THE PREPARATION AND CHARACTERIZATION OF SYNTHETIC LATEXES

by

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ABSTRACT

Several methods of preparing emulsifier-free homopolymer and copolymer latexes have been adapted or developed with the object of producing model colloids with controllable sizes and surface charges. Novel preparations of copolymer latexes with predictable sizes and charge densities were introduced. The diafiltration technique was introduced to clean the latexes with the advantages of efficiency and ease over conventional dialysis or ion exchange. Basic studies of the use of conductometric titrations to characterize the latexes have been made and the applicability of the technique was reconsidered by taking into account the presence of the electrical double layer, ion distribution between surface and bulk, and dissociation of surface groups. Consistent and practical extrapolation methods were developed for the forward and back titrations of latexes to determine stoichiometric amounts of surface charges. The conductometric method developed was applied to study the distribution of various impurities in latexes and criteria were set for latex cleanness with different methods of cleaning. Oscillometric titrations of latex were also used with excellent agreement with the conductometric technique. Electrophoresis studies have shown the presence and desorption of charged oligomers from the surface of emulsifier-free homopolymer latex with dilution or washing. The effect of the presence of these oligomers on the properties of the latexes was examined and found to limit the use of these latexes as model colloids. Comparative electrophoresis measurements of various latexes have shown results that are interpreted in terms of the structure of the latex surface layer. Emulsifier-free copolymer latexes produced in a methanol-water medium are monodisperse and appear to have stable predictable colloidal properties.

RESUME

Plusieurs méthodes de préparation sans l'emploi d'émulsifiant de latex d'homopolymères et de copolymères ont été adaptées ou dévelopées en vue d'obtenir des colloides modèles dont la taille et les charges de surface soient contrôllables.

Nous avons introduit des méthodes originales de préparations de latex de copolymères dont on peut prévoir la taille et la densité de charge.

Nous avons purifié les latex par diafiltration, une technique plus efficace et d'un emploi plus aisé que les techniques conventionnelles telles que la dialyse et l'échange d'ions. L'utilisation des titrations conductimétriques pour la charactérisation des latex a été étudiée sur le plan fondamental et les possibilités d'application de cette technique ont été reconsidérées en tenant compte de la présence de la double couche (électrique), de la distribution d'ions entre la surface et la coeur de phase et de la dissociation des groupes de surface. Nous avons développé des méthodes d'extrapolation cohérentes et d'un emploi commode pour les titrations directes et inverses des latex afin de déterminer les charges stoechiométriques de surface. La méthode conductimétrique que nous avons développée a été appliquée à l'étude de la distribution de diverses impuretés dans les latex; des critères de pureté avec différentes méthodes de nettoyage ont été établis. Nous avons également effectué des titrations oscillométriques des latex: elles sont en excellent accord avec les résultats obtenus par conductimétrie. Des études d'électrophorèse ont montré la présence d'oligomères chargés et leur désorption de la surface de latex d'homopolymères sans émulsifiant lors de la dilution ou du lavage. Nous avons étudié l'influence de la présence de ces oligomères sur les propriétés des latex et nous avons trouvé qu'ils limitent l'emploi de ces latex comme des colloides modèles. Des mesures comparatives de divers latex par électrophorèse ont conduit à des résultats qui ont été interprétés en termes de la structure de la couche de surface du latex. Enfin,des latex de copolymères sans émulsifiant produits dans un système eau-méthanol sont monodispersés; leurs propriétés colloidales sont stables et prévisibles.

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FOREWORD

The study of latexes has been undertaken for several reasons. Latexes can provide the basis for model experiments in colloid chemistry since the shape and size of the particles and their interaction can be controlled. Thus problems of the stability and rheology of suspensions can be studied and the interactions of particles with each other or with surfaces can be investigated. More practically, latexes are often used in papermaking as wet-end additives, saturants, adhesives, coating binders or pigments. The use of latexes, whether in applied or theoretical studies, requires methods of preparation and characterization. This thesis includes several basic and applied aspects of the preparation, purification, and characterization of polymer latexes.

The thesis is divided into eight, more or less independent chapters and is presented as follows:

Chapter I, the general introduction, includes a review of the various applications of latexes, their preparation, purification, the methods used for their characterization, and their utilization as model colloids.

Chapter II deals with the preparation of emulsifier-free homopolymer and copolymer latexes. The control of the surface charge and the size of latexes at high volume fractions are presented.

Chapter III* describes the use of diafiltration in the purification of synthetic latexes in place of conventional methods such as dialysis and ion exchange. The kinetics of cleaning and equilibration are shown as well as the application of the diafiltration technique in latex studies.

Chapter IV** is a study of the conductometric titration of latexes. It examines the latex system on the basis of the theories of conductance of electrolytes and of the model suspension of spheres. A practical and consistant procedure for the determination of the stoichiometric amounts of strong- and weak-acid surface groups based on accounting for the distribution of ions between the surface and the bulk and the dissociation of surface groups is shown.

Chapter V shows how different contaminants affect the conductometric titration curves of latexes. The results are based on the use of model systems in which known contaminants are added to the latex and on the examination of 'as polymerized' latexes during cleaning. Criteria for cleanness are established and proper methods of cleaning are indicated.

Chapter VI presents the successful use of oscillometry in latex titrations. The oscillometric titrations of model acid mixtures and of latexes are compared with conductometric titrations. The results are discussed on the basis of the systems studied and the techniques used.

Chapter VII is an electrophoresis study of the behaviour of emulsifier-free latexes when they are subjected to dilution or continuous diafiltration procedures. The effects of the presence of charged oligomers with emulsifier-free latexes on their use as model colloids are investigated and discussed.

Chapter VIII is related to Chapter VII but deals with the electrokinetic properties of emulsifier-free latexes as a function of electrolyte concentration. The effect of the structure of the surface layer of latexes on their electrokinetic properties is discussed with regard to their use as model colloids.

* Chapter II has been published in J. Colloid Interface Sci. 67, 543 (1978).

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NOMENCLATURE

a = Radius of particles, m.

C = Concentration of solute in the diafiltration chamber and filtrate.

C_o = Initial concentration of a solute in the diafiltration chamber.

C_1 = Initial concentration of inlet feed in diafiltration cleaning or equilibration.

C_p = Total capacitance of oscillometry cell and contents.

C_g = Capacitance of empty cell.

C_s = Capacitance of solution.

c = Electrolyte concentration (mole/l).

D = Particle diameter (nm).

equiv. = Equivalent.

e = Electronic charge (1.602×10^{-19} Coulomb).

F = Formation factor; for sphere $F = \frac{2+\phi}{2+2\phi}$, where ϕ is particle volume fraction.

f = Frequency (Hz, i.e., cycle/second).

I = Ionic strength.

K = Boltzmann Constant (1.3805×10^{-23} JK^{-1}).

K_o = Serum conductance (S cm^{-1}).

K_1 = Latex conductance (S cm^{-1}).

K_{sp} = Specific conductance (S cm^{-1}).

K_{11} = Rate constant of the reaction of M_1 with radical ending with $M_1^{\cdot}$.

K_{12} = Rate constant of the reaction of M_1 with radical ending with $M_2^{\cdot}$.

K_{22} = Rate constant of the reaction of M_2 with radical ending with $M_2^{\cdot}$.

K_{21} = Rate constant of the reaction of M_2 with radical ending with $M_1^{\cdot}$.

l = Litre.

M = Monomer.

(M) = Monomer concentration (mole/l).

ml = Milliliter.

mS = Millisiemens.

meq = Milliequivalent.

N = Number of nuclei.

N_A = Avogadro's number (6.0225 x 10^{23} mole^{-1}).

