilution and centrifugation on the emulsifier distribution, and properties of "cleaned" ion-exchanged latex. The latex properties that are to be discussed are the specific properties of the experimental latex used in this investigation and their relation to the properties of latexes generally.

PARTICLE STRUCTURE AND SIZE

The particles produced from emulsion polymerization of the styrene and butadiene (60:40) are spherical as shown in the electron micrographs Fig. 2 of Ref. 1. The glass transition temperature for these particles has been reported2) to be -8°C, which is the temperature at which the polymer becomes brittle and glass-like and is no longer deformable. Another related characteristic temperature specifically for latex, is the minimum filming temperature (M F T)3, 4), which is the temperature below which a film cannot be formed by drying the latex system. Latexes are classified as soft or hard depending on whether or not they form films by drying under ambient conditions, that is, whether their MFT is below or above room temperature. The styrene-butadiene (60:40) latex has[2)] a MFT of -3°C, and consequently it falls in the category of soft particle latexes, i.e. it coalesces upon drying to give a continuous film at room temperature.

The soft particles can be hardened either by reaction with bromine[5, 6, 7)] which adds to the double bond of the butadiene, or by high energy irradiation[7)]. The hardening of the particles is useful in that it permits their examination in the electron microscope without deformation by the electron beam, and it stops morphological change so that coalescence or filming may be halted and the system examined at any stage. The work done on bromination of latexes[7)] has shown that bromine reacts with all the double bonds, and this suggests that the bromine molecules or Br_3^+ ions have accessibility to the bulk of the polymer forming the particles, and not only the surface.

Particle size determination made by electron microscopy[1)] showed that the latex is a monodisperse system. The number average diameter of the particles prepared and used during the course of this work is in the neighborhood of 3.58×10^{-5} cm, with a ratio of weight average to number average diameters of about 1.02.

DENSITY

The density of the latex particles depends upon, among other factors, the composition of the polymer.

Depending on the ratio of the two components in the styrene-butadiene latex, the density could vary between 0.910 gm/cm^3 and 1.053 gm/cm^3 which are the density of poly(butadiene)8) and poly(styrene)9) respectively.

Since the latex is to be centrifuged, the determination of the density of our styrene-butadiene (60:40) latex particles is necessary in order to know their buoyancy in the dispersing medium, and to be able to calculate the centrifugal force at the applied acceleration. This density is obtained by determining the density of the film produced from latex particles, using the procedure of determining the density of solids. A film was produced from the latex particles either by water evaporation or by centrifugation of a latex-sucrose system. Special care was taken to produce air-free films (by using dilute latex for filming), which were then washed throughly with water and dried in the oven under vacuum. The density of the film was then determined using the pycnometer and distilled water at 20°C as a reference, and was found to be 1.00054 gm/cm^3. This density is comparable with previously9) reported values for the same latex composition and was used for all calculations of the pressures from centrifugation experiments throughout the course of this work.

The closeness of the density of the latex particles to that of the medium and the difference in the temperature coefficients for the two phases make controlled centrifugation of the latex in aqueous medium experimentally difficult. This suggests the need for increasing the difference in density between the two phases, for example by adding sucrose[10)], if the centrifuge is to be used as a tool of investigation.

FILM FORMATION FROM LATEX

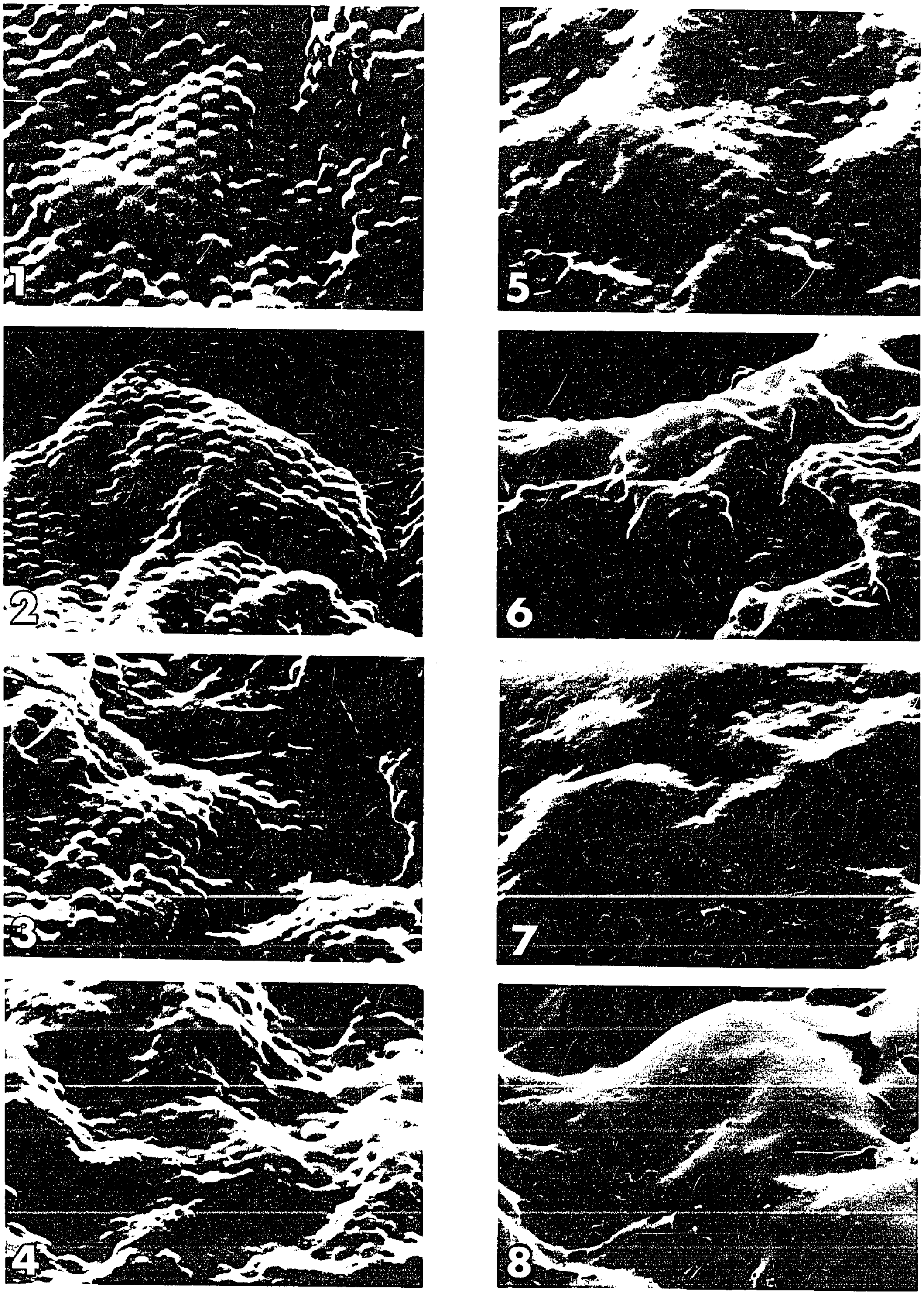
The styrene-butadiene (60:40) latex is transformed into transparent, tough film upon drying at room temperature. The mechanism of film formation from latexes as discussed in Part I, can be summarized as occuring in two stages: particle contact and the initiation of coalescence due to capillary pressure arising from water evaporation, and the propagation of coalescence or completion of filming due to polymer-medium and polymer-air interfacial tension. Though the two stages are superimposed, one can easily find a film more or less at the border between the two stages by following the drying of the latex carefully, and examining it under the electron-microscope. Vanderhoff[11)] found that, at the transparency point of the film formed from styrene-butadiene (67:33) latex which was usually taken as an indication of completion of film formation, the contours of the particles were still visible. On following the aging of this film in the air, the contours were found to disappear after about two weeks.

The films produced in the ultracentrifuge are tough and continuous but not transparent. Examination of these films under the scanning electron microscope[12)] after bromination, showed that the coalescence of the particles in the top surface is more advanced than of those at the bottom. The particles at the bottom were just touching, corresponding to the earliest stage of coalescence. Consequently the ultracentrifuge offered a method of producing films at various stages of coalescence and filming, including the initial phase. The opacity of the film was found to be accompanied by the presence of 5 - 8% of water within the film, distributed in such a way that the top of the film contains less water than the bottom. The aging of this film was followed both in air and under water, by examining samples, brominated after various aging times, using the scanning electron microscope.

The aging in air, over a period of one week is shown in a series of micrographs in Fig. 1. The surface contours of the particles disappear gradually with time. A similar series was produced over the same period of time when aging was carried out under a water surface. This supports the idea that the completion of film formation, after the initiation of the coalescence, is mainly the result of interfacial tensions between the polymer and water or air and is not primarily due to the capillary pressure arising from water evaporation.

The dry, transparent film was found to absorb water when placed again in an aqueous media. This phenomenon is believed to be associated with the alkali-soap content of the film. The polymer film itself, being hydrophobic, does not absorb water, but soap, distributed through the film, can induce the imbibition of water and the film loses its transparency on contact with water. This fact was supported by casting a film from a "clean", ion-exchanged latex which does not contain any soap. After

Figure 1



Change of Film Structure with Time.
Styrene-Butadiene (60:40) Latex

drying, its transparency remained the same by placing it again in water. This problem of water-sensitivity[13)] of dried films is tackled in latex technology by replacing the fixed-alkali soap by a volatile base soap. Such soaps loose their alkali on drying the latex film, and no soap remains, but rather the free fatty acid derived from the soap. Consequently a film of minimum water-sensitivity is obtained.

pH AND AGING EFFECT ON THE LATEX

The pH of the latex as produced is usually between 7 and 8, but this pH does not stay constant for long periods of time, perhaps due to the sorption of CO_2 or due to decomposition of some of the chemical compounds existing in the latex system.

One experiment will be mentioned here because of its historical importance in the development of this research project. The first experiment which was carried out in the development of the ultracentrifuge technique to measure the pressure required for filming was to follow the effect of aging on the latex-sucrose system.

The latex suspension was diluted to 2 gm/100 ml at three different sucrose concentrations (0.56, 0.84 and 1.12 molar) and centrifuged in the usual way for forming a film[10)] at two different rpm (60,000 and 40,000) and at different aging times over a period of 23 days. The films were treated in the usual way, in order to calculate the pressure required for film formation. The results of the experiments are

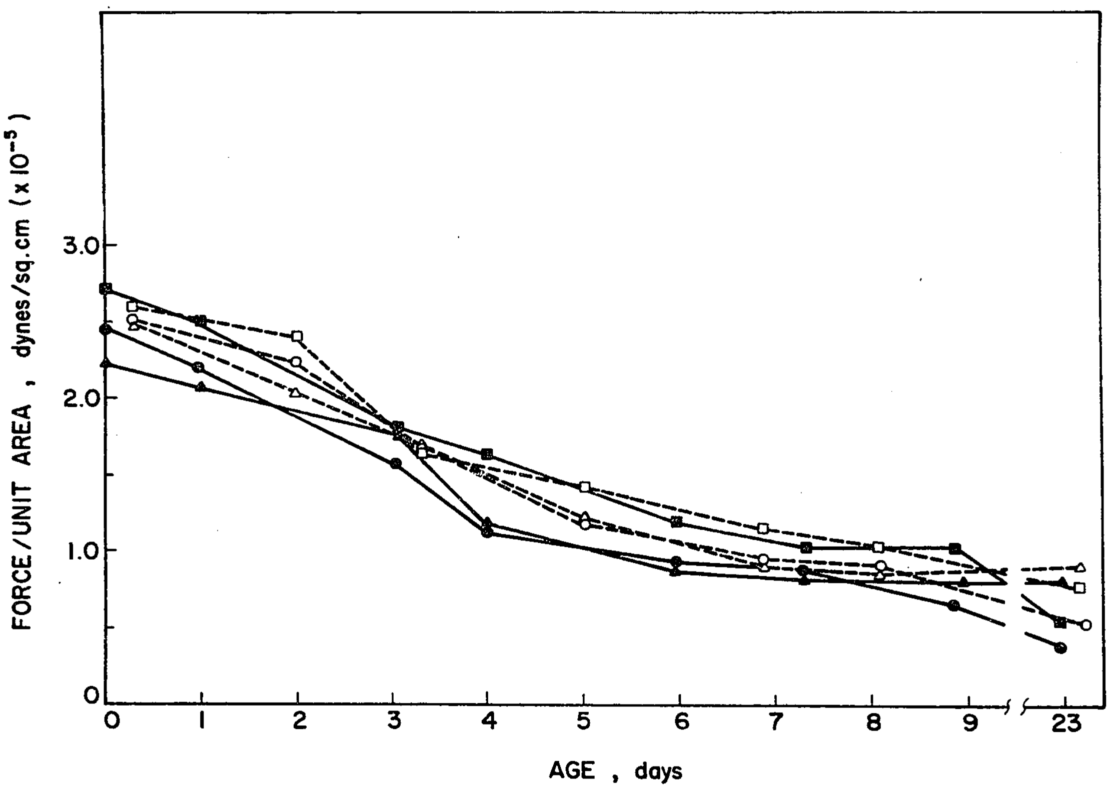


Figure 2. The pressures required for coalescence of 2 gm latex per 100 ml sucrose solution at different aging times as produced by centrifugation of latex-sucrose system at different rpm and different sucrose concentrations:

	rpm	sucrose conc. Molar	sucrose conc. (gm/litre)
(⊖)	60,000	1.12	(384.4)
(○)	40,000		
(▲)	60,000	0.84	(288.4)
(△)	40,000		
(▩)	60,000	0.56	(192.2)
(□)	40,000		

shown in Fig. 2. The pressure required for initiating the filming process decreased by a factor of 4 over a period of two weeks. This demonstrates a continuous destabilization of the latex with an approach to some kind of equilibrium.

The importance of the experiment comes from the many questions it raised at that early stage of the work, which helped in developing the ultracentrifuge technique for our purpose. Some of the questions were: what is the effect of sucrose concentration?, what is the effect of rpm?, what is the time required for equilibrium?, and what does aging involve?. Most of these questions are answered elsewhere10).

A comment on the significance of the aging effect is required at this point in order to understand one characteristic of the latex system. The redistribution of emulsifier due to dilution was first suspected as the reason for the aging behavior. This reason was subsequently rejected on the basis that dilution of the latex to 2% solid content, removes only about 2% of the surface emulsifier from the particles as shown in Fig. 4, and this is unlikely to account for the observed large decrease in the pressure required for coalescence as will be shown in Part V. This reason was rejected also on the basis that the equilibrium between the soap adsorbed on the particle surface and that in the aqueous phase is reached almost instantaneously after dilution, as indicated by surface tension measurements.

The pH of the latex-sucrose system dropped by one unit, from 8 to 7, over the two-week period of aging. As will be shown in Part V, this drop in the pH can account for the observed decrease of the pressure required for initiating the filming process.

This slow change in pH as reflected in the slow destabilization of the latex, could be due to decomposition of chemical compounds remaining after polymerization, or possibly the activity of micro-organisms. This behavior, in general terms, indicates some of the problems involved in storage of latexes, which are solved by lining the containers with materials that are resistant to mild alkalis and mild acids, and by adding small amounts of microbicides13).

PROPERTIES OF THE EMULSIFIER

The emulsifier is essential in the emulsion polymerization of latexes for two main reasons. First, it acts as a micelle generator which provides the main sites for initiation of polymerization; second, it preserves the stability of the latex particles during and after polymerization. The numerous emulsifiers used for polymerization can be divided in four categories depending on the nature of the active hydrophilic group: anionic, cationic, amphoteric and non-ionic.

Anionic emulsifiers are subdivided, in turn, on the basis of the chemical nature of their hydrophilic groups, e.g. alkali salts of organic carboxylic acids (soaps), alkyl sulfates, and alkyl- or alkylarylsulfonates. Anionic emulsifiers are the most widely used in emulsion polymerization, and may be used alone or in a mixture with a non-ionic emulsifier. Since they are anionic in nature, they are expected to be most effective in the alkaline region. They are sensitive to changes in pH, and in acidic media they are transformed into fatty acid.

A fatty acid soap was used in our polymerization procedure. Specifically we used lithium stearate which has a critical micelle concentration14) (2.7×10^{-4} M) very close to its solubility15) limit (3.8×10^{-4} M) at 25°C. This character of the soap gave the essential properties required to prepare a monodisperse latex14, 15) of large particle size, since the number of the generated micelles is limited. At the same time, sufficient soap exists in some form in the system to ensure the stability of the latex.

The amount of soap added for the polymerization step is initially many times greater than the solubility limit but, because of the large specific surface of the latex particles and because of unavoidable losses, it is found that in the final product the particles are incompletely covered by the soap.

Lithium stearate is an aliphatic soap molecule with a chain length of C_{18}, and a terminal hydrophilic group. Its function as a stabilizer is due to the adsorption of the hydrophobic end of the chain on the surface of the hydrophobic polymer particles. The soap molecules are held to the particle surface by a physical adsorption force. Consequently it is expected that the soap molecules are not immobile on the surface, but rather exist in a dynamic equilibrium between adsorption on the surface of the particles and dissolution in the surrounding bulk aqueous phase.

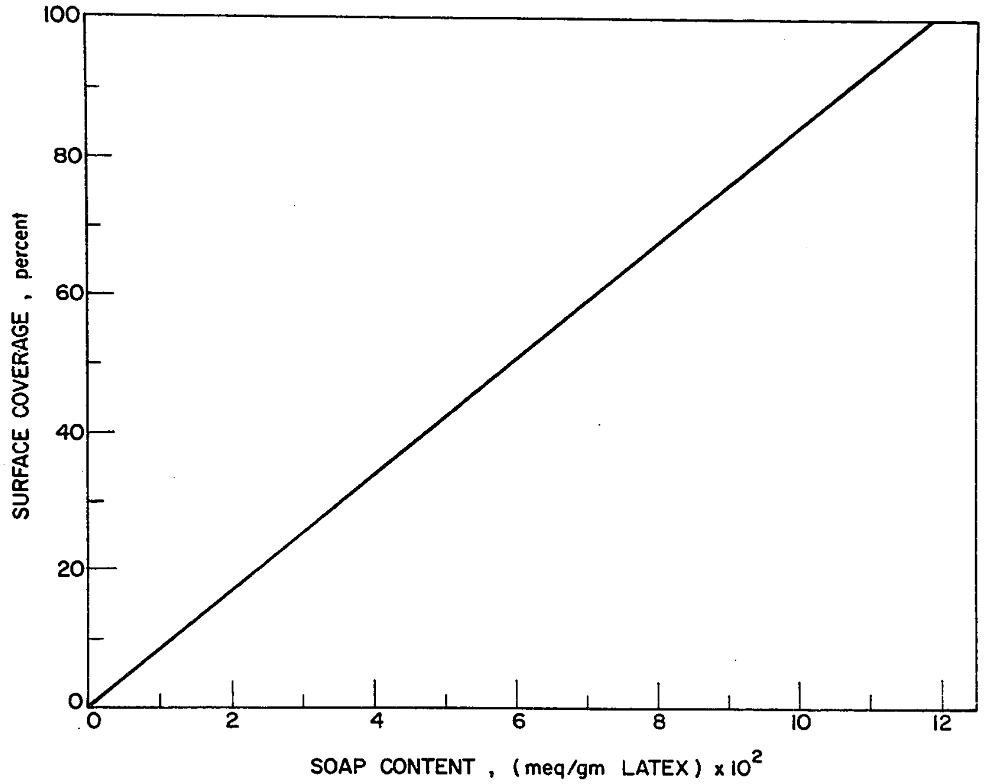


Figure 3. Calculated values of the surface coverage of latex particles from the quantity of soap present. Calculations are based on a particle diameter of 3.58 X 10^{-5} cm and a cross-sectional-area of the stearate molecule of 23.4 $Å^2$.

The quantity of the soap adsorbed on the particle surface may be obtained from the difference between the total soap content in the latex system (as determined by conductometric titration)[16], and the quantity of the soap existing in the aqueous phase (as determined by surface tension measurements)[17]. This soap quantity can be expressed as percent of surface coverage, by reference to Fig. 3. This figure gives the relation between the quantities of lithium stearate soap molecules adsorbed on the particle surface and the corresponding surface coverage for the latex particles used in our work. The calculation of the above relation was made for a particle diameter of 3.58×10^{-5} cm, and assumed[18] that 23.4 $\mathring{A}^2$ was the cross-sectional area of the stearate soap molecule on the surface of the latex particles at complete coverage.

Dilution effect

The solid content of the latex as produced is usually between 25 and 35% (by weight). The total stearate content (7.4×10^{-2} meq/gm) is enough to give 62% surface coverage if it is assumed that all the stearate molecules are adsorbed on the surface. Dilution, in general, results in the desorption of the emulsifier molecules from the particles surface to the aqueous phase. Surface tensions were followed[19] for different latex dilutions at pH = 8, and the corresponding concentration in the bulk aqueous phase was obtained from a reference curve which was previously established for surface tensions of different soap concentrations at the same pH. The percentage of the soap dissolved

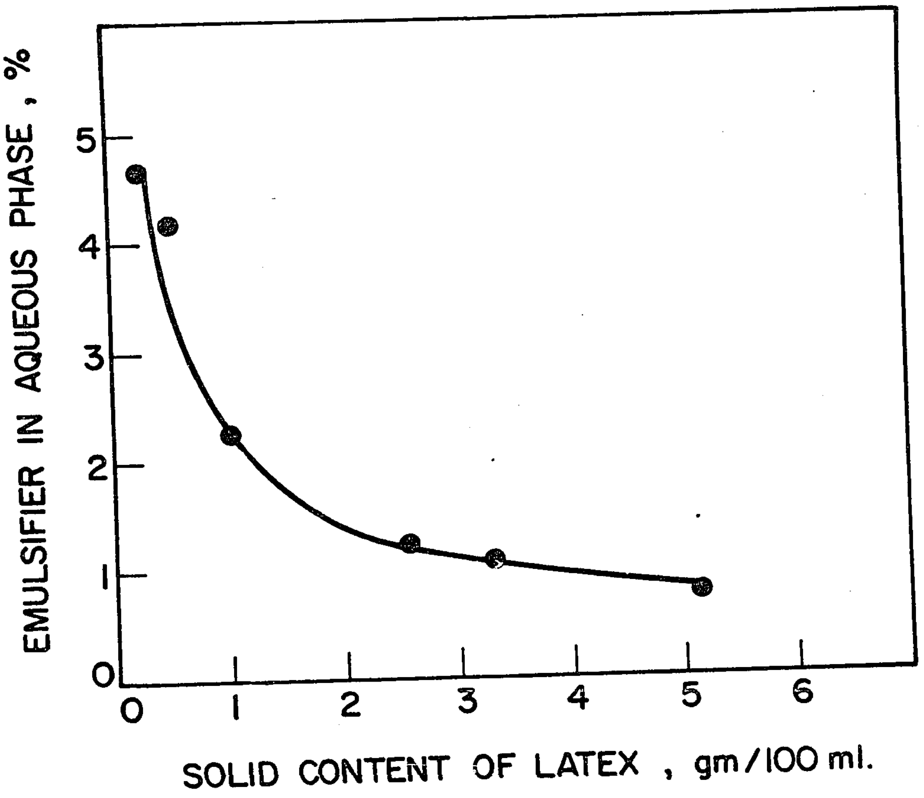


Figure 4. The percentage of lithium stearate soap in the aqueous phase as a function of the solid content of a diluted styrene-butadiene (60:40) latex. pH = 8.

in the aqueous phase to that of the total soap concentration, at different latex solid contents, is shown in Fig. 4. This percentage increases from 0.7% at 5% latex solid content, to 4.6% on dilution to 0.3% solid content. For each dilution a new equilibrium is established between the soap dissolved in the bulk aqueous phase and adsorbed on the particle surface. This equilibrium was found to be reached within a short time after dilution, as reflected in the constancy of the surface tension measured within the first half hour after dilution, and repeated over a period of 3 days. Figure 4 indicates that, initially, a very small amount (less than 1%) of the soap content of the latex system exists in the bulk aqueous phase and that no appreciable soap desorption occurs at the dilutions used in this work (1% and 2% solid contents).

Emulsifier adsorption in the latex-sucrose system

Since a sucrose solution of 0.56 M concentration was used as the dispersion medium for the latex particles during centrifugation experiments, it was advisable to follow the soap adsorption on the particles in a latex-sucrose system. Different concentrations of lithium stearate soap were added to a system of 1% latex in o.56 M sucrose solution, and the surface tensions were followed as described elsewhere17). The surface tension of the latex-sucrose system, Fig. 5, decreased rapidly at first and then slowly with the increase in the soap concentration of the system. The relatively high surface tension, 48 dynes/cm, of the latex-sucrose system with the initial soap content suggests that practically most of the soap is adsorbed on the surface of the particles,

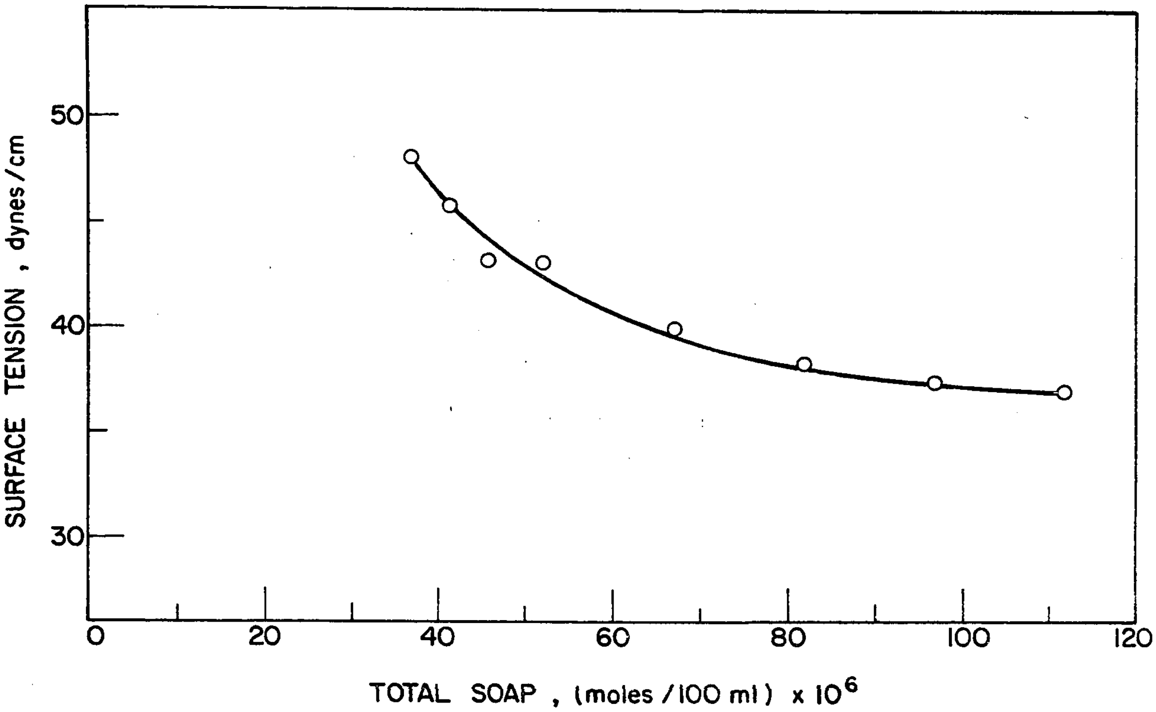


Figure 5. Surface tension of 1 gm latex per 100 ml of 0.56 M sucrose solution with different soap contents.

and that the concentration of the unadsorbed soap molecules dissolved in the aqueous phase is very low. This is the same as previously found for dilutions with water. The quantity of the soap dissolved in the medium for each soap concentration in the system is obtained from the surface tension reference curve (Fig. 2, of Ref. 17). The corresponding quantity of the soap sorbed on the particle surface is calculated by subtracting the soap in the medium from the total soap in the system. The resultant adsorption isotherm of this system is shown in Fig. 6, where the surface saturation is asymptotically reached at soap concentrations near the critical micelle concentration in the bulk aqueous phase. The pH was not controlled during the addition of the soap, but was found to increase from 7.14 to 8.36 in the range of the soap concentrations used. The initial emulsifier content of the latex expressed as total stearate can give 62% coverage of the particle surface. Conductometric titration showed that, at pH = 7.14 the initial ionized-stearate content of the latex system (3.7×10^{-2} meq/gm), is only enough to give 31% coverage of the particles surface. The rest of the emulsifier content is in the form of the un-ionized stearic acid which we assume to be also adsorbed on the surface. As the soap concentration in the system increases, the soap molecules are distributed between the particle surface and the medium in such a way that the surface coverage with soap molecules increases continuously, and the soap concentration in the medium remains below the critical micelle concentration. The adsorption of the soap continues with further addition of soap, until micelles form in the medium, after which the surface

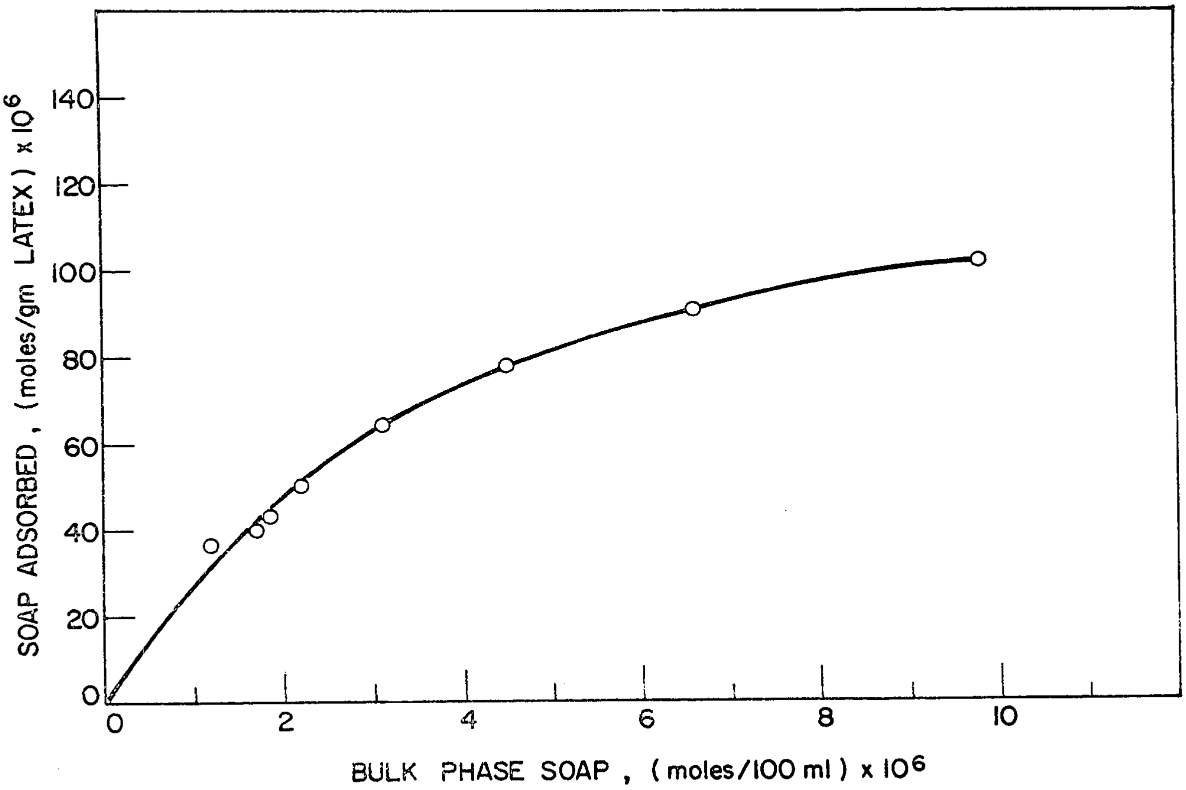


Figure 6. Adsorption isotherm of lithium stearate soap on 1 gm latex per 100 ml of 0.56 M sucrose solution at 25°C.

tension remains almost constant. It is believed that the soap is adsorbed in a monomolecular layer by the polymer particles.

This behavior has been exploited and soap titration is one of the methods used[18, 20)] for determination of the surface area and average particle size of latexes containing fatty acid soaps. The method involves the determination of the soap adsorbed per gram of polymer at the point of micellization, and knowledge of the effective molecular surface area of the soap molecule at this point.

Emulsifier redistribution during filming process in the ultracentrifuge

The weights of the films produced from styrene-butadiene latex, by alternating centrifugation with shaking, were found to be greater than those produced without shaking as shown in Table II of Ref. 10. The explanation given for this observation is that some emulsifier molecules are displaced from the coalescing particles and are gathered in high concentration at a certain level of the floating packed latex layer, preventing further coalescence. The shaking redistributes this emulsifier and the uncoalesced particles, and coalescence proceeds on further centrifugation. The following two experiments were carried out to prove that the emulsifier is being displaced during coalescence of the latex particles under the centrifugal force.

A. Centrifugation With Coalescence. Centrifugations were carried out for 5 ml samples of 2 gm latex per 100 ml of 0.56 M sucrose solutions at 60,000 rpm (acceleration is 153,000 g at 3.8 cm from the center of rotation) for one hour. Several centrifugation runs were carried out, the films produced were dried and weighed, and the serum was collected. Determinations of the emulsifier content of the serum were carried out by conductometric titration, and its solid content was determined by drying. The difference between the emulsifier contents of the original latex system before filming and the serum, gives the emulsifier content of the film. From the latter value and the oven-dry weight of the film, the emulsifier content of the film could be expressed as meq/gm as given in Table I. Comparing this value with the original emulsifier content of the latex, shows that 48.5% of the emulsifier is displaced from the surface of the coalesced particles. This is equated with the emulsifier concentration gained by the serum after centrifugation as shown in Table I.

B. Centrifugation Without Coalescence. Centrifugations were carried out for 25 ml samples of 5 ml latex per 100 ml water (not sucrose solution) in a fixed-angle rotor, at 40,000 and 20,000 rpm (acceleration is 176,000 g and 44,000 g respectively at 9.9 cm from the center of rotation), for about 10 hours. After centrifugation, about 99% of the latex particles were found at the bottom of the tubes in a gel form. The supernatant liquid was separated, and the gel was redispersed into distilled water. Conductometric titrations were carried out for the determination of emulsifier both in the serum and in the redispersed gel. No emulsifier could be detected in the serum, probably due to the very small quantity. However the emulsifier content of the redispersible latex particles, as expressed in meq/gm latex, was found to be very close to the original content of the latex particles before centrifugation.

TABLE I

Effect of Centrifugation, With and Without Coalescence, on the Soap Distribution Between the Particle Surface and the Dispersing Medium of Styrene-Butadiene (60:40) Latex System.

The centrifugation conditions	rpm	Before centrifugation			After centrifugation					
					SERUM		GEL OR FILM			
		Solid content	Emulsifier content		Solid content	Emulsifier content	Latex transformed into film or gel	Emulsifier content	Emulsifier removed from the surface of the coalesced particles	
		(%)	meq/gm latex	meq/100 ml	(%)	meq/100 ml	(%)	meq/gm latex	meq/gm latex	(%)
With coalescence	60,000	2.04	0.068	0.139	0.14	0.074	93.1 (Film)	0.035	0.033	48.5
Without coalescence	40,000	5.36	0.054	0.294	0.06	nil	98.9 (Gel)	0.051	0.003	5.5
	20,000	5.12	0.051	0.261	0.08	nil	98.4 (Gel)	0.049	0.002	3.9

Table I shows that 5.5% of the emulsifier originally existing on the surface of the particles is displaced during centrifugation of the latex-water system at 40,000 rpm and 3.9% at 20,000 rpm, as compared to 48.5% in the case of centrifugation of the latex-sucrose system at 60,000 rpm. These results show that when coalescence is involved in centrifugation of the latex about 50% of the emulsifier covering the particle surface is displaced.

PROPERTIES OF "CLEAN" ION-EXCHANGED LATEX

In order to follow the effect of electrolyte and emulsifier content on the pressure required for coalescence of latex, it was necessary to remove the emulsifier and the salts from the aqueous phase and the particle surface. An ion-exchange technique21) was applied to the latex system. This results in a system of monodisperse particles presumably stabilized by chemically bound sulfate groups and a negligible amount of emulsifier.

The pH of the resultant "clean" latex was in the neighborhood of 4, probably due to the presence of the strongly ionized sulfate groups on the particle surface.

Some of the colloidal changes in the ion-exchanged latex reported earlier by Vanderhoff22) were also observed in our system. The conductance decreased greatly, which is an indication of the low concentration of electrolyte and the ionizable emulsifier molecules.

The viscosity of the latex system during contact with the ion-exchange resin was found to increase greatly, an observation which was reported earlier by Vanderhoff$^{22)}$ on ion-exchanging the styrene latex where the viscosity increased to twice its original value. This behavior put a practical limit on the solid content of the latex that could be ion-exchanged without difficulty. The viscosity behavior of ion-exchanged latex has been reported$^{22)}$ to be non-Newtonian at volume fractions of polymer (Φ) as small as 0.0047, compared to the Newtonian behavior of the original latex at (Φ) below 0.15. The Newtonian behavior was restored by adding a small amount of electrolyte to the ion-exchanged latex. This behavior was explained on the basis of the expansion of the electrical double layers of the particles on removing the electrolyte by ion-exchange, and its decrease in thickness to the original value, when the electrolyte was added to the ion-exchanged latex.