(P) = Initiator concentration (mole/l).

r_1 = Reactivity ratio = (K_{11}/K_{12}).

r_2 = Reactivity ratio = (K_{22}/K_{21}).

SA = Strong acid.

S = Siemens (ohm^{-1})

S_s = Specific surface area (cm^2/cm^3).

T = Absolute temperature (°K).

u = Electrophoretic mobility (cm^2 V^{-1} s^{-1}).

u_t = True mobility (u) deduced from $u_{1/6}$ and $u_{1/2}$.

$u_{1/6}$ = Mobility measured at 1/6 cell depth.

$u_{1/2}$ = Mobility measured at 1/2 cell depth.

V = Volume of the sample in the diafiltration cell.

WA = Weak acid.

z = Valence of counter-ion.

α = Degree of dissociation of weak acid.

ε = Permittivity of the dispersion medium: the product of the dielectric constant of water and the permittivity of a vacuum (8.85×10^{-12} Kg^{-1} m^{-3} s^{4} A^{2}).

ζ = Zeta potential (mV).

κ = Inverse of diffuse layer thickness (m^{-1}).

λ_s = Specific surface conductance (S^{-1} = ohm^{-1}).

λ = Wave length (nm).

μ = Micron (10^{-4} cm).

μm = Micrometer (10^{-6} meter).

μC = Microcoulomb ($10^{-6}C$).

ν = Volume of filtration or feed.

σ_o = Surface charge density ($\mu C/cm^2$).

ϕ = Particle volume fraction.

ψ = Potential at distance (x) from the surface ($\psi = \psi_o$ at the surface).

ψ_o = Surface potential (mV).

CHAPTER I

GENERAL INTRODUCTION

INTRODUCTION

Latexes are defined for the purposes of this thesis as stable dispersions of polymer particles in water--specifically the suspensions obtained by emulsion polymerization or similar processes. The term 'latex' is widely applied to a variety of synthetic products of commercial importance , and its original use to designate natural products of various plants has been largely subordinated, at least by polymer chemists.

The production of polymers in the form of latexes is one of the main processes in polymer technology for the latexes can be prepared from many monomers and comonomers producing polymers of different mechanical properties and different size and size distribution characteristics. Many polymers are produced on an industrial scale in the form of latexes; these include polystyrene, styrene-butadiene copolymers, butadiene-acrylonitrile rubbers, neoprene, polyvinyl chloride, and acrylic polymers.

The preparation of polymers by emulsion polymerization has several advantages over the other three basic polymerization methods, ie., bulk, suspension and solution polymerization. These advantages are:

(a) It is superior to bulk polymerization in that heat transfer presents no difficulty during the polymerization.

(b) Unlike suspension polymerization, there are no coalescence complications in the emulsion technique; this makes the latter suitable for the preparation of stickly, rubbery polymers.

(c) Among the free radical polymerization techniques, emulsion polymerization is characterized by very high rates because the polymerization is activated in a very large number of separate loci at the same time.

(d) There is no need for toxic solvents in emulsion polymerization.

The main disadvantage of emulsion polymerization is the surface contamination by ions, emulsifiers, and oligomers or polyelectrolytes that are produced in situ. These contaminants adversely affect many of the physical properties of the polymer. Another disadvantage is the very high molecular weight produced in some cases, but this can be controlled by using chain transfer agents (modifiers).

The high fluidity and ease of mixing, stirring, and transporting are properties of latexes that can be used to advantage whether the latex is to be used as such or is to be converted to bulk polymer. Solid polymer may be obtained by coagulating and separating the latex or by spray drying for subsequent molding or extrusion.

In addition to their use in the production of solid polymers, latexes have many industrial applications. They are used to produce continuous coatings of different characteristics (e.g., latex-based paints and textile coatings). In the paper industry, latexes are utilized in at least four processes: (a) adding the latex to pulp stock before papermaking; (b) saturating dried paper by introducing latex into the fibre structure by impregnation; (c) coating the paper surface by using the latex as a pigment binder and (d) using latex-based adhesives in gluing. The utilization of latex in the above processes results in improvements in the mechanical properties of paper, its appearance, and printability.

Latex compounds are used as a binder for nonwoven fabrics; the function of the polymer is to bond together a loose web to produce a coherent whole. Another important use of polymer latexes is in carpet backing.

Monodisperse latexes, particularly polystyrene, have been found suitable as model colloids and are extensively used in various fields of science and medicine. The major uses of monodisperse latexes are in the calibration of instruments (e.g., electron microscopes, light scattering equipment, and particle counting devices such as the Coulter-counter), and in research. Latex fixation tests for pregnancy and rheumatoid arthritis are available today.

Latexes provide suitable model systems for testing many current theories in colloid and surface science; they can be prepared as monodisperse spherical particles whose size and surface charges can be varied and characterized.

There can be no doubt that synthetic polymer latexes have many important uses and applications in various industries and in the physical and medical sciences. Most of these applications are based on the surface properties of the latexes. The study of the preparation, purification, and surface characterization of latexes and their use as model colloids is of considerable importance and is well justified.

LATEX PREPARATION

Emulsion polymerization in the presence of emulsifiers is the conventional process used to prepare latexes for industrial applications and for scientific purposes. The preparation of latexes in the absence of emulsifiers is also known and is used mainly for scientific investigations. In order to overcome complications in latex applications due to the presence of emulsifiers, interest in emulsifier-free latexes from the industrial point of view has increased in recent times.

Although only emulsifier-free latexes were used in this study, a summary of the emulsion polymerization mechanism conventionally used is given here as an historical background and as a basis for the study of emulsifier-free polymerization.

Conventional Emulsion Polymerization (Emulsifier Present)

In these systems, a surfactant is used to emulsify the sparingly soluble monomer and is added in excess so that surfactant micelles are also present. Monomer and emulsifier are both present in the dispersed droplets, in the micelles, and in the solution; most of the monomer is in the droplets and most of the emulsifier in the micelles.

Harkins (1) and Smith and Ewart (2) have discussed such systems, and the mechanism and kinetics have been worked out. Experimental results are frequently in accord with the above theories, particularly for systems based on styrene polymerization.

In the styrene system, it is assumed that persulfate decomposes in the aqueous phase according to:

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

The sulfate ion-radical produced reacts with monomer in the aqueous phase [eqs. (2) - (4)];

$$SO_4^{-}\cdot + M \longrightarrow \cdot MSO_4^{-} \qquad (2)$$

$$\cdot MSO_4^{-} + M \longrightarrow \cdot MMSO_4^{-} \qquad (3)$$

$$\cdot MMSO_4^{-} + M \longrightarrow \cdot MMMSO_4^{-} \qquad (4)$$

As these reactions proceed, the hydrophobic character of the oligomeric ion radical increases until it confers surface active properties. Free radical oligomers of this type can enter (by adsorption) monomer-swollen micelles, and once in the micelles, they continue to grow until another radical enters and causes termination, mainly by combination, i.e.:

$$\cdot M(M)_n SO_4^- + \cdot M(M)_m SO_4^- \longrightarrow SO_4^- (M)_{n+m+2} SO_4^- \qquad (5)$$

According to this mechanism, the monomer-swollen micelles are transformed into monomer-swollen polymer particles of much greater size. As the monomer is consumed in the polymer particles, a supply is maintained by diffusion of the monomer from the droplets through the aqueous phase.

Particle initiation continues until all the micelles have disappeared either by capturing radicals and becoming polymer particles, or by disbanding to supply neighboring micelles, which have captured radicals, with emulsifier. According to (1,2), the disappearance of the micelles separates the initiation stage from the particle growth stage; in the latter, a constant number of particles continues to grow until the supply of monomer or radicals is exhausted.

All particles formed in the above manner should be stable if there is sufficient emulsifier in the system to stabilize them during the growth stage. The number of particles formed, therefore, depends on the concentration and nature of the surfactant.

It should be mentioned that other mechanisms for particle formation in emulsion polymerization in the presence of emulsifiers have also been suggested. Roe (3) assumes that particles are formed outside surfactant micelles and that particle formation stops when the surface of particles has grown to such a size that the emulsifier concentration in the aqueous phase is below the critical micelle concentration (CMC). As shown by Roe (3), this assumption leads to the same expression for particle number as the one obtained from the Smith-Ewart theory (2).

The number of growing particles and the amount of monomer available for growth determine the final particle size. The ratio of the time needed for initiation and for growth determines the monodispersity of the latex; the shorter the time needed for producing a constant number of polymeric growing particles and the longer the time for their growth, the better the monodispersity (4). Thus the nature and concentration of the emulsifier used, the monomer and initiator concentrations, and the polymerization conditions control the size and size distribution of the produced latexes.

Emulsifier-free Polymerization

Although the Smith-Ewart theory gives a fairly good prediction of particle number for sparingly soluble monomers (e.g., styrene), it does not explain the preparation of latexes in the absence of emulsifiers (5-7). Priest (8) and Fitch et al (9) have proposed a mechanism which implies that nuclei are formed in the aqueous phase by precipitation of oligomeric radicals above a critical length. Nucleation in the aqueous phase seems to be a plausible mechanism for emulsifier-free polymerization of monomers even though they may be only sparingly soluble at the polymerization temperature.

It is assumed that, in the emulsifier-free polymerization of styrene, oligomeric-free radicals are formed in the aqueous phase in a manner similar to that given by Eqs. (1-4). Several mechanisms of nucleation have been proposed (6,10):

(a) The growing free radicals in solution become insoluble and precipitate on themselves.

(b) The growing free radicals achieve a critical chain length and concentration at which they become surface active and undergo micellation.

(c) The growing free radicals undergo termination followed by nucleation by coagulation of the terminated species.

It is unlikely that any one of these mechanisms alone would describe particle nucleation for all monomers since the solubility and the hydrophobicity of the monomer would be expected to have profound effects on the initial processes occurring in the solution (5,6,10).

By one or more of the above mechanisms, nucleation will occur in the aqueous phase. The result is the formation of a large number of nuclei (N/cm^3). The rate of nuclei formation depends on the rate of initiation, i.e., oligomer formation.

According to Goodwin et al (6), the nuclei formed are immediately able to absorb monomer and swell. They are, however, unstable in the colloidal sense since they are stabilized by a small number of endgroups of the oligomers forming them. As a result, these nuclei coagulate under the ionic strength conditions of the medium to an extent and at a rate which can be predicted by the kinetics of coagulation processes (6,11). It is predicted that rapid coagulation occurs until the new particles formed by aggregation of nuclei acquire a radius and a surface charge density large enough to prevent further coagulation.

The particle number is shown schematically in Fig. 1 as a function of polymerization time. Up to the maximum, the number of particles is due to two opposing processes, that is, nucleation and coagulation. The number of particles increases until the rate of nucleation equals that of coagulation (the maximum in Fig. 1). Past the maximum, the particle number decreases by coagulation until the particles acquire considerable stability;

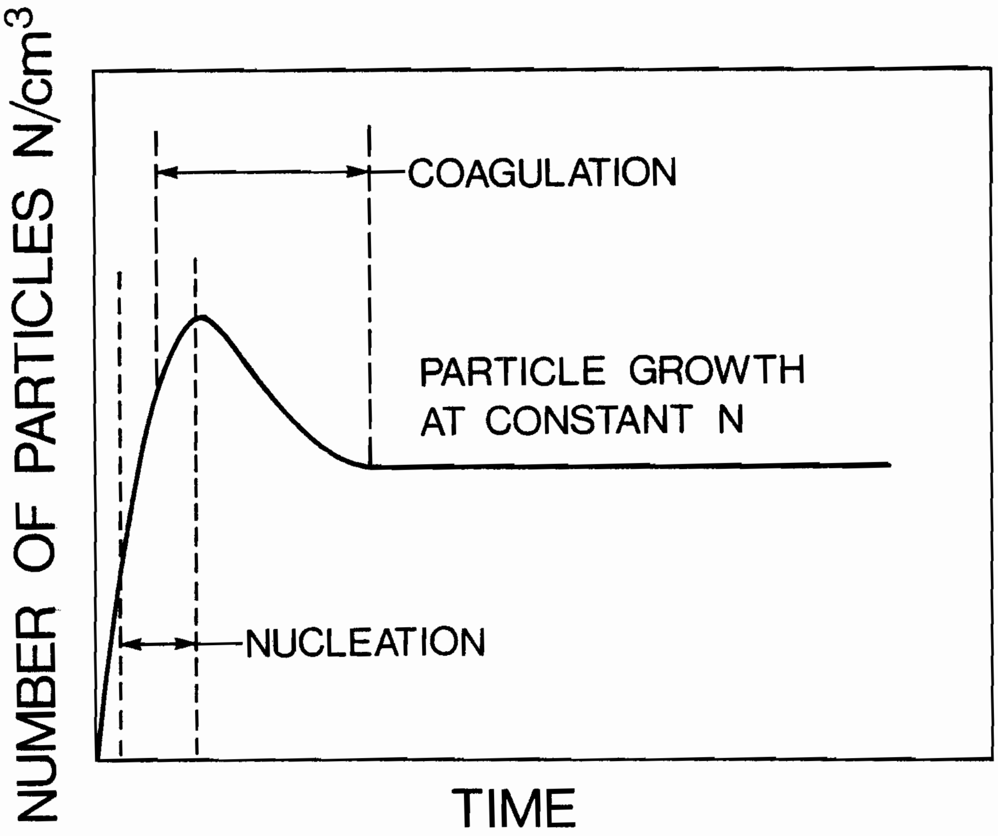

Figure 1: Schematic diagram showing the variation in the total number of particles per unit volume as a function of time during emulsifier-free polymerization (after Ref. (6)).

the particle number thereafter becomes constant. The particles then swell with monomer and grow by capturing radicals until the monomer or radicals are exhausted.

Several experimental results obtained with emulsifier-free systems are clearly understood on the basis of the above mechanism. Examples of such results are:

(a) Increasing the ionic strength decreases the colloidal stability of the particles. Coagulation, therefore, leads to fewer colloidally-stable growing particles, and hence to final large particle sizes (6).

(b) Increasing the initiator concentration at a constant ionic strength leads to the formation of a larger number of oligomers and to supersaturation at lower degrees of polymerization, thus forming a large number of nuclei. The final number of growing particles will therefore be large, and the final particle size small.

(c) Increasing the temperature increases the solubility of the monomer and the decomposition rate of the initiator; this results in a final small particle size (6,7). Another adverse effect of temperature is the decrease in the colloidal stability of particles, but the first two effects predominate over the last.

(d) Changing the solvent affects the solubility of the monomers and oligomers as well as the colloidal stability of the system. Increasing the solubility of the monomers affects the nucleation stage and the rate of reaction (12). Decreasing the dielectric constant affects the coagulation stage and hence the final particle size (12).

(e) Utilizing functional comonomers in emulsifier-free systems results in stabilization of the nuclei. Coagulation, therefore, decreases, resulting in a final decrease in the particle size (13).