The appearance of interference colors in our ion-exchanged latex systems has been noted and is taken to be evidence of the uniformity of particle size. This property has been previously observed and explained by Vanderhoff$^{23)}$, and Krieger$^{24)}$ and others. Uniform particles can maintain themselves in orderly array under the influence of the long range electrostatic repulsive forces that are characteristic of double layers. Under appropriate conditions of concentration these arrays diffract light, and consequently colors are observed. While the spacing in our latex system is assumed to be the result of mutual repulsive forces among the particles, it has been suggested$^{23)}$ that arrays may also result from potential energy minima at separation distances where attractive and repulsive forces balance each other.

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PART IV

AN ULTRACENTRIFUGATION TECHNIQUE FOR THE STUDY OF LATEX COALESCENCE

ABSTRACT

The use of the ultracentrifuge to determine the minimum pressure required for coalescence of latex particles is described. The extent of coalescence is found to reach an equilibrium value after a short centrifugation time and this equilibrium provides the basis for calculating the required pressure. Displacement of the emulsifier from the coalescing latex particles affects the equilibrium but can be taken into account. The stability of styrene-butadiene latex was quantitatively followed over the pH-range by means of this technique. The maximum stability occurs between pH 8.8 and pH 10.7 but stability decreases outside these limits and the latexes are unstable below pH 2 and above pH 12.

INTRODUCTION

The theory of film formation from latexes has been extensively discussed by several authors[1-3]. Briefly, the current view of the film-forming process is as follows. As the water evaporates, the particles are brought together so that their stabilizing layers are in contact. The pressure forcing the particles together is increased by the force arising from the water-air interfacial tension, until the stabilizing layers are ruptured and polymer-polymer contact is formed. Once this occurs, the coalescence of the particles is promoted by the forces arising from polymer-water and polymer-air interfacial tensions successively.

The purpose of this part is to describe a technique that has been developed to determine the minimum pressure required for the initiation of coalescence. The measurement provides a method for investigation of the stability of latexes and the mechanism of film formation.

The method is based on the consideration that in centrifugation of a latex, the force pressing particles together in the packed layer varies more or less linearly with the thickness of the bed. Coalescence occurs if the force exceeds a certain minimum.

ULTRACENTRIFUGATION TECHNIQUE

Centrifugations are carried out in cellulose nitrate tubes (capacity 5 ml each) in a swinging bucket rotor SW-65 which holds three tubes. A Beckman L2-65 ultracentrifuge is used for all runs. The maximum rpm is 65,000 (the acceleration at 3.8 cm from the center of rotation is 180,000 g) at a controlled temperature. Since the density of the polymer is near unity, a nonelectrolyte solute is needed to raise the density of the medium without affecting the latex stability. Sucrose solutions were chosen to play this rôle. The concentrations are such that the buoyancy effect is negative and the latex particles are forced to the top. Concentrated latex (30% solid content) is diluted to 2gm/100 ml, using a 0.56 M solution of sucrose. The latex-sucrose system is centrifuged at the desired rpm, and at a controlled temperature of 20°C, for a certain period of time greater than the flotation time. At the end of the run, the floating layer consists of two parts, a complete film on the top and a redispersible part underneath. The film is recovered, washed free of the attached redispersible particles as well as of occluded sucrose, and is dried in the oven (105°C).

The mass of uncoalesced latex may be obtained from the difference between the original weight of latex charged and the weight of the film.

RESULTS

Monodisperse styrene-butadiene (60:40) latex with number average diameter of particles = 3,200 Å, was used throughout this work.

Centrifuging 5-ml samples of 1 gm latex/ 100 ml of 0.56 M sucrose solutions at 60,000 rpm for different times resulted in weights of film that were independant of the run duration (Fig. 1). This indicated that an equilibrium is established in the filming process during the first 30 min of centrifugation.

The film was brominated4) directly after the run and the two faces were examined by the scanning electron microscope5). Figure 2 shows that coalescence is more advanced in the particles at the upper face than in those at the bottom. The close packing of the particles in the film is clearly indicated in the micrographs of Fig. 2 and by the amount of aqueous medium left in the interstices between the particles, which was found to be 5%-8% of the weight of the film.

The force tending to bring about coalescence of the particles is considered to be cumulative from the bottom of the latex layer to the top. Since an equilibrium is attained, the force calculated on the bottom surface of the film (the boundary between the dispersible and the nondispersible layers), may be taken as the minimum force F of film formation.

The force F can be calculated from the following equation:

$$F = m(1 - d_1/d_2)a'$$

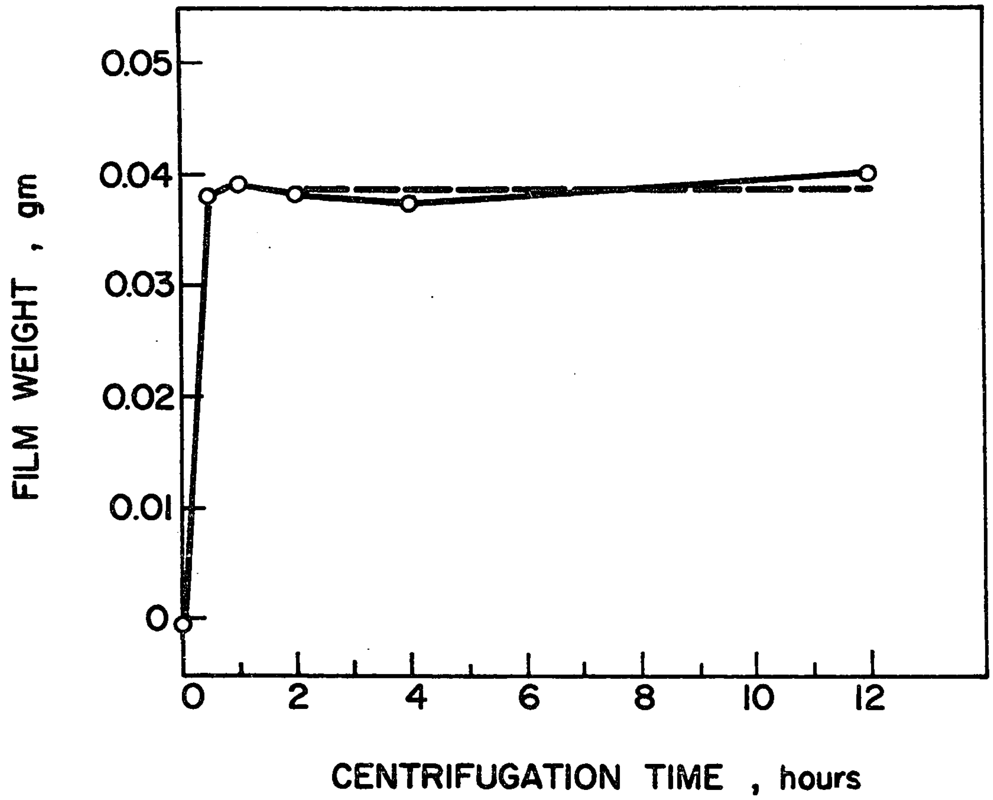
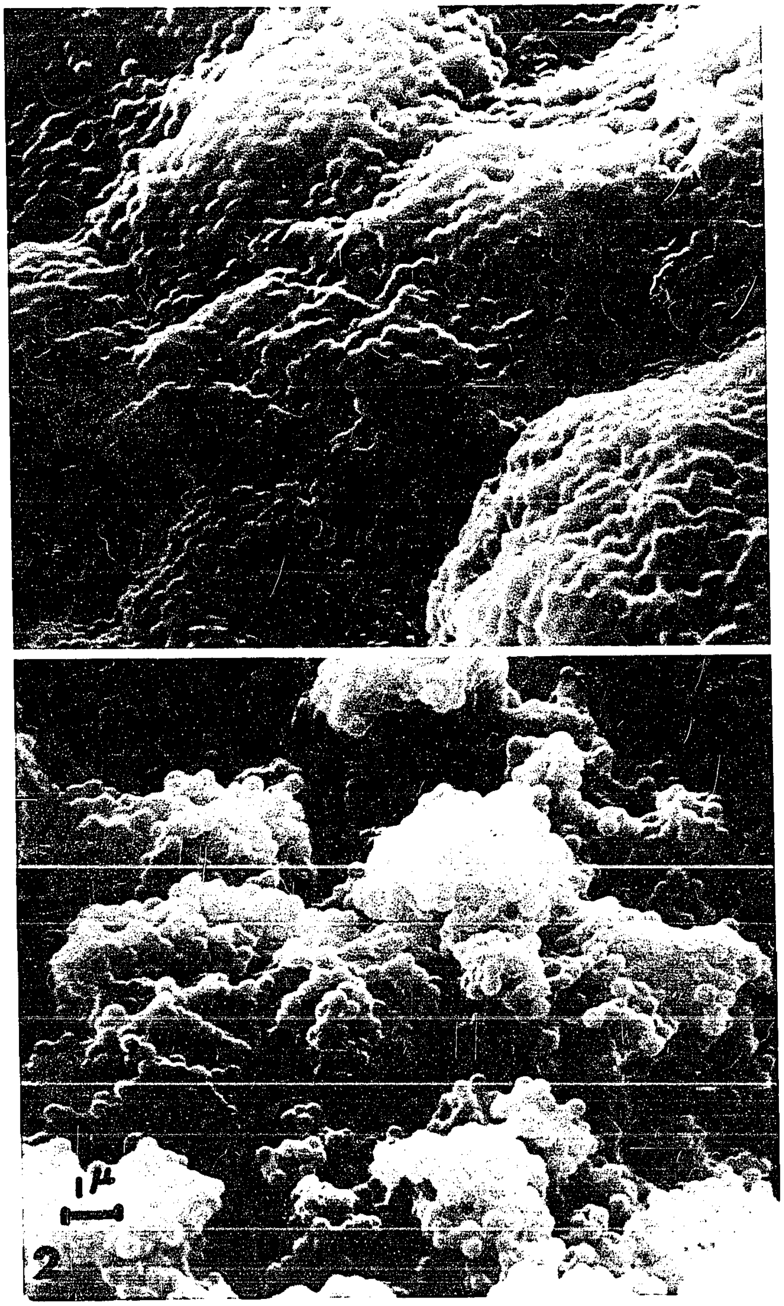


Figure 1. Establishment of equilibrium in the coalescence of latex particles under centrifugation at 60,000 rpm. Latex, 0.05 gm in 5 ml of 0.56 M sucrose solution.

<u>Figure 2</u>

Figure 2. Scanning electron micrograph comparison between top (1) and bottom (2) surface structure produced from styrene-butadiene (60:40) latex by the centrifugation technique.


1μ
2

where m is the mass of the uncoalesced particles (grams), d_1 and d_2 are the densities of the medium and the polymer, respectively (grams/cubic centimeter), $(1 - d_1/d_2)$ is the buoyancy (dimensionless), $\underline{\acute{a}}$ is the acceleration (centimeters/square second) = $\omega^2 R$, where R is the radius of rotation (centimeters), ω is the angular velocity (radians per second). At the top of the tube where R = 3.8 cm, we obtain $\underline{\acute{a}}$ = 153,000 g, for 60,000 rpm and $\underline{\acute{a}}$ = 68,000 g for 40,000 rpm, where g is the gravitational constant.

The calculated force F (in dynes) is divided by the cross section area of the centrifugation tube (1.37 cm^2), to be expressed in units of force/unit area or pressure ($dynes/cm^2$).

The method was applied to the study of the effect of pH on latex stability. Centrifugation of 5-ml samples of 2 gm latex/100 ml of 0.56 M sucrose solution at different pH values was carried out at 60,000 rpm for 1 hour.

The stability curve, Fig. 3, shows the oven-dry weights of the films produced at different pH values. The total weight of the latex charged to the tube (0.10 gm) is transformed into film below pH 1.8 and above 12.3. These represent the two regions of instability on the pH scale.

The pressures required for coalescence, calculated from the corresponding masses of the uncoalesced particles, are shown in Fig. 4. The pressures required for coalescence of the most stable latex with pH values between 8.8 and 10.7, where no film was produced under the applied centrifugal force, could be estimated by extrapolation of the two arms of the curve.

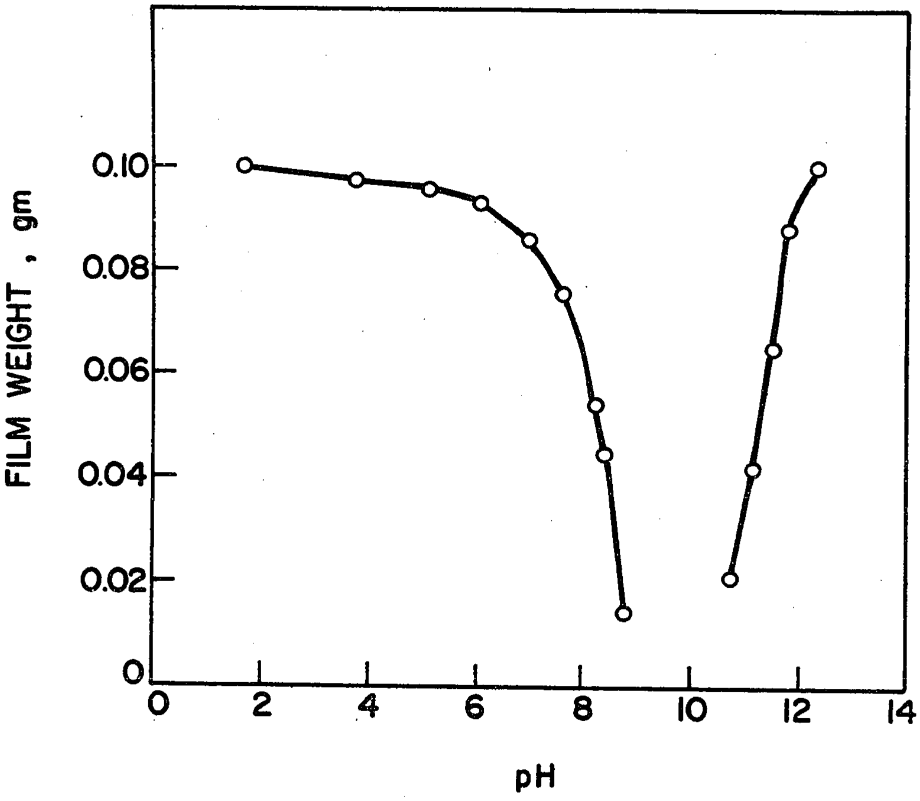


Figure 3. Stability curve of styrene-butadiene latex particles. Produced by centrifugation of samples of 0.10 gm latex/5 ml of 0.56 M sucrose solution at 60,000 rpm.

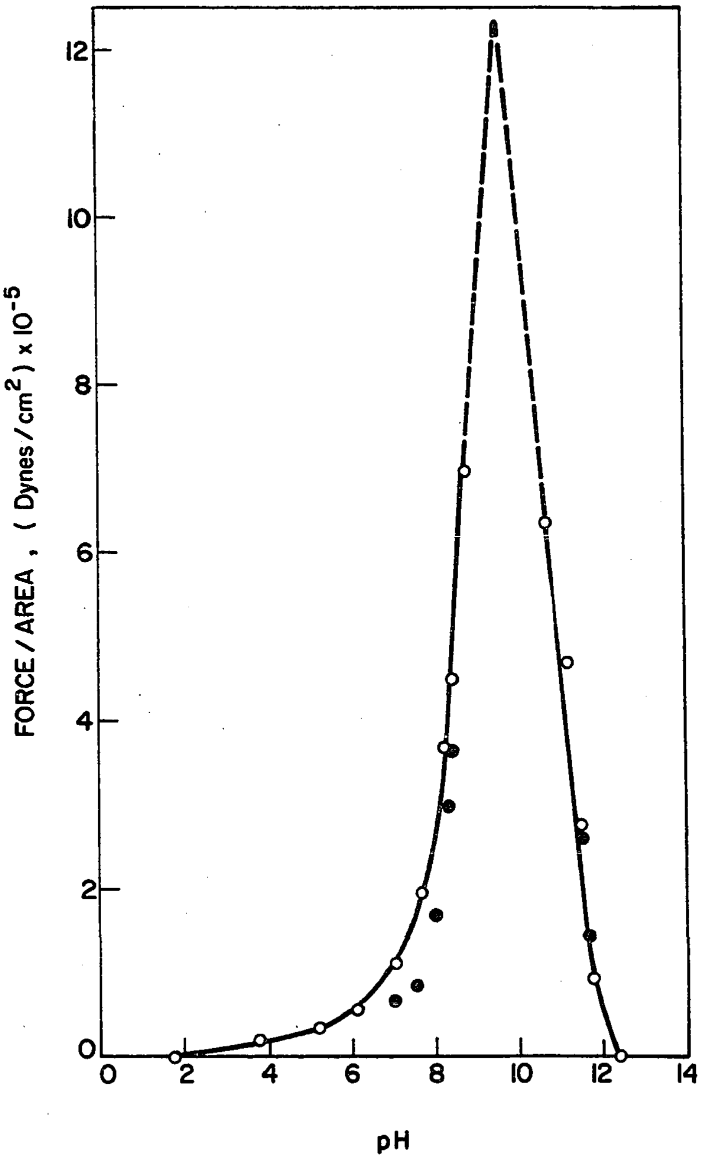


Figure 4. Pressure required for coalescence of latex particles over the pH range. (o) pressures obtained from centrifugation of 0.10 gm latex in 5 ml sucrose solution. (●) minimum pressure from the extrapolations in Fig. 5. The pressure is calculated using the cross-section area of the centrifugation tube.

Experiments were carried out to study the effect of the different variables on the calculated force.

1. Effect of Sucrose Concentration. Two effects were anticipated: the possibility of a concentration gradient's developing under the applied centrifugal force, and the effect of viscosity of the medium on the film formation.

The development of a concentration gradient with respect to sucrose can occur with prolonged operation at the highest centrifugating speeds6). This could result in a loss of buoyancy and a decrease in the force acting to produce filming. An experiment to reveal the extent of the concentration change has shown that in 2 hours at 60,000 rpm, a homogeneous sucrose concentration of 19.6% (d = 1.0795 gm/cm^3) produced concentrations of 18.5% (d = 1.0745 gm/cm^3) at the top and of 20.9% (d = 1.0855 gm/cm^3) at the bottom. Thus at the shorter times characteristic of the experimental program, the buoyancy change involved in filming is less than 6%. The viscosity of the medium may affect the rate of diffusion of any emulsifier displaced from the coalescing particles, as discussed in detail later. Consequently it might affect the establishment of equilibrium in the filming operation.

Three different concentrations of sucrose were used in centrifuging samples with the same latex concentration (2 gm latex per 100 ml of sucrose solution) at 60,000 rpm. Though the weights of the produced films were different, the pressures calculated are very close to each other and do not vary in any systematic manner, as shown in Table I. This shows that within the range of the viscosities of the

TABLE I

Effect of Sucrose Concentration and Speed of Rotation on the Pressures Required for Coalescence of Styrene-Butadiene (60:40) Latex at Two pHs

Sucrose			Pressure (dynes/cm^2) X 10^{-5}			
Concentration	Viscosity	Density	rpm 60,000		rpm 40,000	
gm/l (molar)	(20°C) (centipoises)	(20°C) gm/cm^3	pH = 7.6	pH = 6.7	pH = 7.6	pH = 6.7
192.2 (0.561)	1.786	1.0718	1.8	1.0	1.8	1.0
288.3 (0.842)	2.573	1.1083	1.8	0.8	1.8	0.8
384.4 (1.123)	3.806	1.1443	1.6	0.9	1.8	0.8

medium used, the calculated pressures are not significantly affected.