In emulsifier-free systems, it has been found that the low solubility of monomers limits the preparation of latexes to small volume fractions (5-7). Homola et al (12) have demonstrated that the addition of methanol to increase the solubility of monomer (styrene) allows the preparation of latexes in the absence of emulsifiers at volume fractions as high as 40%. The preparation of latexes at high volume fractions has also been possible in the copolymerization of styrene and functional comonomers (13).

Emulsion Copolymerization

Emulsion copolymerization is used to prepare several important polymers such as styrene-butadiene, styrene-acrylonitrile, and carboxylated latexes. This technique provides ways to prepare latexes with a wide range of mechanical properties (e.g., the styrene-butadiene system of different monomer ratios (14,15)) and latexes with different colloidal properties (e.g., the styrene-itaconic acid system (15,16)). In the case of water-insoluble pairs, such as styrene and butadiene or styrene and acrylonitrile, the composition of the copolymer formed in the emulsion system is almost the same as that produced by bulk polymerization (14). This is because the entire propagation reaction occurs in the monomer-swollen polymer particles which can absorb the two comonomers. The composition of the copolymer formed, as compared to the monomer mixture from which it is derived, depends on the "monomer reactivity ratios" (15), i.e., $r_1 = K_{11}/K_{12}$ and $r_2 = K_{22}/K_{21}$ where K's are the rate constants for the reaction of monomers M_1 or M_2 with the polymer radical which has end derived from 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 or the other monomer unit. When $r_1 = r_2^{-1} = 1$, the polymerization is considered to be "ideal copolymerization" where the copolymer formed from any mixture of two monomers at any instance during polymerization has the same composition as the monomer feed. An example close to "ideal polymerization" is provided by the styrene-butadiene monomer pair with $r_1r_2 = 1.08$ (14). The polymer produced here is a random copolymer with a final composition close to that of the monomer feed.

When one of the monomers is highly water soluble (e.g., itaconic acid) and the other is only slightly soluble (e.g., styrene), the composition of the polymer produced by emulsion polymerization is different from that produced by homogeneous polymerization. In this system, most of the itaconic acid is dissolved in the aqueous phase and the 'oil' phase is almost pure styrene. Correspondingly, the monomer dissolved in the polymer particle is almost pure styrene and the observed reactivity ratios are markedly different in emulsion and in homogeneous polymerization (15,16).

The copolymerization of styrene and strong-acid functional comonomers (styrene p-sulfonic acid) is also known and has been used to introduce sulfonate groups onto the surface of latexes (13). Juang and Krieger (13) have assumed that such polymerization starts in the aqueous phase with water soluble monomer (styrene sulfonate) and that this monomer is depleted initially. The distribution of the functional groups in the polymerization products has not however been studied.

The use of functional comonomers in emulsion polymerization is found in many applications. For example, carboxylated latexes prepared with itaconic acid comonomer are known to have considerable mechanical stability and are preferred binding agents in paper coatings (17). In the case of copolymerization with functional comonomers, no emulsifier is required since the functional groups of the particles and polyelectrolytes produced during polymerization act as stabilizers.

The following points summarize the experiences reported with model emulsifier-free latexes:

(a) the control of particle size is achievable for conventional latexes (19),

(b) the control of the surface charge remains difficult especially for persulfate initiated systems (6,18),

(c) the copolymerization mechanism is not yet well understood (13), and

(d) the effect of the solubility of the monomer(s) on the mechanism of particle formation is not established (12).

LATEX CHARACTERIZATION

Latex Purification

The use of latexes as model colloids requires a well-characterized, clean surface (20). In order to achieve this, all the impurities must be removed and all the functional surface groups should be in the acid or basic form. The 'as polymerized' latex contains unreacted monomer, initiator decomposition products, emulsifiers, oligomers and polyelectrolytes produced in situ (21), and electrolytes (6,7) or non-electrolytes (22) added to the polymerization recipe.

Unreacted volatile components, such as styrene or methanol (12), are removed by flash evaporation or by steam distillation under vacuum. Soluble impurities are conventionally removed by dialysis (23) or by ion exchange (20).

Dialysis cleaning is based on the concentration difference of impurities between the two sides of the membrane; diffusion is the only driving force in dialysis. Although dialysis is still used extensively in latex purification, it has the following limitations:

(a) the pores can be blocked by impurities (24),

(b) the transport can be changed or limited by modification of pore properties due to adsorption of some components (24),

(c) the membrane material may change chemically or biologically, desorb, and re-adsorb on the latex resulting in its contamination (25),

(d) the pore size in the conventional dialysis membrane is small and may not allow the passage of high molecular weight impurities,

(e) the dialysis procedure is long and requires effort.

Ion exchange is used for latex purification from ionic impurities and ionic emulsifiers (20). The process is based on the abstraction of low molecular weight ionic components by a mixed-bed, ion-exchange resin. Although ion exchange can achieve lower conductivities of latexes, in most cases it has the following limitations:

(a) the removal of high molecular weight components is uncertain,

(b) ion exchange does not remove non-ionic impurities,

(c) the ion-exchange resin may contaminate the latex (26),

(d) the resin does not remove difficultly desorbed species.

The lattice and the type of ion-exchange resin determine the performance of ion-exchange cleaning (18). In order to eliminate the possibility of latex contamination from the resin, van den Hul and Vanderhoff (27) employed a procedure for resin purification from leachable polyelectrolytes and gave some criteria for its cleanness.

A dispute exists as to the proper method of cleaning. Several investigators (6,18,25) have prepared latexes with similar recipes, have obtained fairly good agreement with regard to particle size, but have failed to get reliable results regarding surface charge. The reason for such discrepancies is attributed to the lack of consistant and reliable methods of cleaning. Thus the following problems are related to the purification of model latexes:

(a) non-ionizable solutes are not removable by ion-exchange resins and are slowly removed by dialysis,

(b) particulate contaminants such as aggregates of oligomers or polyelectrolytes are difficult to remove by conventional procedures, i.e., dialysis or ion exchange.

(c) adsorbed oligomers and difficultly-desorbed material cannot be removed simply and the desorption process may be very slow.

The purification of latexes for use as model colloids thus requires overcoming the above problems by introducing more satisfactory cleaning methods.

Surface Charge Characterization

(A) Origin of Surface Charge

Normally the charge on the latex can be due to either bound or adsorbed functional groups. Bound surface groups are polar groups covalently bonded to the polymer chains forming the latex particles. Adsorbed functional groups are due to the adsorption of functional surfactant or polyelectrolyte molecules. Unlike bound surface groups, adsorbed functional groups are removable by proper cleaning. In conventional polymerization, surfactants sometimes become permanently fixed in the surface and are not removable by conventional cleaning methods (18). For the purposes of this study, we consider only bound functional groups especially those of anionic emulsifier-free latexes initiated with $K_2S_2O_8$.

The surface charges of the cleaned polystyrene latexes used for the purposes of this study are due to functional groups from one or both of the following sources:

(a) endgroups derived from the initiator and/or modifications of such endgroups, and

(b) functional groups provided by a comonomer.

When $K_2S_2O_8$ is used as the initiator, sulfate, hydroxyl, and/or carboxyl groups may appear on the surface depending on the polymerization conditions. Two mechanisms are proposed to explain the reactions leading to the production of hydroxyl and carboxyl groups in the persulfate initiation:

(a) Hydrolysis of the sulfate ion radical to produce hydroxyl radicals (28):

$$\cdot SO_4^- + H_2O \longrightarrow HSO_4^- + \cdot OH \qquad (6)$$

The hydroxyl radicals initiate the polymerization and the resulting surface hydroxyl groups are readily oxidized by persulfate to carboxyl groups.

(b) Hydrolysis of sulfate surface groups, i.e.,

$$R - C - O - SO_3^- + H_2O \longrightarrow R - C - OH + HSO_4^- \qquad (7)$$

This reaction may occur after polymerization upon storage (29). McCarvill et al (30,33) have indicated the possibility of sulfate group hydrolysis upon extensive dialysis and also the possibility of catalyzing such reaction by the resin during ion-exchange cleaning. The resulting surface hydroxyl groups are readily oxidized by persulfate to carboxyl groups. In using latexes as model systems, the production of carboxyl groups is undesirable since they are not dissociated under acid conditions. The hydrolysis of sulfate surface groups creates a problem by decreasing the particle charge upon storage or purification.

Reactions leading to the production of carboxyl groups in persulfate initiated polymerizations are thought to be hampered under alkaline conditions and enhanced under acid conditions (28). Furusawa et al (31) have found that the polymerization of polystyrene with a persulfate initiator in the presence of an alkaline buffer produces latexes with only sulfate groups. However, Stone-Masui and Watillon (19) have reported the presence of carboxyl surface groups in emulsifier-free polystyrene latexes prepared in alkaline buffers. Wu (32) has also indicated that the presence of metal-ion contaminants in the system catalyzes side reactions leading to carboxyl groups and that the results of controlling such reactions depend on the type of buffering system used. The control of such side reactions in persulfate initiation is not completely understood.

Since sulfate groups are not suitable as surface charges for model colloids for the above reasons, several ways are suggested to introduce non-hydrolyzable sulfonate groups instead:

(a) The use of selected redox systems such as persulfate-bisulfite with a trace of heavy metal-ion as the catalyst has been used by McCarvill and Fitch (30) to produce sulfonate surface groups.

(b) Juang and Krieger (13) have used styrene sulfonate as a functional comonomer to introduce sulfonate surface groups. Production of carboxyl endgroups has however been observed and attributed to the reactions resulting from $K_2S_2O_8$ initiation.

(c) It has been suggested that switching to initiators other than persulfate may be beneficial. Details of such trials can be found elsewhere (34). Other routes of introducing surface charges in latexes are also known; these include surface sulfonation (35) and conversion of surface chloride groups to sulfonate by reaction with sulfites (34).

(B) Nature of Surface Groups

It is thought that the surface charges of cleaned homopolymer latexes are the endgroups of the high molecular weight polymer chains forming the latex particle and that these endgroups are located on the surface. However, emulsifier-free latexes have been shown to contain a large amount of extractable oligomers and these latexes may be formed from such oligomers at one stage (21). Goodall et al (36) have found that the presence of these oligomers complicates the characterization of emulsifier-free latexes.

Smitham et al (17) have proposed that steric stabilization effects may be associated with the presence of carboxyl surface groups; these groups may not be located at the interface but attached to polymer chains protruding into the solution. The use of functional comonomers to introduce surface groups may be associated with the formation of polyelectrolytes or polyelectrolyte chain segments on the surface.

The following problems are therefore seen as being related to the nature of the surface charge:

(a) The identity of surface groups and their dissociation properties are often incompletely known.

(b) The groups may be subject to reactions such as hydrolysis or oxidation.

(c) Difficulties are encountered in controlling the type of surface groups produced in persulfate initiated polymerizations with or without functional comonomers.

(d) Unwanted substances (such as oligomers of polyelectrolytes) are produced during the polymerization; these substances are difficult to remove and complicate the behaviour of latexes.

(e) The location, disposition and orientation of surface groups at or near the polymer/water interface are not readily established.

Titration of Surface Functional Groups

The surface charge of cleaned latexes is normally determined by conductometric titration (18,20,38). The conductometric technique is based on the change of the slope of the conductivity curve as an acid is titrated with a standard base. In the titration of free acid mixtures, for example, the slopes of the conductivity curves are the algebraic sum of the equivalent conductances of ions involved in reactions; the extrapolation of such conductivity curves leads to stoichiometric endpoints in most cases. In the titration of latex, however, the picture is different and the titration of surface acid groups is complicated by the existance of double layer and counter-ions, dissociation of surface groups, and distribution of ions between the surface and bulk that affects the conductivity. The endpoints are frequently not sharp and their identification is difficult.

For the determination of the surface charge of latexes, many investigators employ the extrapolation techniques normally used for free acid mixtures,but difficulties have been encountered in the interpretation of the results.

Recent theoretical reviews have appeared on the use of potentiometric and conductometric titrations of strong- and weak-acid latexes to obtain information about the structure of the double layer (39,40). These reviews have considered the distribution of ions in the double layer in both weak- and strong-acid titrations. No specific emphasis has been put on the determination of endpoints by titration.

The amount of weak acid can be determined by employing a back titration of the weak-acid salt with standard strong acid. This procedure has been used by Maron et al (41) to determine the amount of soap in a latex. Hen (42) has used the back titration of weak-acid latex to which an excess of alkali was added.

Electrokinetic Properties

The interpretation of electrophoretic mobility data obtained under different experimental conditions of surface charge and ionic strength is based on theoretical calculations using several assumptions. Among these assumptions are: the location of the charges on the surface, and the formation of a double layer at the interface in an ideal way (43).

Electrophoresis has been used as a technique in latex characterization. Ottewill and Shaw (44) have used this technique to study dissociation characteristics of latex surface groups and to investigate the electrokinetic properties of latexes and the applicability of corrections made for converting mobilities to ζ-potentials (45).

The conversion of electrophoretic mobilities to determine surface potentials or surface charge densities that characterize the latex requires knowledge or assumptions concerning the structure of the surface layer and the charged interface (46). When this departs from ideality, e.g., the presence of a polymeric stabilizer (47,48) or nonlocalization of surface groups, the interpretation becomes more complicated.

The following problems are thus related to latex characterization by available methods:

(a) A suitable conductometric titration procedure has not yet been established.

(b) Interpretation of electrophoretic mobilities of latexes is apt to be uncertain since the structure of the surface layer (identity and location of groups) is different from the model on which calculations are usually based.

REFERENCES

1. Harkins, W.D., J. Am. Chem. Soc. 69, 1428 (1947).
2. Smith, W.V. and Ewart, R.H., J. Chem. Phys. 16, 592 (1948).
3. Roe, C.P., Ind. Eng. Chem. 60, 20 (1968).
4. LaMer, V.K., Ind. Eng. Chem. 44, 1270 (1952).
5. Kotera, K., Furusawa, K. and Takeda, Y., Kolloid Z.u.Z. Polymere 239, 677 (1970).
6. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Brit. Polymer J. 5, 347 (1973).
7. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Colloid Polymer Sci. 252, 464 (1974).
8. Priest, W.J., J. Phys. Chem. 56, 1077 (1952).
9. Fitch, R.M., Prenosil, M.B. and Sprick, K.J., J. Polymer Sci. C27, 95 (1969); Fitch, R.M. and Tsai, C.H., in 'Polymer Colloids' (R.M. Fitch, ed.), Plenum, New York (1971).
10. Munro, D., Goodall, A.R., Wilkinson, M.C., Randle, K. and Hearn, J., J. Colloid Interface Sci. 68, 1 (1979).
11. Ottewill, R.H. and Shaw, J.N., Discuss. Faraday Soc. 42, 154 (1966).
12. Homola, A.M., Inoue, M. and Robertson, A.A., J. Appl. Polymer Sci. 19, 3077 (1975).
13. Juang, M.S. and Krieger, I.M., J. Polymer Sci. 14, 2089 (1976).
14. Mayo, F.R. and Walling, C., Chem. Revs. 46, 191 (1950).
15. Bovey, F.A., Kolthoff, I.M., Medalia, A.I. and Meehan, E.J., 'Emulsion Polymerization', Vol. IX in High Polymer Series, Interscience, New York (1955).