2. Effect of Rotation Speed. The latex-sucrose system was centrifuged at two different rpm (60,000 and 40,000). Though the weights of the produced films were different, the calculated pressures were similar, as shown in Table I.

3. Effect of Film Thickness. As the film is being formed, its thickness increases in the direction away from the center of centrifugation. In calculating the force of coalescence, the radius of centrifugation used is the distance from the center of rotation to the top of the film (3.8 cm). The average thickness of the film produced from 5 ml of 2 gm latex per 100 ml of sucrose solution centrifuged at 60,000 rpm, is of the order of 0.05 cm. This represents an increase of 1.3% in the centrifugal force applied at the bottom face of the film. This effect was neglected in all the calculations.

4. Effect of Repeated Centrifugation. Further experiments were carried out by centrifuging 5-ml samples of 2 gm latex per 100 ml of 0.56 M sucrose solution at 60,000 rpm. The results, shown in Table II, showed that although the weight of the film is not increased by increasing the centrifugation time from 2 hours to 6 hours, a second film could be produced by centrifuging the uncoalesced particles for 1 more hour after removing the first film and shaking the contents of the tube. Furthermore, the weight of the film was greater, if, instead of 2 hours uninterrupted centrifugation, the latex-sucrose mixture was centrifuged for 1 hour, and the contents were shaken and then centrifuged without removing the film (Table II).

TABLE II

Effect of Centrifugation Time and Shaking on the Weight of Film Produced by Centrifugation of Samples Containing 0.1 g latex per 5 ml of 0.56 M Sucrose Solution.

Centrifugation time (hours)	Film	Weight of Film (grams)
6	1st	0.073
2	1st	0.072
1	2nd	0.014
	1st & 2nd	0.086
1 shake 2	1st & 2nd	0.086

The observation that second and subsequent films are obtained only by shaking the contents of the tube can be explained in the following way. As coalescence of the particles in the upper layers is proceeding, emulsifier molecules are displaced owing to the decrease in the surface area. The close packing of uncoalesced latex particles at the lower face of the film hinders diffusion of the displaced emulsifier molecules, and consequently their concentration in this region is relatively high. The latex particles in this region are prevented from coming into contact by the displaced stabilizer, which may exist as sorbed molecules or as micelles or undissolved particles. Consequently, further coalescence is prevented. On shaking, the stabilizer and the uncoalesced latex particles are redistributed in the serum and, on recentrifugation, further coalescence occurs.

The displacement of the emulsifier molecules during the particle coalescence was proved experimentally7) by centrifuging the latex under forces below and above the force required for coalescence. Conductometric determination of the emulsifier in the serum showed that in the case of particle coalescence about 50% of the emulsifier covering the surface of the particles was displaced to the serum, whereas in the case of noncoalescence, negligible displacement of emulsifier to the serum was detected. The phenomenon of emulsifier displacement and its effect on the equilibrium in the filming process has been observed to varying degrees with different concentrations of latex. This indicates that the pressure, calculated from the first film obtained by the centrifugation of any latex concentration used through this work, is not the minimum pressure required for coalescence but is higher than the required value.

The procedure was consequently modified to overcome this problem of emulsifier redistribution. Stability curves for different latex concentrations were established by centrifuging latex-sucrose mixtures at several pH values. The weights of the first films, produced from different latex concentrations at the same pH value, were interpolated from stability curves similar to that of Fig. 3, and were plotted as shown in Fig. 5. The line at any specific pH value is extended to its intersection with the horizontal axis. The intercept represents the minimum mass of latex particles that would produce a film under the applied centrifugal force at this specific pH value if no stabilizer displacement took place. This is the mass required to calculate the minimum pressure required for coalescence at the specific pH value. The calculated minimum pressures for different pH's are shown in Fig. 4.

DISCUSSION

An ultracentrifugation technique has been developed to determine the minimum pressure required for the initiation of latex particle coalescence.

The basic principle of the technique is to determine the minimum mass of the latex particles which can produce a film under an applied centrifugal force. The minimum force is obtained by multiplying

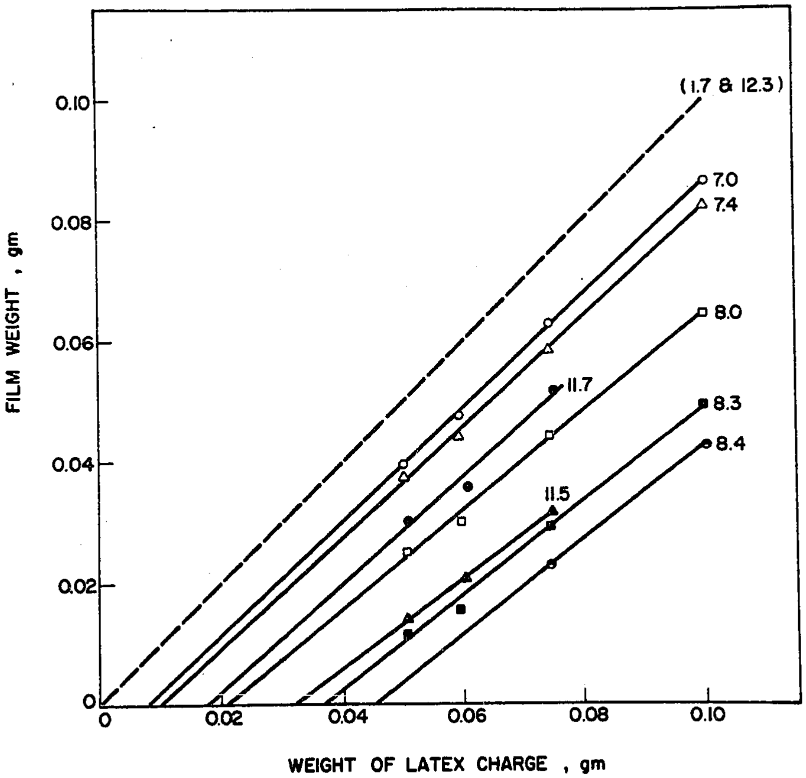


Figure 5. Weights of the films produced from different latex concentrations by centrifugations at 60,000 rpm at designated pH values.

this mass by the buoyancy of the medium and the acceleration.

On centrifugation, the latex particles may be considered as being forced into a layer at the top, or conversely the aqueous medium is drained from the interspaces to form a layer of serum below the particles. Consequently the centrifugal force is acting to bring the latex particles into close proximity and to initiate their coalescence. In this respect, it resembles the capillary force arising from the water-air interfacial tension during the evaporation of the aqueous medium in the usual way of forming a film.

For practical purposes, it is necessary to use concentrations of latex sufficient to produce films that can be handled and weighed. The use of such concentrations of latex leads to complications owing to the displacement of the emulsifier molecules from the surface of the coalescing particles and their increased concentration at the lower boundary of the film. The established equilibrium is then determined by the displaced emulsifier and is not a reflection of the force required to produce coalescence of latex particles with their original stabilizer coverage. Consequently the mass of the uncoalesced latex particles left after filming is larger than the mass which would be obtained if the stabilizer were not displaced.

This effect is minimized by decreasing the concentration of latex charged to the tube and is illustrated in Fig. 5, by the inclination of the lines representing the weights of the films produced from different latex concentrations at designated pH values. In the ideal case where no displacement of emulsifier occurs during coalescence, the line would be inclined at 45 degrees. The fact that the inclination of the lines in Fig. 5 is less than 45 degrees illustrates the effect of emulsifier displacement in decreasing the mass of the produced film and consequently increasing the mass of the uncoalesced latex particles left after filming.

The minimum pressures calculated from the mass at the intersection points of these lines with the X-axis are plotted in Fig. 4. The uncorrected pressures obtained from the centrifugation of 2 gm latex in 100 ml of 0.56 M solution of sucrose approximate the minimum pressure to the extent shown in Fig. 4. The approximation would be closer as the concentration of latex is lower and the coalesced film is thinner.

The 45-degree line through the origin in Fig. 5 represents the weights of the films produced from latex at pH values less than 2 and above 12. These are the two regions of instability of the latex where all particles charged to the tube are transformed into film on centrifugation. The stability of the latex system between these two pH limits is represented in Fig. 4 by the pressure required for coalescence. It reaches its maximum between pH 8.8 and pH 10.7. The stability of the latex is very sensitive to small changes in pH and can readily change owing to absorption of CO_2 from air.

The minimum pressure required for coalescence could presumably be obtained by varying the rpm instead of varying the concentration of the latex. Extrapolation of the weights of the films produced by centrifuging a certain concentration of latex at different rpm's would provide an estimate of the minimum rpm required to produce a film.

The corresponding acceleration could be used together with the total mass m of the latex charged to the tube to calculate the minimum pressure for coalescence.

The mean centrifugal force transmitted per particle to initiate coalescence can be calculated by dividing the minimum coalescence force by the number of particles in the layer. For the latex-sucrose system at pH 8.75, the force transmitted per particle is 0.54 X 10^{-3} dynes, independent of the rpm or sucrose concentration.

The minimum pressures required for coalescence were measured in preliminary work by a different method employing Millipore filters. The method is similar to the porous plate technique which has been applied in soils8), textile materials9), and pulp fibers10, 11). The apparatus is the same as previously described10), with the main difference being that a Millipore filter replaces the porous plate. A styrene-butadiene latex sample (5% concentration) is placed on a wet Millipore filter, and hydrostatic tension is applied from below. When equilibrium is reached the applied tension is equal to the capillary pressure. The onset of coalescence is detected by attempted redispersion of the latex particles in water. Although the establishment of equilibrium was difficult to determine in these experiments, the minimum applied tension resulting in the filming of the latex system in the pH range from 7.0 to 8.4, were typically between 1.6 X 10^5 dynes/cm^2 (= 12 cm Hg) and 4.0 X 10^5 dynes/cm^2 (= 30 cm Hg). These pressures compare reasonably with the pressures subsequently obtained from the centrifugation technique for the same range of pH values, i.e.,

1.1×10^5 dynes/cm^2 to 5.2×10^5 dynes/cm^2, and confirm that the capillary force required to produce coalescence during drying is sensibly estimated by centrifugation technique.

The minimum pressures for latex coalescence measured by centrifugation or capillary pressure are of the order of pounds per square inch as compared to the hundreds of pounds per square inch that have been previously[2, 3] calculated as the pressure exerted upon the particles during the evaporation of water.

The coalescence of latex particles under the conditions of the present experiments was found to be time independent in contrast to the coalescence of oil emulsions during centrifugation in Vold's work[12]. In the latter case the rate of coalescence was studied and related to the rate of thinning of the intervening film[13]. The applied force exceeded the force of repulsion between the particles and coalescence continued throughout the reported centrifuging time. With latexes the film thinning is believed to be comparatively rapid but the forces between particles provide a substantial and continuing barrier to complete coalescence.

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PART V

A STUDY ON THE INTERPARTICLE FORCES IN LATEXES USING THE ULTRACENTRIFUGATION TECHNIQUE

ABSTRACT

The ultracentrifugation technique[1], was applied to study the effect of pH and of emulsifier and electrolyte contents on the minimum pressures required to coalesce styrene-butadiene (60:40) latex stabilized with stearate soap. The method provides a measure of the force opposing coalescence of the latex particles, which correlates qualitatively with the primary maxima in the force-interparticle distance curves calculated according to DLVO theory. The study suggests that stability of this latex system is dominated by the electrostatic repulsive force and is controlled by factors influencing this force, specifically coverage of the particle surface with potential-determining ions and the thickness of the double layer, as modified by the concentration of univalent electrolytes.

INTRODUCTION

The practical importance of latexes often lies in their ability to form films. This involves the coalescence of the latex particles and is usually accomplished by the development during drying of capillary forces that are sufficient to overcome the barriers or repulsive forces opposing particle approach. A study of the mechanism of coalescence and film formation requires knowledge of the magnitude and nature of the forces acting between the particles.

An ultracentrifugation technique has been developed1) for determining the minimum force required for the initiation of coalescence. The method is based on the consideration that in centrifugation of a latex-sucrose system, the force pressing particles together in the packed layer varies more or less linearly with the thickness of the bed. Coalescence occurs if the force exceeds a certain minimum. The effects of pH, emulsifier content, and electrolyte content on the force required for coalescence of latex particles have been investigated using this technique. The importance of these measurements go beyond the investigation of the mechanism of film formation; they are significant in relation to latex stability in general.

It is the purpose of this part to discuss the centrifugal approach to the investigation of the filming of latexes in the light of existing theories of colloidal stability.

RESULTS

Effect of Emulsifier Content. In order to study the effect of different soap concentrations on latex coalescence, an ion-exchanged latex[2)] was used and lithium stearate was added as the emulsifier. To insure the presence of the emulsifier in the ionizable soap form, pH = 10 was maintained during these experiments. Since the "clean" latex after the ion exchange procedure usually has a pH value near 4, the pH of the latex was adjusted to a value slightly less (e.g. 9) than the required pH before the addition of any soap in order to avoid the precipitation of stearic acid. The final adjustment of the pH was carried out prior to the centrifugation experiments.

Centrifugations of 5 ml samples of 0.8 gm and 2 gm latex/100 ml of 0.56 M sucrose solutions with different soap concentrations at pH = 10, were carried out at 60,000 rpm for one hour. The oven-dry weights of the films produced at different soap contents are shown in Fig. 1. The reference points on the Y-axis of the graph were obtained by centrifuging the "clean" latex at pH 12.3, where the total weight of the latex charged to the tube is transformed into film. The pressures required for coalescence, calculated from the corresponding masses of the uncoalesced particles are shown in Fig. 2. Two straight line plots (1 and 2) with different slopes were obtained for the two different concentrations of latex. This discrepancy is due to emulsifier displacement[3)] and its effect on the establishment of equilibrium during

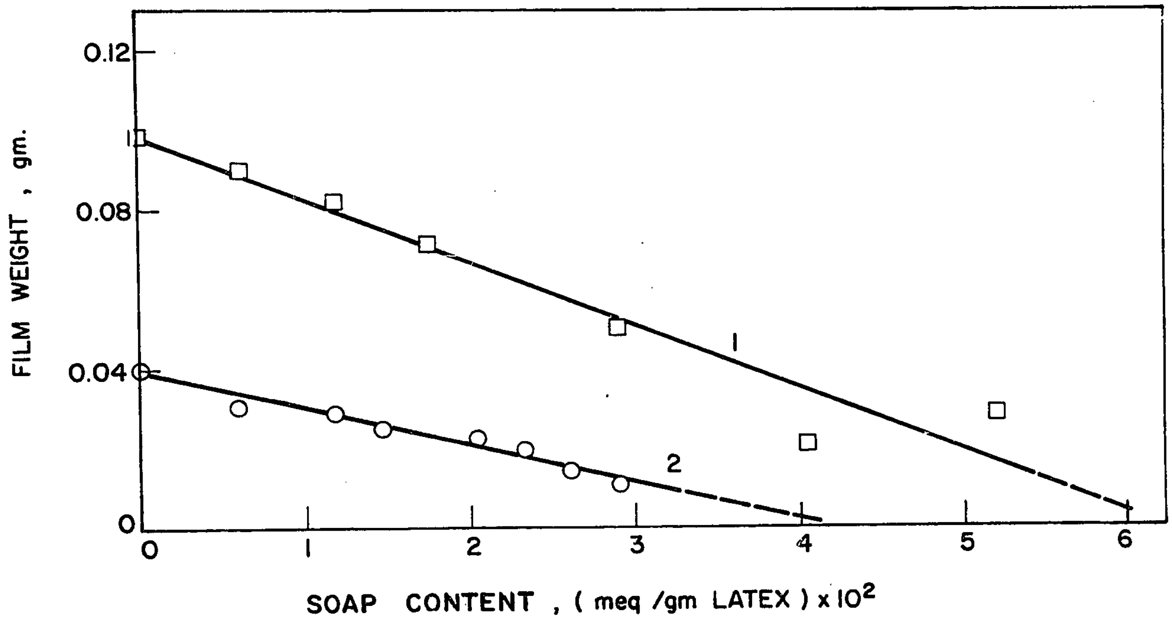


Figure I. Weights of the films produced from two latex concentrations (1) 0.098 gm and (2) 0.039 gm, per 5 ml of 0.56 M sucrose solution, at different soap contents, by centrifugations at 60,000 rpm at pH = 10.

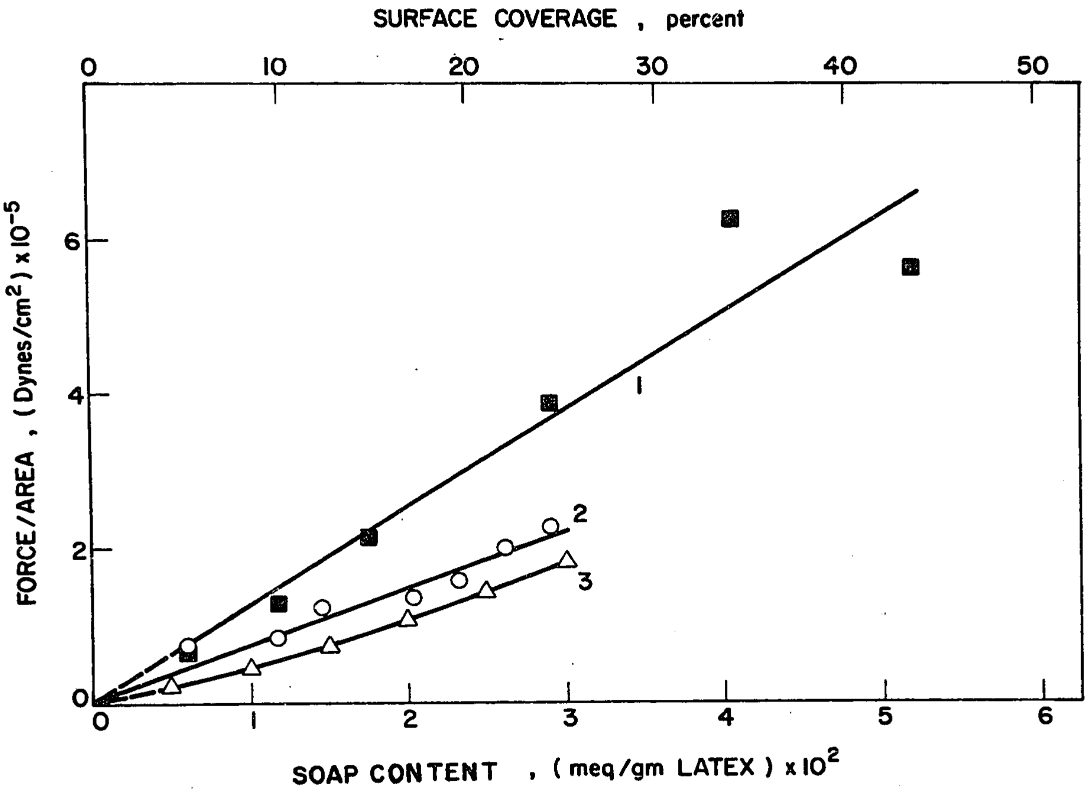


Figure 2. Pressures required for coalescence of latex particles with different soap contents at pH = 10,

(1) pressures obtained from centrifugation of 0.098 gm latex in 5 ml of 0.56 M sucrose solution,

(2) pressures obtained from centrifugation of 0.039 gm latex in 5 ml of 0.56 M sucrose solution,

(3) minimum pressures obtained from the extrapolations in Fig. 3.

the filming process of latex under centrifugation as discussed earlier[1)]. The soap displacement during filming results in an increase in the surface coverage of the particles at the boundary between the uncoalesced particles and the film, as compared to the original surface coverage. Consequently the soap concentration plotted in Fig. 2 does not correspond to the true surface coverage that determines the barrier to coalescence and neither of the two straight lines represent the required pressure-soap content relationship.