16. Fordyce, R.G. and Ham, G.F., J. Am. Chem. Soc. 69, 695 (1947).

17. Greene, B.W. and Sheetz, D.P., J. Colloid Interface Sci. 32, 96 (1970).

18. Stone-Masui, J. and Watillion, A., J. Colloid Interface Sci. 52, 479 (1975).

19. Bradford, E.B. and Vanderhoff, J.W., J. Appl. Phys. 26, 864 (1955); Vanderhoff, J.W., Bradford, E.B., Trakowski, H.L. and Wilkinson, B.W., J. Polym. Sci. 50, 265 (1961).

20. Vanderhoff, J., van den Hul, H.J., Tausk, R.J.M. and Overbeek, J.Th.G. in 'Clean Surfaces: Their Preparation and Characterization for Interfacial Studies' (G. Goldfinger, ed.), Marcel-Dekker, New York (1970).

21. Goodall, A.R., Wilkinson, M.C. and Hearn, J., J. Polym. Sci. 15, 2193 (1977).

22. Woods, M.E., Dodge, J.S. and Krieger, I.M., J. Paint Technol. 40, 541 (1968).

23. Ottewill, R.H. and Shaw, J.N., Kolloid Z.u.Z. Polymere 215, 161 (1967).

24. Brodnyan, H.A. and Kelley, I.L., J. Colloid Interface Sci. 20, 7 (1965).

25. Yates, D.E., Ottewill, R.H. and Goodwin, J.W., J. Colloid Interface Sci. 62, 356 (1977).

26. Shenkel, J.H. and Kitchner, J.A., Nature 182, 131 (1958).

27. van den Hul, H.J. and Vanderhoff, J.W., J. Colloid Interface Sci. 28, 336 (1968).

28. Kolthoff, I.M. and Miller, I.K., J. Am. Chem. Soc. 73, 3055 (1956).

29. Everett, D.H. and Gültepe, M.E. in 'NATO Advanced Study Institute - Polymer Colloid Reprints', The Norwegian Institute of Technology, Trondheim (1975).

30. McCarvill, W.T. and Fitch, R.M., J. Colloid Interface Sci. 64, 403 (1978).

31. Furusawa, K., Norde, W. and Lyklema, J., Kolloid Z.u.Z. Polymere 250, 908 (1972).

32. Wu, W.D., Ph.D. Thesis, Lehigh University (1977).

33. McCarvill, W.T. and Fitch, R.M., J. Colloid Interface Sci. 67, 204 (1978).

34. Liu, L. and Krieger, I.M. in 'Emulsion Latices and Dispersions' (P. Becher and J. Judenfreund, eds.), Dekker, New York (1978).

35. Chan, F.S. and Goring, D.A.I., Canadian J. Chem. 44, 725 (1966).

36. Goodall, A.R., Hearn, J. and Wilkinson, M.C., J. Polym. Sci. 17, 1091 (1979).

37. Smitham, J.B., Gibson, D.V. and Napper, D.H., J. Colloid Interface Sci. 45, 211 (1973).

38. van den Hul, H.J. and Vanderhoff, J.W., J. Electroanal. Chem. 37, 161 (1972).

39. Davis, J.A., Leckie, J.O., J. Colloid Interface Sci. 65, 331 (1978).

40. Healy, T.W. and White, L.R., Advances in Colloid and Interface Sci. 9, 303 (1978).

41. Maron, S.H., Elder, M.E. and Ulevitch, I.N., J. Colloid Sci. 9, 89 (1954).

42. Hen, J., J. Colloid Interface Sci. 49, 425 (1974).

43. Overbeek, J.Th.G. in 'Colloid Science' (H.R. Kruyt, ed.), Vol. I, Elsevier, Amsterdam (1952).

44. Ottewill, R.H. and Shaw, J.N., Kolloid Z.u.Z. Polymere 218, 34 (1967).

45. Ottewill, R.H. and Shaw, J.N., J. Electroanal. Chem. 37, 133 (1972).

46. Wiersema, P.H., Loeb, A.L. and Overbeek, J.Th.G., J. Colloid Interface Sci. 22, 78 (1966).

47. Brooks, D.E. and Seaman, G.V.F., J. Colloid Interface Sci. 43, 670 (1973).

48. Brooks, D.E., J. Colloid Interface Sci. 43, 687 (1973).

CHAPTER II

PREPARATION OF EMULSIFIER-FREE HOMOPOLYMER AND COPOLYMER LATEXES

ABSTRACT

The preparation of several emulsifier-free homopolymer and copolymer latexes in different ways has been investigated in order to produce model colloids. The sizes of homopolymer latexes prepared with different recipes and under varied conditions agreed well with the results of Goodwin. Novel preparations of copolymer latexes with controllable sizes, amounts and types of surface charges in the presence of methanol have been introduced.

INTRODUCTION

Monodisperse latexes for use as model colloids or dispersions can be synthesized by methods of emulsion polymerization employing specified surfactant systems and carefully controlled conditions (1,2). Such methods were frequently used until it was found that polymer colloids (latexes) could be synthesized by simple emulsifier-free recipes (3-5) to give a high degree of monodispersity without the problems of desorbable emulsifiers.

Emulsifier-free polystyrene latexes have been frequently described. The initiator used is generally a persulfate which results in sulfate groups on the surface of the latex particles which constitute the stabilizing charges. Some of the sulfate groups, however, undergo hydrolysis and oxidation resulting in variable amounts of hydroxyl and carboxyl groups (5,6).

Juang and Krieger (7) have attempted to overcome the problem of hydrolyzable surface groups (sulfate) and variable surface charge by the incorporation of non-hydrolyzable strong-acid groups in the polymer by the use of an ionic comonomer. However, the reported results still show a variable surface charge of sulfonic acid groups from the comonomer and resulting amounts of carboxyl groups from the initiator.

The two emulsifier-free syntheses mentioned above are briefly explored in this paper and are compared with a novel synthesis based upon latex polymerization in a water-methanol medium. The latter syntheses include ionic comonomers to contribute a fixed stabilizing charge.

MATERIALS AND METHODS

Materials

All the distilled water used was distilled three times in all-Pyrex apparatus. The $K_2S_2O_8$ was recrystallized twice from distilled water. Styrene monomer was purified by distillation at 40 to 45°C in an atmosphere of N_2 at a pressure of 5 mm Hg. The distillation was performed shortly before the polymerization.

Functional copolymers were used as supplied. The (NaSS) sodium styrene p-sulfonic acid was obtained from the Fairfield Chemical Co., and the itaconic acid was from the Eastman Kodak Co.

Latex Preparation

(a) Flask Method. A two-litre, three-necked, round-bottomed flask was used in some preparations in the manner described by Goodwin et al (4,5). N_2 bubbling was used for the duration of the experiment. The stirring rate was 350 rpm. The polymerizations were continued for 24 hours in all cases.

(b) Bottle Method. Polymerizations were conducted in narrow-mouthed 250 or 500 ml Pyrex bottles fitted with standard stoppers. The procedure was the same as that of Homola et al (8) who used a tumbling water bath at a speed of 35 rpm. The bottles were charged, freed from oxygen by O_2-free N_2 gas, then sealed in the same way as (8). The polymerization was continued for 24 hours.

Latex Cleaning

Unreacted styrene and methanol were removed from the latexes by repeated flash evaporation under vacuum after diluting the latexes with distilled H_2O. The latexes were then cleaned by the diafiltration procedure with distilled H_2O (9) until equilibrium was reached as judged by conductivity. Prior to conductometric titrations, the latexes were further deionized by ion-exchange resins cleaned according to (10) until a constant conductance was reached.