In order to overcome this problem of soap redistribution and its interference with the calculation of the minimum pressures required for initiation of coalescence, a procedure similar to that previously applied[1)] was used. In this case the weights of the films produced from different latex concentrations at the same soap concentration, were interpolated from Fig. 1 and were plotted as shown in Fig. 3. The line at any specific soap concentration is extended to its intersection with the horizontal axis. The intercept represents the latex charge that would just produce incipient film formation. Under this condition, there is no coalescence and no stabilizer displacement. This latex charge is identified with the mass of uncoalesced latex required to calculate the minimum coalescence pressure.

The calculated minimum pressures obtained in this way with different soap contents are shown in Fig. 2 by curve 3. This is fairly close to curve 2 representing the pressures obtained without correction using the lower (0.8%) latex concentration. Curve 3 represents the

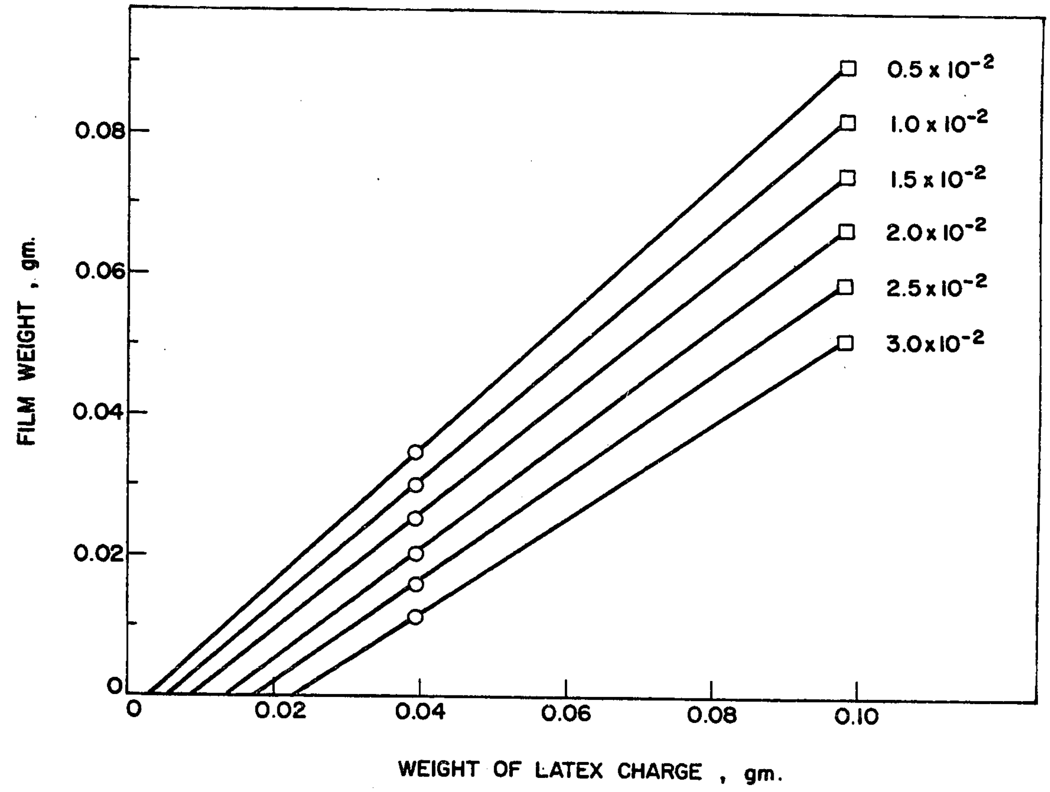


Figure 3. Weights of the films produced from two latex concentrations at the designated soap contents in meq/gm latex as interpolated from Fig. 1.

desired pressure-surface coverage relationship and shows a continual increase in the pressure required for initiation of coalescence with increase of the surface coverage by the ionizable soap molecules.

The calculation of the percentage of particle surface coverage from the soap content of the system used in these experiments was based on an assumed cross-section area of 23.4 $\mathring{A}^2$ for the lithium stearate soap molecule$^{4)}$ at complete packing of the surface. The corresponding percentages of surface coverage are given on the top scale of Fig. 2, based on the assumption that the total amount of the soap in the latex system is adsorbed on the surface of the particles.

This assumption is supported by auxiliary experiments$^{3)}$ in which the soap distribution between latex particles and solution was determined. The total soap as obtained by conductometric titration was compared with the soap in the bulk. The dissolved soap was determined by measuring the surface tension relative to a concentration-surface tension calibration curve. It was found that the fraction of soap in solution increased with dilution of the latex but at 0.8% latex amounted to no more than 5% of the total.

pH-Effect. The effect of pH on the coalescence of latexes both with and without emulsifier was examined. Centrifugations of 5 ml samples of 2 gm latex/100 ml of 0.56 M sucrose solution at different pH values were carried out at 60,000 rpm for one hour.

The stability curve, Fig. 3 of Part IV, shows the oven-dry weights of the films produced from latex with a known constant emulsifier content at different pH's. The pressure required for coalescence at a certain pH, as calculated from the corresponding mass of the uncoalesced particles, was again found to be dependent on the latex concentration. This behavior was consistant with the observation of the displacement of the emulsifier during centrifugation. The procedure previously discussed[1)] was used to eliminate this effect of emulsifier redistribution and to establish a pressure-pH relationship at a specified emulsifier coverage. The corrected pressures required for coalescence of latex with emulsifier at different pH's are shown in Fig. 4, by curve 1. The pressures required for coalescence of latex without emulsifier are calculated directly from the weights of the uncoalesced particles without any need for correction, since there is no emulsifier displacement and no concentration dependence. These are also shown in Fig. 4, by curve 2.

The pressures required for coalescence of "clean" latex are very low over the whole pH-scale. The small "hump" which appears at pH = 10 may be due to a small residual amount (0.6×10^{-2} meq/gm latex) of emulsifier after ion-exchanging the latex.

The pressures required to coalesce latex which contains emulsifier are far higher than those required for "clean" latex, and their magnitude depends very much on the pH value. Curve 1 in Fig. 4 shows the effect of pH on the pressures required to coalesce a latex system which has a constant emulsifier content. The emulsifier content (expressed as total stearate) of the system is that which results from the polymerization conditions and is determined to be 6.5×10^{-2} meq/gm latex. This represents about 55% surface coverage for the

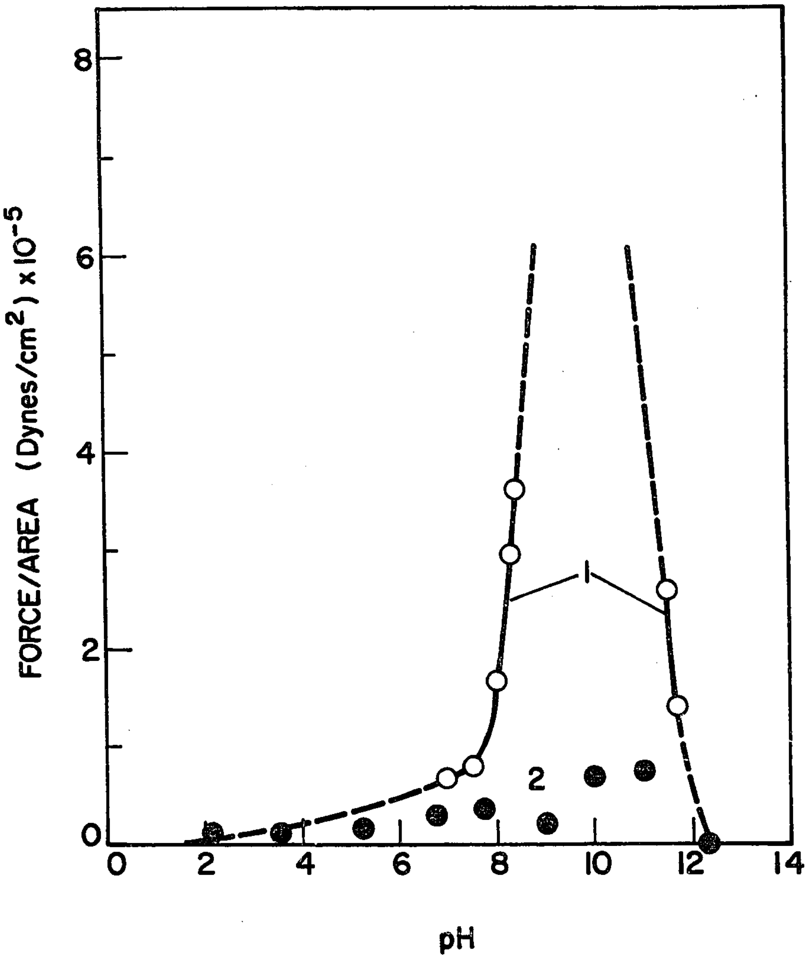


Figure 4. Minimum pressures (after correction for soap displacement during centrifugation) for coalescence of latex particles over the pH scale as obtained by centrifugation of 0.1 gm latex in 5 ml of 0.56 M sucrose solution.

(1) Pressures for latex with a constant stearate content of 6.5 X 10^{-2} meq/gm latex.

(2) Pressures for ion-exhanged "clean" latex. The stearate content does not exceed 0.6 X 10^{-2} meq/gm latex.

Pressures were calculated using the cross-section area of the centrifugation tube (1.37 cm^2).

particles, if all the stearate (soap and stearic acid) is adsorbed on the surface of the particles.

The first arm of curve 1, Fig. 4, from pH 6 to 9, shows the effect of varying the soap to acid ratio of the emulsifier in the system on the coalescence of latex. As the pH increases, the ratio of the stearate soap to the stearic acid in the system increases. Since 95% or more of the emulsifier content is adsorbed on the particle surface, increasing the pH results in increasing the concentration of the ionizable soap molecules on the surface and a decrease of the un-ionized stearic acid molecules. The corresponding pressures required for initiation of coalescence increase first slowly and then rapidly as the pH approaches 10.

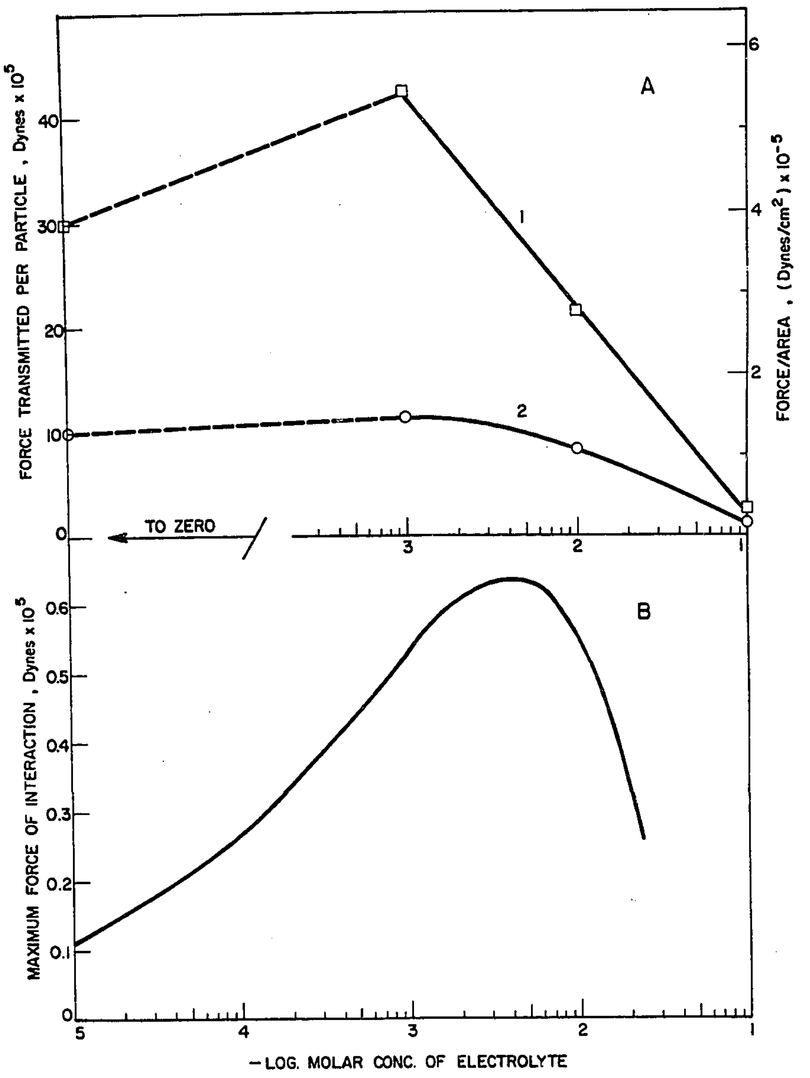
The bulk electrolyte concentration through this pH-range (6-9) is determined by the products of polymerization, e.g. potassium sulfate (about 6×10^{-3} M). It may be considered to vary with pH only to the small extent determined by the free soap molecules existing in the medium surrounding the particles, since the added alkali is used in transforming the stearic acid into soap and the cations are held near the particle surface as counter-ions to the adsorbed stearate. After the pH is reached at which the total stearate content of the system is transformed into the ionized soap form, any further increase in the pH by adding excess alkali results in an increase of the electrolyte content of the system without changing the surface coverage of the particles. Consequently the descending arm of the pressure-pH curve 1, is explained as an effect of electrolyte concentration on latex coalescence.

Effect of Uni-Univalent Electrolyte. The effect of sodium chloride concentration on the coalescence of latex was studied. The latex was first ion-exchanged to remove almost all of the electrolyte and soap; then lithium stearate soap was added at pH = 9 to give a certain surface coverage of the particles. The required amount of electrolyte was added and then the final adjustment of pH to a value of 10 was carried out prior to centrifugation. Centrifugations of 5 ml samples of 2 gm latex/100 ml of 0.56 M sucrose solutions which contain a known soap and electrolyte content at pH = 10 were carried out at 60,000 rpm for one hour.

The pressures (dynes/cm^2) required for coalescence were calculated in the usual way from the weights of the uncoalesced latex particles. The results for latex particles with two different original surface coverages of 24% and 10% (2.9×10^{-2} and 1.2×10^{-2} meq/gm latex respectively) are shown in Fig. 5A. The minimum pressure required for coalescence was also expressed in units of force (dynes) transmitted per particle to initiate coalescence simply by dividing the minimum coalescence pressure by the calculated number of particles per unit cross-section. These pressures were not corrected for the effect of the soap displacement during centrifugation which, if taken into consideration, should decrease the magnitude of the pressures particularly for the case of high surface coverage. The observation that the shape of the curve is the same for both high and low surface coverage suggests that taking the effect of soap displacement into consideration for the calculation of the pressures, would change only the magnitude and not

Figure 5-A. Pressures required for the coalescence of 0.1 gm latex in 5 ml of 0.56 M sucrose solution at different uni-univalent electrolyte contents, obtained from centrifugation of latex with two different soap contents, (1) 2.9 X 10^{-2} meq/gm latex, and (2) 1.2 X 10^{-2} meq/gm latex. The pressure is calculated using the cross-sectional area of the centrifugation tube (right ordinates). The corresponding force transmitted per particle is also given, as calculated by dividing the total force by the number of particles per cross-sectional area of the tube (left ordinates).

Figure 5-B. The theoretical variation of the maximum force of interaction between two particles as a function of electrolyte concentration, as determined from the maxima of the curves given in Fig. 9.


FORCE TRANSMITTED PER PARTICLE , Dynes x 10^5
0
10
20
30
40
FORCE/AREA , (Dynes/cm^2) x 10^{-5}
2
4
6
A
1
2
TO ZERO
3
2
1
B
MAXIMUM FORCE OF INTERACTION , Dynes x 10^5
0
0.1
0.2
0.3
0.4
0.5
0.6
5
4
3
2
1
−LOG. MOLAR CONC. OF ELECTROLYTE

the shape of the curve. Consequently these curves are a qualitative expression of the trend by which the electrolyte affects the pressures required for initiation of coalescence.

For a given surface coverage the pressure required for coalescence, after an increase at low electrolyte concentrations, decreases substantially with further increases of the electrolyte concentration.

DISCUSSION

The stability of lyophobic colloids in general depends upon the energy of interaction among the suspended particles. The chief forces influencing the stability are the following.

1. Forces of attraction of the London-van der Waals dispersion type.
2. Forces of repulsion due to interaction of the electrical double layers that are generally present around the particles.
3. Forces of repulsion due to the steric hindrance and the solvation of the adsorbed layers.

In the DLVO theory5, 6) of colloidal stability the energy of interaction between the approaching particles is considered to be determined by the first two forces. The total potential energy of interaction V_T for two particles at a given separation is given by:

$$V_T = V_R + V_A \qquad (1)$$

where V_R is the potential energy of repulsion and V_A is the potential energy of attraction. The identity and qualitative relationship of the chief variables determining the two potential energies are shown in the following equations which are derived using broadly simplifying assumptions.

The potential energy of electrostatic repulsion for spherical particles of equal size is given by 7)

$$V_R = 4.62 \times 10^{-6} \quad (a\ \gamma^2/v^2) \exp(-\kappa H) \qquad (2)$$

$$\gamma = (\exp(Z/2) - 1)/(\exp(Z/2) + 1) \qquad (3)$$

$$Z = v\ e\ \psi_\delta/kT \qquad (4)$$

where v is the valency of counter ion, a is the radius of the particle, H is the distance between the particles surfaces, e is the electronic charge, ψ_δ is the Stern potential, and

$$\kappa = (8\ \pi\ n\ v^2 e^2/\varepsilon\ kT)^{1/2} \qquad (5)$$

where $1/\kappa$ is the thickness of the diffuse double layer, n is the number of ions of electrolyte per cm^3, ε is the dielectric constant of the medium.

The potential energy of attraction for two spherical particles of equal size and at very short distances is approximately given 8) by:

$$V_A \quad = \quad - A \cdot a/12\ H \qquad (6)$$

where A is the Hamaker constant.

The combination of the electrostatic repulsive energy V_R with the attractive energy V_A leads to a potential energy curve such as that shown schematically in Fig. 6a. The hump which exists in the potential energy curve represents a potential energy barrier, which must be overcome if two particles are to attain coalescence. Its height is considered to account for the apparent stability of the colloidal particles, and is determined by the parameters of equations (2) and (6). From a shelf-life stability point of view, if the energy barrier is sufficiently higher than the available thermal energy, say $V_{T\ (max.)} > 25$ kT, the colloid is absolutely stable9) whereas with a lower barrier approximating kT, a proportion of the colliding particles can acquire sufficient kinetic energy to surmount the barrier and consequently rapid aggregation or precipitation results.

Since in the ultracentrifuge technique, it is the force acting between the particles that is being determined rather than the potential energy, it is more convenient to consider the force-interparticle distance curves instead of the potential energy curves. These curves are directly related since the force F is given by:

$$F \quad = \quad - dV/dH \qquad (7)$$

i.e. the potential gradient in the direction of the line joining the centres of the two interacting particles, where H is the interparticle separation.

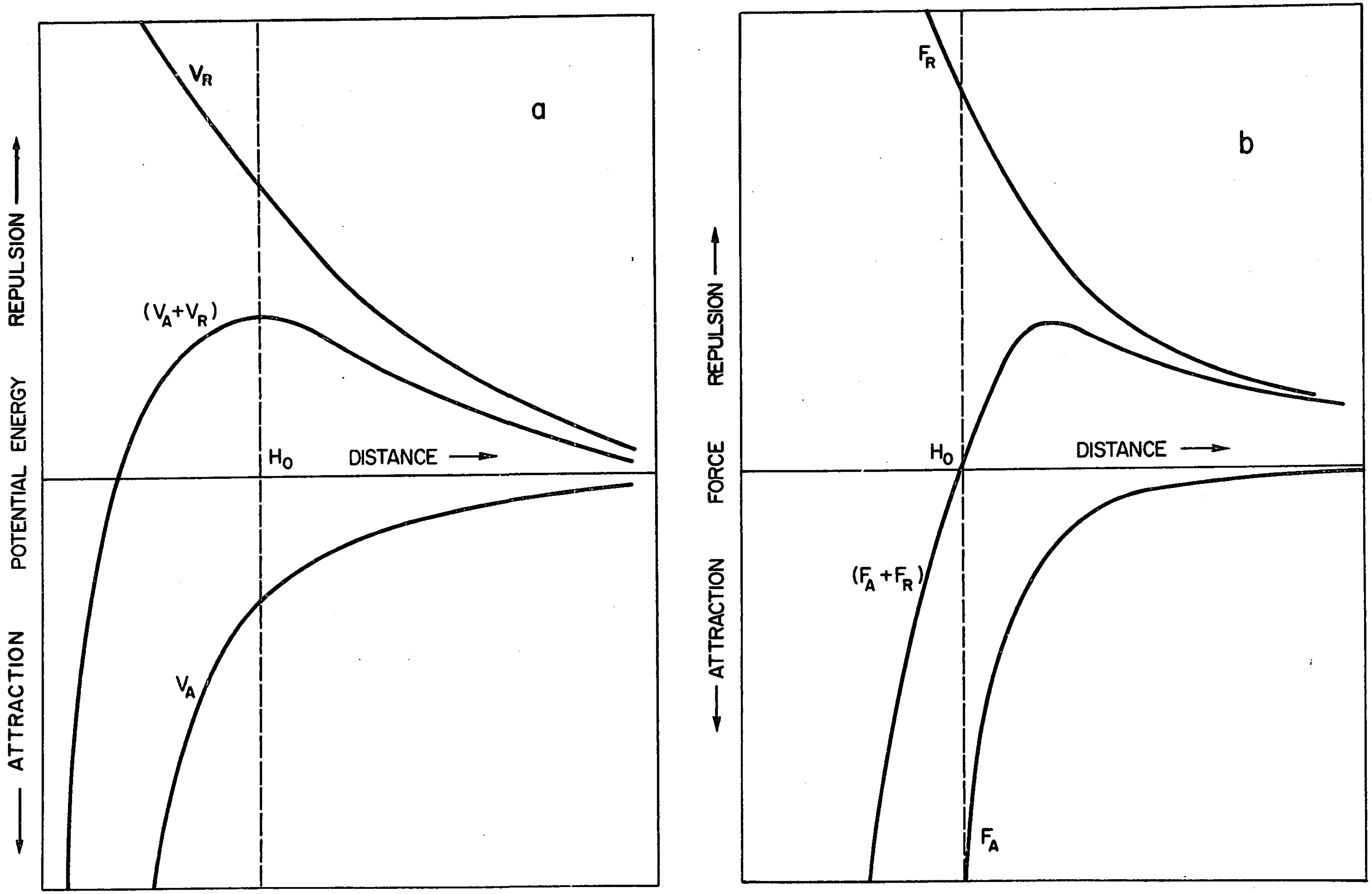
The potential energy curves and their corresponding force curves are given in Fig. 6a, b respectively, which show that the behavior of the system at large interparticle separations is governed mainly by the electrostatic repulsion, whereas at small separation it is determined by the attractive force. The behavior of the two particles at separations intermediate between these two extremes is governed by the combination of the two forces of opposite sign but of comparable orders of magnitude. At separations greater than H_0, dV/dH is negative and the resultant force operative between the particles is repulsive. At separations smaller than H_0, dV/dH is positive and the resultant force is attractive. At $H = H_0$, the forces of electrostatic repulsion are just balanced by the forces of attraction. The maximum in the force curve corresponds to the maximum slope of the corresponding potential energy curve and it represents the force which must be applied to the particles to pass the energy barrier and to initiate coalescence. From the coalescence point of view, these are the forces that should be compared with the force obtained from the ultracentrifugation experiments for the coalescence of latex particles, or with the capillary forces that are developed during film formation by evaporation.

Though the DLVO theory is widely accepted as the basis for explaining the stability of colloidal systems, yet in some particular cases a number of factors, other than those accounted for in the theory, may have to be considered. An example is the stability of a dispersion of carbon in paraffins with adsorbed dodecyl benzene as stabilizer.

Figure 6 (a and b). Schematic representation of the effect of interparticle distance upon (a) the potential energy of interaction between two particles (b) the force acting between the particles.

Note that at the distance H_0, the potential energy passes through a maximum and the attractive and the repulsive forces are equal.

The maximum in the force curve represents the maximum slope of the potential energy curve.


a
V_R
(V_A+V_R)
H_0
DISTANCE ⟶
V_A
REPULSION ⟶
POTENTIAL ENERGY
⟵ ATTRACTION
b
F_R
H_0
DISTANCE ⟶
(F_A+F_R)
F_A
REPULSION ⟶
FORCE
⟵ ATTRACTION

In this case, the electrostatic repulsion is assumed10) to be unimportant and the stability is accounted for by considering the decrease in the number of configurations of the adsorbed aliphatic molecules due to steric hindrance when the particles approach each other giving rise to an entropic repulsion. Ottewill11) emphasized the importance of the repulsive forces arising from the solvation of the adsorbed molecules in addition to those arising from changes in configurational entropy as in the stabilization of polystyrene latexes by adsorbed non-ionic surface-active agents. An alternative visualization of the barrier opposing coalescence can be related to the mechanical strength of the adsorbed emulsifier film and any tightly-bound water molecules12).

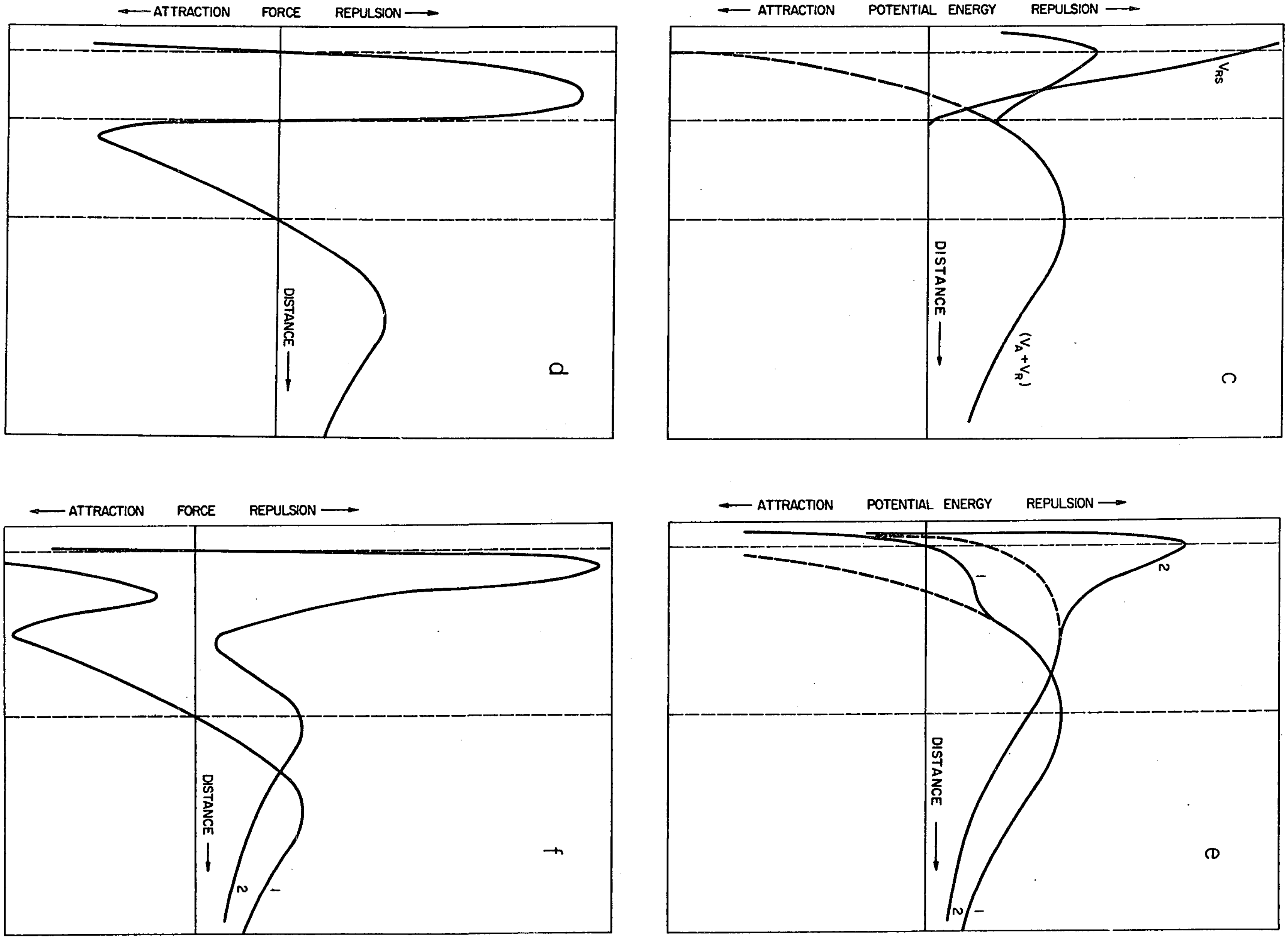
The effect of the adsorbed layers can be accomodated into the scheme of the DLVO theory, when their contribution to the interaction energy can be formulated, since the three potential energies are presumably additive. Some attempts have been made to calculate the contribution of the entropic repulsion13, 14, 15) and the repulsion due to solvation11) of the adsorbed emulsifier molecules and to construct the total potential energy curve by the addition of these repulsive energies to the van der Waals attractive energy.

The most complicated situation arises when the three potential energies (attractive V_A, electrostatic repulsion V_R, and steric repulsion V_{RS}) are operating at the same time. Lyklema16) points out that, due to the long-range action of the electrostatic repulsion V_R, a contribution of the steric repulsion is not felt as long as V_R is high enough to prevent close approach. However, when the maximum in $(V_R + V_A)$ is not quite high enough to stabilize the dispersion, a minimum can develop at distances approximately twice the thickness of the adsorbed layer, followed by another energy barrier due to the contribution of the steric repulsion.

Depending on the magnitude of the steric repulsive energy V_{RS}, and the shape of the curve representing the potential energy of interaction due to $(V_R + V_A)$ different types of potential energy curves can result of which two are shown schematically in Fig. 6 c and e. The corresponding force curves are also given in Fig. 6 d and f. The relative contribution of the steric and the electrostatic factors in the stabilization of the latex system depends to a great extent, among other factors, on the nature, dissociation constant, and concentration of the emulsifier, the effect of interaction between the emulsifier molecules and the solvent, and the type and concentration of electrolyte. Though the precise nature of the balance between these two repulsive factors is not yet understood, some experimental evidence has been given17) for the presence of both steric and electrostatic repulsion in the stability of polystyrene latex by potassium palmitate.

Since, in our latex system, the force required for coalescence was appreciable only with the emulsifier in its ionized form while the un-ionized emulsifier apparently provided no barrier to the coalescence at low pH, it is assumed that the electrostatic effects predominate. In fact, our experimental results can be accounted for qualitatively by the

Figure 6 (c, d, e and f). Schematic representation of some possible effects of the addition of the steric repulsion on the shape of the total potential energy curves (c and e); and the corresponding force curves (d and f). The dashed curves omit the contribution of the steric repulsion energy V_{RS}.


ATTRACTION
FORCE
REPULSION
DISTANCE
d
ATTRACTION
POTENTIAL ENERGY
REPULSION
V_{RS}
DISTANCE
(V_A+V_R)
c
ATTRACTION
FORCE
REPULSION
DISTANCE
2
1
f
ATTRACTION
POTENTIAL ENERGY
REPULSION
1
2
DISTANCE
2
1
e

basic DLVO theory, as explained in the following paragraphs.

The emulsifier effect, Fig. 2, showed that the force required for the coalescence increases with the increase of surface coverage with ionized stearate soap molecules (C_{18}), at least up to 25% (3×10^{-2} meq/gm latex). Mazur et al.[18)] studied the zeta potential of polystyrene in relation to the soap concentration for various aliphatic soap systems ranging from C_8 to C_{16}, in the absence of salts. Their studies showed that the potential was low at low soap concentration, and it increased as the soap increased until a critical concentration was reached above which a decrease in the potential occurs. This behavior was typical for each of the soaps in this homologous series, they differ only in the magnitude of the potential and the soap concentration at which the maximum occurs.

An explanation of our results may be found in assuming a similar increase of the zeta-potential with the increase of the surface coverage at the low surface coverages used in our experiments. The increase in the zeta-potential, in turn, should result in an increase of the repulsive force as calculated from the derivative of equation (2) with respect to H when ψ_δ is identified with the zeta-potential. Consequently the maximum force in the force-interparticle distance curve should increase with the increase of surface coverage. The complete investigation of the effect of increasing the surface coverage on the force required for coalescence of latex particles requires accurate determinations of the zeta-potential for different surface coverage, and more ultracentrifugation data, which are not available at the present time.

The behavior of the latex on changing the pH from 6 to 9 as expressed by the pressure required for coalescence in Fig. 4, curve 1 may be explained on the basis of conversion of stearic acid to soap and effectively increasing the surface coverage of the particles with the potential-determining ions, as discussed in the previous paragraph. The explanation of the behavior of latex at pH higher than 10 as given in the same figure, is considered to be the effect of electrolyte concentration on the coalescence, as discussed below.

An explanation for the effect of electrolyte on the latex coalescence, shown in Fig. 5-A, was sought in terms of the theory of colloidal stability by trying to correlate the forces opposing coalescence, as obtained from centrifugation experiments, with the corresponding values calculated from DLVO theory.

The total effect of electrolyte on the latex coalescence may be found in the effects which the ionic strength of the latex system have on 1) the adsorption of the anion by the latex particles, and on 2) the thickness of the double layer around the particles. The effect of the ionic strength on the adsorption of soap anions on the latex particles that concerns us here is the contribution of the adsorbed anions to the potential ψ_δ, which is required for the calculation of the repulsive force F_R. To assess this effect, the only experimentally accessible value of potential to be identified with ψ_δ, is the zeta-potential which is obtained from electrophoretic measurements as will be discussed shortly. The effect of the ionic strength on the thickness of the double layer can be calculated from equation (5) for different electrolyte contents of the latex system.

Potential energy curves for the interaction of latex particles were constructed using equations (2) and (6), by substituting suitable values for the various parameters. The particle radius $\underline{a}$ was taken to be 1.75×10^{-5}cm, $\underline{v} = 1$, and the various values of κ were calculated from equation (5) by substituting different values of ionic concentrations $\underline{n}$ (ions/cm^3) over the range of electrolyte concentrations used in our experiments ($10^{-5} - 2.3 \times 10^{-2}$ M). The value of γ was calculated from equations (3) and (4). The potential ψ_δ was taken to be 50 mV and was assumed to be constant for the different electrolyte concentrations.

Mazur et al.[18)] reported that the electrophoretic mobility of styrene latex stabilized with palmitate (C_{16}) soap remained constant with a many-fold change in the electrolyte concentration. This behavior and the inference of a constant potential was substantiated experimentally by measurements of electrophoretic mobilities using our latex system. The mobilities U of the ion-exchanged latex containing 0.05% by weight solids and 4.7×10^{-2} meq stearate soap/gm latex (40% surface coverage) have been measured by conventional electrophoretic techniques, in the presence of various amounts of sodium chloride at pH = 10. The zeta-potential ζ was calculated from Henry's equation:

$$U = (C) \cdot \frac{\zeta \ \varepsilon}{\pi \ \eta} \qquad (8)$$

where η is the viscosity and (C) is a numerical factor which, depending on κ and $\underline{a}$, varies[19)] between 1/4 and 1/6. This equation was found to be satisafactory for the calculations of zeta-potential over the range

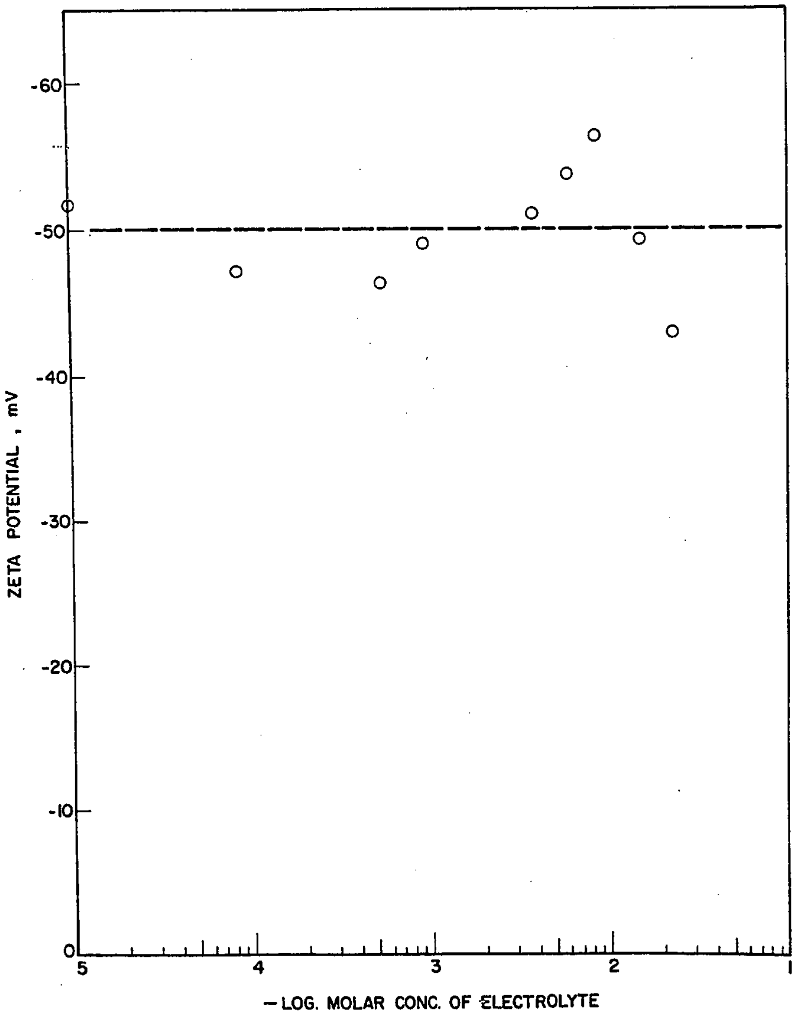


Figure 7. The influence of the concentration of sodium chloride on the zeta-potential of styrene-butadiene latex.

of (κa) and mobilities observed in our measurements according to the criterion set down by Overbeek et al 20).