Latex Characterization

(a) Particle Size Analysis. Particle sizes were determined from shadowgraph (Nikon) examinations of transmission electron micrographs of the latexes. The average particle diameters were based on at least 50 particles.

(b) Conductometric Titrations. Conductometric titrations were performed by using a Radiometer Model CDM3 (Copenhagen) conductivity meter on 100 ml of latex in most cases. Bubbling of N_2 gas was continued during the titrations. All the titrations were conducted at 25°C. Back titrations with HCl were made in most cases.

The surface charge density of latexes was calculated according to the extrapolation method described in (11).

Examples of the conductometric titrations of cleaned latexes prepared in the presence of 30% methanol are shown in Fig. 1.

RESULTS

Homopolymer Emulsifier-Free Latexes

Preparation

Emulsifier-free polystyrene latexes were prepared following the procedures outlined under 'Methods' using $K_2S_2O_8$ as the initiator. Details

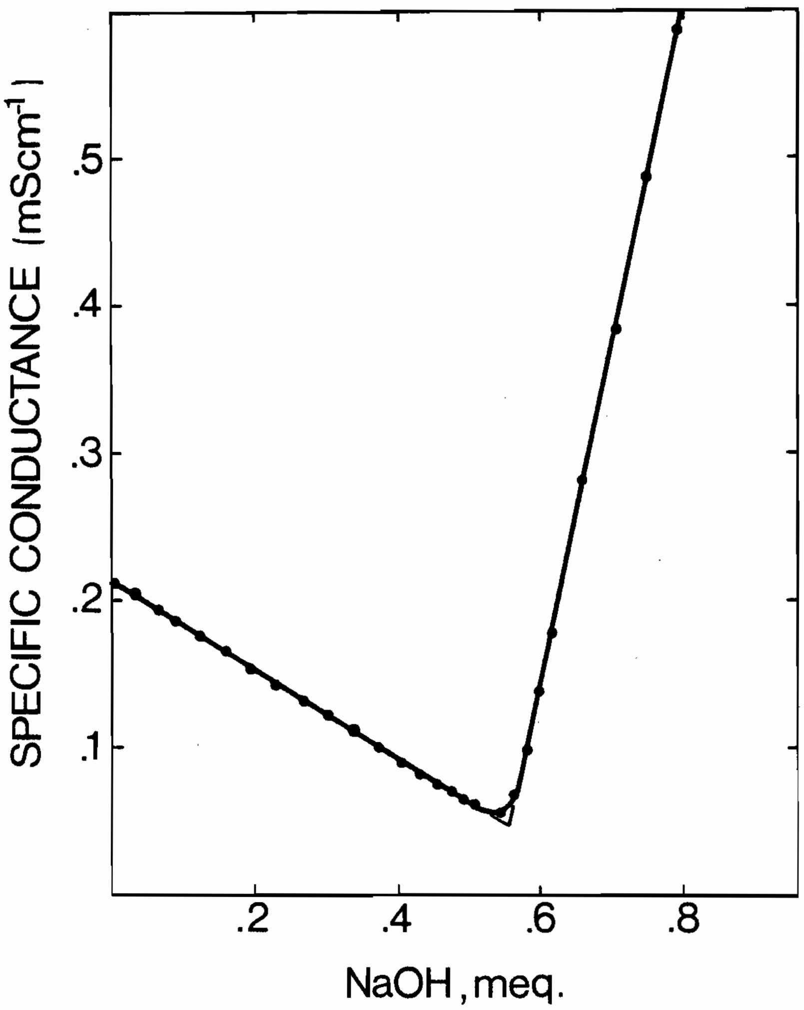

Figure 1a: Example of the titration curve of copolymer latex (LNSS-5) prepared with styrene and NaSS in a mixture of H_2O - CH_3OH.

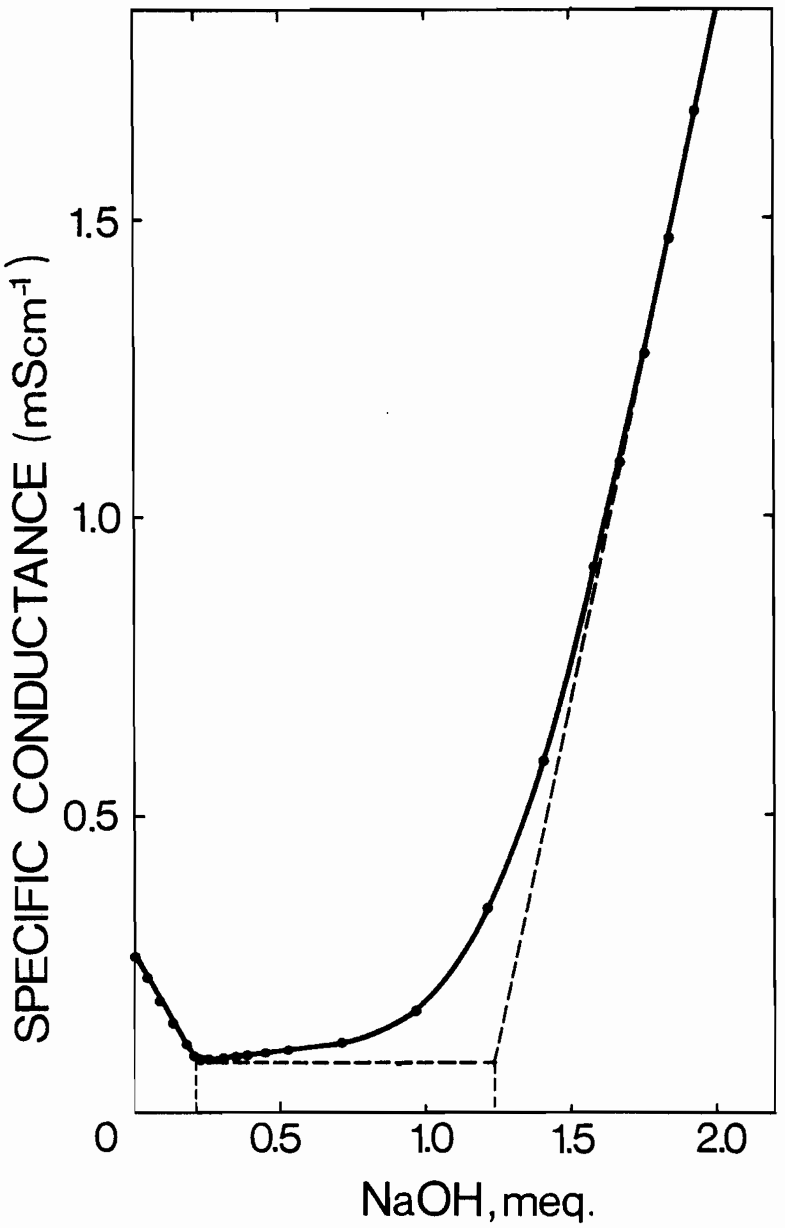

Figure 1b: Example of the titration curve of copolymer latex (LSIT-4) prepared with styrene, NaSS, and itaconic acid in a mixture of H_2O - CH_3OH.

of the recipes, polymerization conditions, particle sizes and surface charges of the latexes obtained are shown in Table I.