The zeta-potentials at different electrolyte concentrations are plotted in Fig. 7, over the range of electrolyte used. Similar behavior showing a maximum was previously reported for the effect of electrolytes on similar systems of paraffin particles 21) and sulfonated polystyrene latex 22). Our results for the zeta-potentials are fairly well approximated by 50 mV over the range of electrolyte concentration used, as shown in Fig. 7.

The Hamaker constant A was arbitrarily taken to be 1×10^{-12} ergs.

For the given system of latexes, equations (2) and (6) may be re-written as

$$V_R = 1.66 \times 10^{-11} \exp(-\kappa H) \tag{9}$$

$$V_A = -\frac{0.146 \times 10^{-17}}{H} \tag{10}$$

from which V_R and V_A can be calculated for different values of κ at different interparticle separations. The sum of V_R and V_A gives the total potential energy of interaction between two particles at different distances of separation. Some of the results are represented by the potential energy curves at different electrolyte concentrations in Fig. 8, with the potential energy expressed in ergs and in multiples of kT (4.1×10^{-14} ergs).

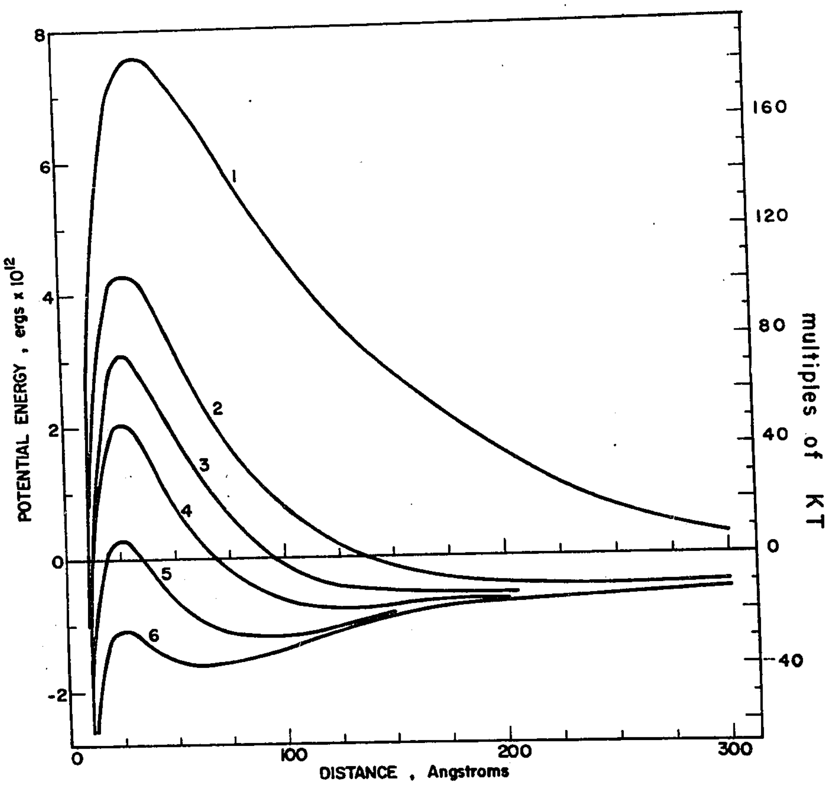


Figure 8. The influence of the concentration of uni-univalent electrolyte on the total potential energy of interaction of two spherical particles, as calculated using particle radius = 1.75×10^{-5}cm, $A = 10^{-12}$ erg and ψ_δ = 50mV.

The curve numbers for different electrolyte concentrations (equivalents/1000 cm^3) and the corresponding κ (cm^{-1}) are:-

(1) 9.4×10^{-4} ($\kappa = 1 \times 10^6$) ; (2) 3.8×10^{-3} ($\kappa = 2 \times 10^6$) ;

(3) 5.9×10^{-3} ($\kappa = 2.5 \times 10^6$) ; (4) 8.5×10^{-3} ($\kappa = 8 \times 10^6$) ;

(5) 1.5×10^{-2} ($\kappa = 4 \times 10^6$) ; (6) 2.3×10^{-2} ($\kappa = 5 \times 10^6$) .

The corresponding force-interparticle distance curves were calculated from equations (11) and (12), of the repulsive force F_R and the attractive force F_A which were obtained from the derivatives with respect to interparticle separation H, of equations (9) and (10) respectively:

$$F_R = 1.66 \times 10^{-11} \kappa \exp(-\kappa H) \tag{11}$$

and

$$F_A = -\frac{0.146 \times 10^{-17}}{H^2} \tag{12}$$

The resultant total force of interaction between two particles at different interparticle distances for different electrolyte concentrations, as obtained from the sum of F_R and F_A, are shown in Fig. 9.

The effect of electrolyte concentration on the height of the barrier in the potential energy curves and the force curves respectively must be clearly distinguished. The increase in the electrolyte concentration results in a continuous decrease in the height of the potential energy barrier; whereas the height of the force barrier increases first gradually with increasing electrolyte concentration, passes through a maximum at about 4×10^{-3} M, and then decreases rapidly with further increase in the electrolyte concentration as shown in Fig. 5-8. From the shelf-life stability point of view, all latex-electrolyte systems which are represented by potential energy curves above curve number 5 in Fig. 8 are very stable since they all have a potential energy barrier greater than 25 kT. Other systems which are represented by

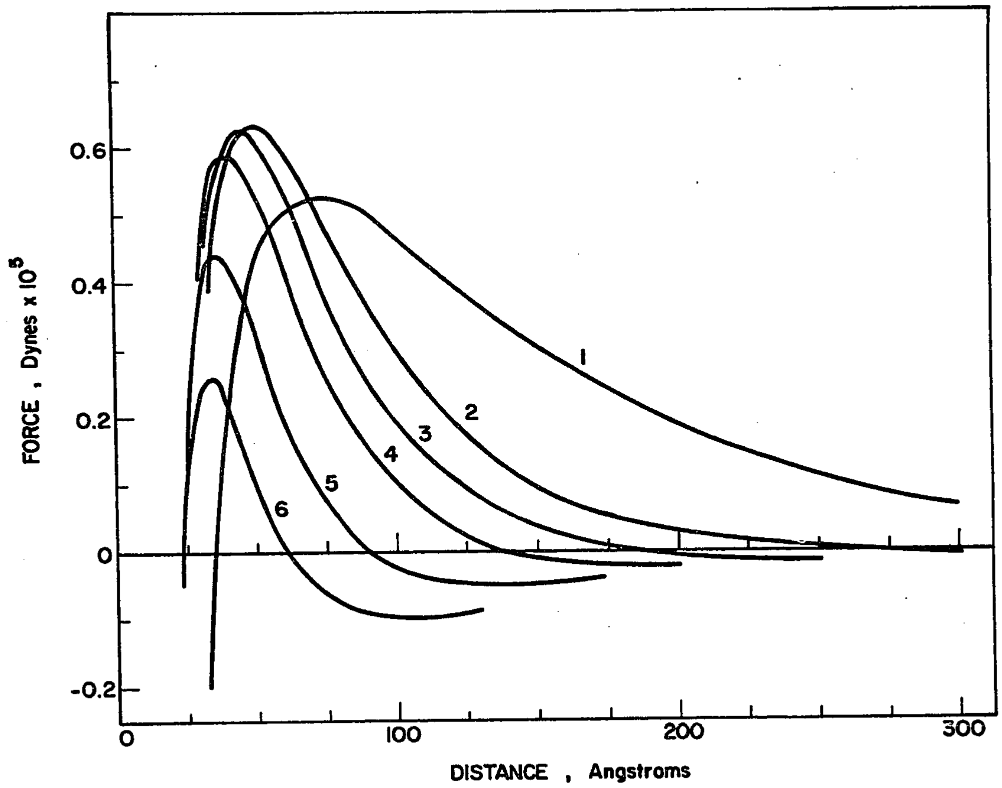


Figure 9. The influence of the concentration of uni-univalent electrolyte on the total force of interaction of two spherical particles as calculated using the same data that were used for calculating the potential curves of Fig. 8. The maxima in these curves represent the forces which must be applied on the latex particles for the initiation of coalescence.

curves below curve number 5, are less stable, and the stability is decreased by increasing the electrolyte concentration which results in a progressively decreasing barrier. Ultimately, the thermal energy, which results in collisions due to Brownian motion of the particles causes rapid coagulation. From coalescence point of view the maxima of the various force curves for different electrolyte concentrations as shown in Fig. 9, are the ones which should be compared with the forces obtained from the ultracentrifugation experiments for the coalescence of latex particles as in Fig. 5-A and 5-B.

There is no intention, considering the arbitrary assumptions made, of making a quantitative comparison between the experimental and the theoretical calculations of the force required for coalescence of latex particles. It is only possible to show that the trend of the experimental results of the electrolyte effect can be accounted for by the properties of the force-distance curves.

The force required for coalescence of latex particles at different electrolyte concentrations as obtained by the ultracentrifugation technique can be compared with the theoretical calculations as shown in Fig. 5-A and B. The force required for coalescence of latex particles with high surface coverage is higher than that required for low surface coverage, as shown by the plots 1 and 2 in Fig. 5-A. This is due to the increase of the repulsive force between the particles as a consequence of the increase in the number of the potential-determining ions on the surface of the particles.

The experimentally determined values of the force required for coalescence at different electrolyte concentrations are always much higher than the theoretically calculated values. Similar order of magnitude differences have been observed by Ottewill et al.[23)] at separations near the maximum in the pressure-interplate distance curve for a montmorillonite system. They attributed this behavior to the barrier resulting from structural boundary layers of water and to the inadequacy of the electrostatic repulsion model at such small separations.

In the latex systems these considerations of solvation and theoretical shortcomings are also applicable, and additional uncertainties exist. Uncertainty concerning the structure of the particle surface and the nature and orientation of the adsorbed emulsifier and its solvation makes any assignment of the Hamaker constant rather arbitrary at the present time. Further, the origin $H = 0$ for equations (11) and (12) cannot be clearly specified and may even be different for the two equations.

Another uncertainty is the transmission of force between spherical particles in a packed bed which should be a function of the packing (cubic or hexagonal) and the orientation of the packed structure to the force. The force transmitted per particle should be reduced, as a first approximation, by dividing by the number of contact points the particle makes in the direction of the force, if one requires an indication of a single particle-particle interaction.

Concluding remarks.

The experimental determination, by the centrifugation method, of the force required for initiation of coalescence provides a measure of the height of the force barrier in the force-interparticle distance curve and is thus a measure of latex stability. It is to be noted however that this technique neither identifies the force barrier as due to electrostatic or steric factors, or both; nor does it indicate the separation at which the peak occurs. The variation of the stability with the amount of surfactant, the pH and the elctrolyte concentration is consistent in trend with the predictions of the DLVO theory but this does not preclude the possibility of other factors playing a significant role. A more complete description of the interparticle interactions will require additional information to be provided by the application of auxiliary techniques.

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APPENDICES

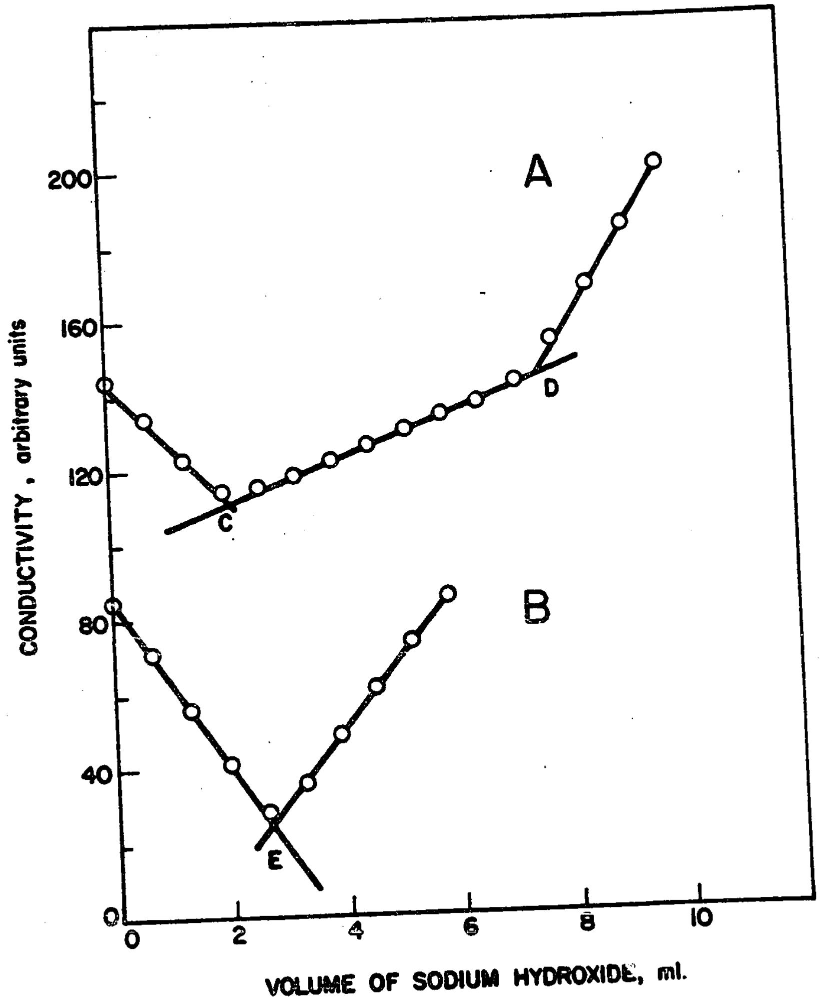
APPENDIX I

CONDUCTOMETRIC TITRATION OF SYNTHETIC LATEXES

The indirect titration method developed by Maron et al[1)] was used for the determination of the soap and fatty acid or free alkali content of the latex. The method is summarized as follows. The latex is diluted with equal volumes of isopropyl alcohol and water, a known excess of hydrochloric acid is added, and titration with standard base is carried out using conductance measurements to follow the course of the titration.

In a typical procedure, about 5 gm of latex (20% solid content) is diluted successively with 20 ml of distilled water and 20 ml of isopropyl alcohol. Excess of 0.1 N hydrochloric acid is then added, and the mixture is titrated with o.02 N sodium hydroxide solution. The sodium hydroxide was added from a pre-calibrated syringe mounted on and operated with the vernier of a traveling microscope. In this way, small and accurate portions of alkali are added. Constant stirring is maintained during additions. Conductivity measurements are made after each 0.3 ml additions of sodium hydroxide. The titrations were carried out in a 100 ml beaker with a double-wall for controlling the temperature at 25°C by circulation of water. Conductivity meter type CDM2 (RADIOMETER, Copenhagen), is used to follow the conductivity cell which has two unprotected platinum electrodes.

Fig. 1-A shows a typical conductance curve of latex. V_C gives the volume of sodium hydroxide required for neutralization of the excess



<u>Figure 1</u>. Typical conductometric titration curves for latex-emulsifier systems using 0.0205 N sodium hydroxide.

A. Conductivity titration of a sample containing 1.77 gm latex, 1 ml of 0.1 N hydrochloric acid was added before titration.

B. Conductivity titration of a sample containing 1.44 gm "clean" ion-exchanged latex, 0.5 ml of 0.1 N hydrochloric acid was added before titration.

hydrochloric acid added. $(V_D - V_C)$ is the volume of sodium hydroxide required for reaction with the total fatty acid (i.e. the initial free fatty acid content of the latex plus the soap content which is now in acid form after reaction with the hydrochloric acid). Thus the total number of milliequivalents of soap and fatty acids present in the latex sample is equal to $N_b(V_D - V_C)$, where N_b is the normality of alkali used for titration. Assuming that the volume of the hydrochloric acid added in the first place was V_A with a normality of N_a, then $(V_AN_a - V_CN_b)$ represents the milliequivalents of the acid which must have been consumed by the latex constituents.

Various information can be obtained from such titrations as given in the following cases.

1. <u>When $N_b(V_D - V_C) > (V_AN_a - V_CN_b)$.</u> This indicates that there must have been fatty acids present in the initial latex samples, and Equations 1 to 3 are used to calculate the amounts (in meq) of the different forms of the emulsifier content.

Soap $\quad S = (V_AN_a - V_CN_b) \quad (1)$

Total stearate $\quad Y = N_b(V_D - V_C) \quad (2)$

Free fatty acid $\quad X = Y - S \quad (3)$

2. <u>When $N_b(V_D - V_C) < (V_AN_a - V_CN_b)$.</u> This indicates that there must have been free alkali present in the initial latex, and Equations 4 to 6 should be used instead of 1 to 3.

Soap $\quad S = N_b(V_D - V_C) \quad (4)$

which in this case is equal to the total stearate in the system.

Total alkalinity $Z = (V_A N_a - V_C N_b)$ (5)

Free alkali $K = Z - S$ (6)

3. $\underline{\text{When } N_b(V_D - V_C) = (V_A N_a - V_C N_b)}$. This indicates that the latex contained neither free alkali nor free acid but only soap which is given by $N_b(V_D - V_C)$.

4. $\underline{\text{When } V_C N_b > V_A N_a}$. This implies that free strong acid groups are present, since more base is consumed in the titration of the strong acid than the hydrochloric acid originally added. This case is obtained on titrating an ion-exchanged latex where all the soap and fatty acid groups have been removed, and the sulfate groups are present on the surface of the latex particles.

The conductometric titration of the "clean" ion-exchanged latex, Fig. 1-B, showed that the emulsifier content is negligible as reflected by the disappearance of the flat portion (C-D) of the titration curve. The point of intersection E gives the quantity of the strong acid groups on the surface of the particles which, in this specific case amount to 0.0033 meq/gm latex. This value corresponds to 1.80 μcoulomb/cm^2 for particle diameter of 3.58×10^{-5} cm, which is comparable with values reported by Vanderhoff$^{2)}$, for a polystyrene latex of similar preparation.

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APPENDIX II

SURFACE TENSION MEASUREMENTS FOR THE DETERMINATION OF SOAP IN THE AQUEOUS PHASE OF THE LATEX SYSTEM.

Latex systems containing fatty acid soaps owe their stability to the attachment of the anions to the particles by physical adsorption. In such cases, an equilibrium exists between the stabilizer in the bulk phase and that adsorbed on the particles. In order to determine the fraction of the total soap (determined by conductometric titration), which is responsible for the stability of the latex, it was necessary to find a way to determine the quantity of the soap dissolved in the bulk phase.

Surface tension measurements were used1, 2, 3) to determine the soap content in the bulk phase of the latex system, since the latex particles with the adsorbed soap layer do not themselves affect the surface tension.

Surface tensions were determined at 25°C by the Wilhelmy plate method4) which, according to Zettlemoye et al5), is reliable for surfactant solutions. The experimental set-up is described by Padday6). For our purpose, a vertical platinum plate, suspended from the arm of a CAHN type electrobalance, just touches the surface of the suspension contained in a covered beaker. The balance was calibrated in such a way as to read directly the additional pull on the plate, i.e. the force in grams, without detaching the plate from the surface during the measurements.

The force on the plate was followed with time as shown in Fig. 1, where the force in grams is plotted against the square root of time.

Equilibrium, as indicated by the levelling-off of the curve in Fig. 1, is reached after about one hour for Curve 1 which is typical of latex-sucrose-soap system. Curves 2 and 3 are typical of sucrose-soap systems which contain no latex particles, and show the longer time required for equilibrium. These differences in the time required for equilibrium between the two systems may be explained by the diffusion controlled process of reaching equilibrium, where the soap molecules adsorbed at the sucrose-air interface have to be in equilibrium with the soap molecules in the bulk phase. In the case where latex particles exist with their adsorbed layers of soap molecules (Curve 1), the particles could be envisioned to be acting as a reservoir which contains a high concentration of soap molecules located within a very short distance from the interface, and ready to furnish the soap molecules required to establish equilibrium at the air interface. In the case where latex particles are not present (Curve 2 or 3), the soap molecules required for equilibrium at the air interface have to be furnished from the bulk phase and the molecules have probably to diffuse farther and equilibrium is delayed. The fact that the force at which equilibrium is reached for Curve 2 is almost equal to that of Curve 1, though the soap content of the latter is about 40 times higher, is an indication of the adsorption of most of the soap on the surface of the particles in the case of Curve 1 while the amount dissolved in the aqueous phase and responsible for the surface tension is very small.

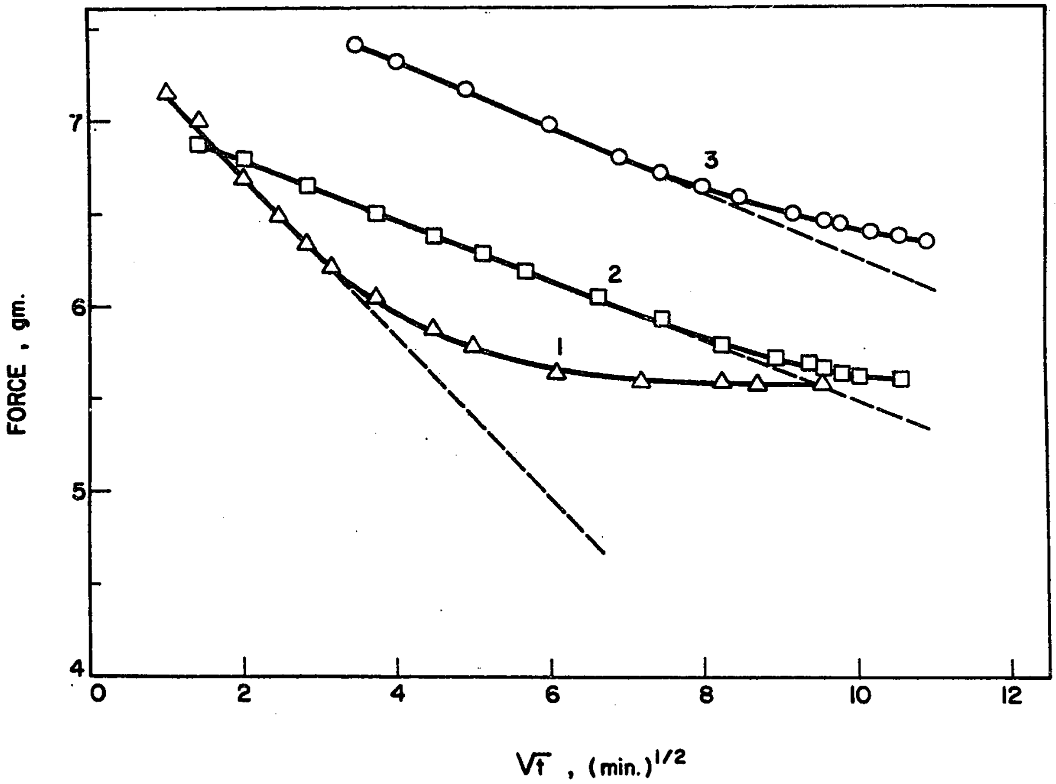

Figure 1. The variation of the force required to keep the edge of the platinum plate in contact with the surface of the suspension, with the square root of time t. Equilibrium force is taken at the levelling-off of the curves.

(1) 2 gm latex/100 ml of 0.56 M sucrose solution containing a total soap concentration of 7.4 X 10^{-4} M.

(2) 2 X 10^{-5} M lithium stearate soap in a solution of 0.56 M sucrose.

(3) 8 X 10^{-6} M lithium stearate soap in a solution of 0.56 M sucrose.

In order to eliminate the effects of evaporation, the measurement-chamber of the balance was humidified with the same suspension prior to measurements and a glass cover was installed on the top of the beaker with a small opening for the hanging plate.

The force in grams at the equilibrium point was used as W to calculate the surface tension γ according to

$$\gamma = W.g/R \tag{1}$$

where $R = 2(L + d)$; L is the width of the plate (cm), and d is the thickness of the plate (cm), g is the gravitational constant. For the plate used in our experiments, $g/R = 8.3342 \text{ sec}^{-2}$. Special precautions were taken to insure the wettability of the platinum plate so that the contact angle could be considered equal to zero.

Surface tensions were determined for different concentrations of lithium stearate soap in 0.56 M sucrose solution, as shown in Fig. 2. This curve is used as the reference for obtaining the emulsifier concentration in the aqueous phase of the latex-sucrose system.

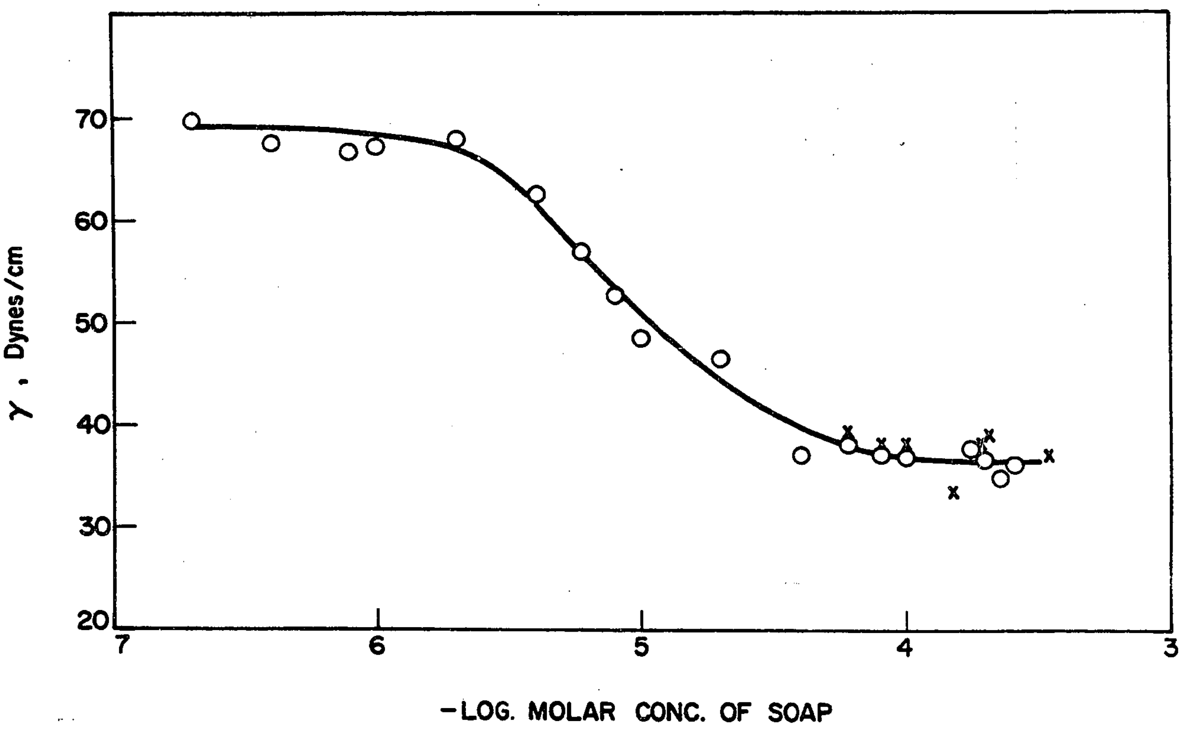

Figure 2. Reference curve for the surface tension (γ) of different lithium stearate soap concentrations in 0.56 M sucrose solutions.

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APPENDIX III

ION-EXCHANGE FOR LATEX "CLEANING"

Latexes, as produced from emulsion polymerization, contain sufficient emulsifier to give about 60% coverage of the particle surface. Also various salts exist in the dispersing medium as by-products of the ingredients added during the polymerization. In order to study the effect of emulsifier at lower surface coverage, and the effect of electrolyte on the stability of latex, it was necessary to remove both emulsifier and electrolytes from the system. The ion-exchange technique as reported by Vanderhoff et al[1)] represents the basis for this method of removing the emulsifier and electrolyte from the styrene-butadiene (60:40) latex.

One of the most important features of the technique is conditioning the ion-exchange resins to remove completely any soluble polyelectrolytes.

The resins selected were the 20-50 mesh DOWEX 50W - X4 which is the sulfonate salt (H^+ form) of a 96:4 styrene-divinylbenzene copolymer, and DOWEX 1-X4 resin which is the analogous trimethylammonium salt. The ion exchange capacity of the DOWEX 50W resin (OH^- form) is 1.2 meq/ml (wet volume). The lower degree of crosslinking (4%) was used to facilitate the removal of soluble polyelectrolyte and the pickup of emulsifier anions. The procedure given by Vanderhoff[1)] for conditioning the resins was strictly followed, which is summarized as follows.

Separately the resins were washed until no more colored material was removed. Then each resin was separately eluted consecutively with 3N Na OH, hot water, methanol, cold water, 3N H Cl, hot water, methanol, and cold water. This cycle was repeated four times, and the last cycle was completed by conversion of DOWEX 50W resin to the H^+, and of DOWEX 1 resin to the OH^- form, by elution with an excess of 3N H Cl and 3N Na OH respectively. The resins were rinsed copiously with double distilled water to remove the excess acid and alkali.

The procedure of applying the ion exchange technique reported by Vanderhoff1) comprised mixing 300 - 500 ml latex with 5-fold excess (estimated from the emulsifier and electrolyte content) of mixed resin under agitation for two hours, and then filtering through a sintered-glass Buchner funnel to remove the resin beads and titrating an aliquot. The process was repeated until a constant value was obtained for the surface charge, as determined by the conductometric titration.

Several trials were carried out until a suitable procedure for the application of the ion-exchange technique was mastered. The following remarks represent the general guide line for applying the ion-exchange technique to our latex system. (1) The mixed resin and the DOWEX 1 were agitated alternately with the latex in a batch technique. (2) The mixed resin used was of a quantity and composition such that the DOWEX 1 was in 5-fold excess with respect to anion content of the latex and DOWEX 50W was equivalent to the cation content. (3) Conductometric titrations were carried out after each step in order to estimate the amount of the resin to be used in the next step. (4) The pH of the latex suspension during agitation with DOWEX-1 was adjusted to 10 with sodium hydroxide in order to transform all the stearate anion into the completely dissociated soap form. (5) The time of contact with the resin was more than 5 hours.

In a typical ion-exchange process, 600 ml of 16% (by weight) of styrene-butadiene latex were agitated with the resin according to the previous guide-lines. The results, as followed step by step, are shown in Table I.

The decrease in the solid content given in Table 1, is partly due to adsorption of some latex on the resin surface, and partly due to dilution with distilled water used for washing during filtration. The decrease in the pH of the latex system on using the mixed resin is due to the effectiveness of DOWEX-50W in removing all the cations from the medium rapidly. The slight rise in the pH of the latex system on agitation with DOWEX-1 is due to the removal of some anions from the medium and the release of their corresponding cations to form alkali.

The stearate content of the ion-exchanged latex system is reduced from 6.27 X 10^{-2} meq/gm (original), to 0.56 X 10^{-2} meq/gm. This is indicated by the disappearance of the flat portion of the titration curve in Fig. 1-B of Ref. 2. This reduction in the stearate content corresponds to a change in the surface coverage from 53% to about 5%. The stability of the latex system with such low surface coverage is attributed to the residual sulfate end groups of the polymer chains, which are in the ionized form.

TABLE I

Step-by-Step Record of Ion-Exchanging Styrene-Butadiene with DOWEX-50W (D-50) and DOWEX-1 (D-1) Resins.

Step	pH		Duration of contact	Solid content	Stearate content
	Before	After	(hours)	(%)	(meq/gm)
Original	7.6	--	--	16	0.0627
Mixed Resin (D-1 : D-50) (5 : 1)	7.6	3.9	7	14.9	0.0425
D-1	9.7	11	5	12.6	0.0150
Mixed Resin (D-1 : D-50) (10 : 1)	11	10	7	12.2	0.0119
D-1	9.8	10.6	11	12.2	0.0060
Mixed Resin (D-1 : D-50) (5 : 1)	10.6	4	5	10.9	0.0056

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APPENDIX IV

A- pH Measurements

The pH-value of the latex-sucrose system is measured using a Corning pH-meter Model 7, and a Fisher microprobe combination electrode. It is adjusted just prior to the centrifugation run by careful addition of dilute solutions of either sulphuric acid or lithium hydroxide to the latex-sucrose system during vigorous stirring.

B- Scanning Electron Microscopy

Examination of the surface morphology of some of the produced films was carried out in a scanning microscope Stereoscan 2-A Model (Cambridge Instrument Company, Cambridge, England), (Figs. 1 of Part III, and 2 of Part IV).

In order to prevent further coalescence of the particles, and preserve the morphology of the surface, the film was brominated1) with bromine-water. The sample was then washed with distilled water, dried and coated with conducting material (Au/Pd, 60:40) in a vacuum chamber.

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CLAIMS TO ORIGINAL RESEARCH

The work reported in this thesis was primarily designed to measure the force required to initiate coalescence of latex particles under various conditions. This has been achieved together with several original accomplishments and findings.

(1) Preparation and characterization of the monodisperse styrene-butadiene (60:40) latex system required for this work.

(2) It has been shown that the consolidation or "further gradual coalescence" of films after inter-particle contact is independent of the presence of a polymer-air interface.

(3) It has been demonstrated that the surface coverage of the latex particles by stabilizer is not greatly changed by dilution down to 0.5% solid contents.

(4) It has been demonstrated that the centrifugation of the latex system, when coalescence is involved, results in the displacement of about 50% of the emulsifier originally covering the coalesced particles.

(5) Development of an equilibrium technique, which involves the use of the ultracentrifuge and the dispersion of the latex particles in sucrose solution, for the determination of the minimum pressure required for the initiation of particle coalescence.

(6) It has been proved that equilibrium is reached within a very short centrifugation time. The study of this equilibrium is in contrast to the study of rate of coalescence of oil emulsions during

centrifugation in Vold's work[1].

(7) It has been proved that the minimum pressures required for coalescence measured by the ultracentrifugation technique are two orders of magnitude lower than those previously suggested[2].

(8) It has been proved that coalescence of the latex particles occurs if the applied centrifugal force exceeds a certain minimum.

(9) It has been demonstrated that the minimum pressure required for initiation of particle coalescence provides a measure of the force barrier in the force-interparticle distance curve, which corresponds to the maximum slope of the potential energy curve, and so, is related to latex stability.

(10) The pH sensitivity of latex stability has been shown to be controlled by the changes in the ratio of the ionized to the non-ionized emulsifier content of the system. The sensitivity of the latex stability to CO_2 absorption is explained on this basis.

(11) It has been shown that the ion-exchanged "clean" latex has a very low barrier for the initiation of coalescence and this is independent of the pH value.

(12) Increasing the surface coverage of the latex particles with ionized emulsifier molecules has been shown to result in increasing the stability of the latex system.

(13) Increasing the electrolyte concentration of the latex system, at a given stabilizer coverage of the particles, has been shown to increase the force required for coalescence at low electrolyte concentrations. This trend is reversed at higher concentrations and the

required force decreases with electrolyte concentrations.

(14) It has been demonstrated that the stability data of the ultracentrifugation technique correlate qualitatively with the DLVO theory, and that the stability of this specific latex system is dominated by electrostatic factors.

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SUGGESTIONS FOR FURTHER WORK

The ultracentrifugation technique has been successfully used to determine the force required to initiate coalescence of latex particles under equilibrium conditions. This force correlates qualitatively with the force barrier in the force-interparticle separation curves for latex systems in which the stability is dominated by electrostatic factors.

The significance of the minimum force as a stability measurement suggests its application to variables other than those studied here. These include the effect of multivalent cations, temperature, non ionic, cationic and anionic stabilizers, polymeric stabilizers, built-in stabilizers (carboxylated latexes etc.), copolymer composition and particle size.

The reasons for the lack of quantitative agreement between the repulsive forces calculated from DLVO theory with the experiments should be examined further. The geometry of interaction, the surface migration of stabilizer during particle approach, the definition and application of the DLVO theory to the surface layer structure of soap stabilized colloids, and the concept and role of ζ-potential, all require further examination.

The demonstration that an equilibrium force balance is realizable and can be defined, suggests that alternative techniques for the force measurement should be sought, that would be more convenient and informative than the measurement based on centrifugation. Methods based on hydrodynamic or electrical forces are possibilities.