Properties

The latexes prepared by this method were all monodisperse. Their size varied with the recipe and polymerization conditions and followed the predictions of Goodwin et al (4,5) that are summarized in the empirical equation:

$$\log D = 0.238 \left[\log \frac{(I)(M)^{1.723}}{(P)} + \frac{4929}{T} \right] - 0.827 , \qquad (1)$$

where D is the particle diameter (nm) and (I), (M), (P) and T are the ionic strength, monomer concentration, initiator concentration and the absolute temperature respectively. The agreement is shown in Fig. 2.

The monodispersity of these latexes and the ready control of particle size suggest the reliability of this procedure when particle size is the main consideration.

The appearance of weak-acid groups (Table I) follows the experience of others who have attributed these to the hydrolysis of the sulfate groups and the oxidation of some of the resulting hydroxyls to carboxyl groups (4,6). The process is inhibited by the presence of an alkaline buffer but is not prevented as Furusawa et al (12) suggest.

While the hydrolyzability of the surface sulfate groups represents a deficiency in these latexes, a more serious drawback is the desorbability of functional groups when the latexes are diluted or thoroughly washed. This behaviour is documented elsewhere (13).

TABLE I

Properties of Homopolymer Emulsifier-free Latexes

Latex Code	Styrene mole/l	$K_2S_2O_8$ mole/l	Temperature °C	Diameter Observed nm	Diameter Predicted (5) nm	Total Charge Density $\mu C/cm^2$	Strong Acid $\mu C/cm^2$	Weak Acid $\mu C/cm^2$	Method
L 11	0.600	0.001	70	362	412	-	-	-	Flask
L 10	0.500	0.001	70	395	382	-	-	-	"
LS 1-2	0.400	0.001	70	340	349	3.90	2.40	1.50	"
L 17	0.871	0.025	70	467	480	-	-	-	"
L 13*	0.871	0.037	70	550	483	4.37	3.40	0.97	Bottle
L 14*	0.871	0.037	70	462	483	3.81	3.26	0.55	"
LM	0.871	0.037	60	650	609	-	-	-	"
LS 3-4	0.400	0.001	60	460	443	3.70	2.40	1.30	Flask
L 6	0.435	0.00062	90	275	234	-	-	-	"

* 2×10^{-4} M K_2HPO_4 was added to the polymerization recipe.

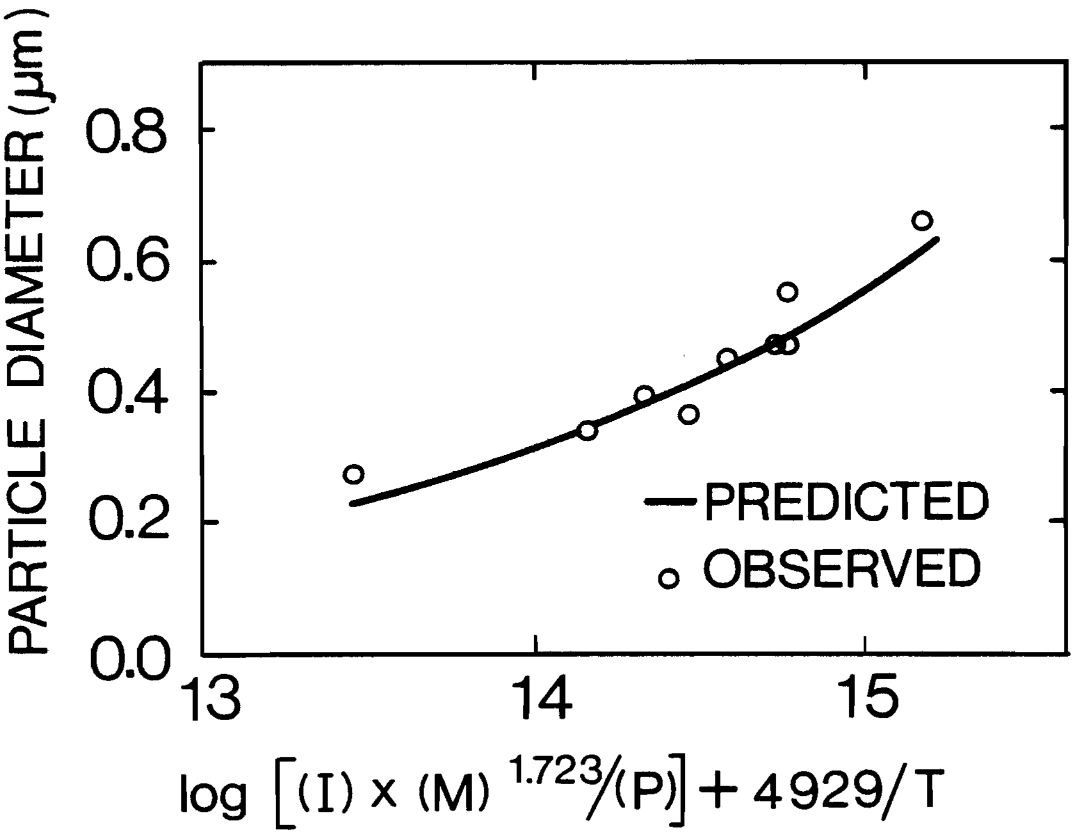

Figure 2: Comparison between the particle sizes of emulsifier-free latexes produced in this work (Table I) and those predicted by Goodwin et al (4,5) according to their empirical equation (1).

Copolymer Emulsifier-Free Latexes

Preparation

These latexes were prepared without an emulsifier using NaSS comonomer and persulfate initiator employing the bottle polymerization method. The recipes, conditions and characteristics of these latexes are summarized in Table II. The copolymerization with itaconic acid is also shown in Table II.

Properties

The introduction of NaSS to emulsifier-free recipes has several effects. The particle size is substantially reduced and is not varied by the range of polymerization conditions employed. The proportion of weak-acid groups has been found to increase in these latexes (Table II).

The continued influence of hydrolyzable groups on the final surface charges suggests that control of surface groups remains a problem with these copolymer latexes and indeed the production of weak-acid groups is unexpectedly high. These results do not appear to be at variance with those of Juang and Krieger (7).

Copolymer Emulsifier-Free Latexes Prepared in a Water-Methanol Medium

Preparation

These latexes were prepared in a mixture of H_2O - CH_3OH (2:1 volume) by bottle polymerization using $K_2S_2O_8$ as the initiator. They were prepared with high solid contents (37%) in one step. NaSS, itaconic acid, or an itaconic acid-NaSS mixture were used as comonomers. All the polymerizations were made at 60°C. Details of these recipes are given in Tables III and IV.

Properties

The investigation of the latexes prepared in the presence of methanol has been restricted to the effect of the amount of comonomer(s) added.

TABLE II

Properties of Copolymer Latexes Prepared Without Methanol
(Styrene = 0.871 mole/l; $K_2S_2O_8 = 3.7 \times 10^{-3}$ mole/l; Temperature = 60°C)

Latex Code	Initial pH	Electrolyte Added, M	Comonomer mole/l	Diameter nm	Total Charge Density $\mu C/cm^2$	Strong Acid $\mu C/cm^2$	Weak Acid $\mu C/cm^2$
LM (Control)	-	-	-	660	-	-	-
L 15	-	-	3.9×10^{-2} NaSS	120	-	-	-
L 18	-	-	1.5×10^{-2} NaSS	118	-	-	-
L 19	7.5	-	"	114	2.85	0.90	1.95
L 20	7.5	4×10^{-3} Na_2SO_3	"	115	-	-	-
L 21	7.5	"	"	115	-	-	-
L 22	7.5	4×10^{-3} $NaHSO_3$	"	113	-	-	-
L 23	7.5	"	"	112	1.95	0.90	1.05
L 36	-	-	7.5×10^{-3} Itaconic Acid	677	-	-	-

TABLE III

Properties of Latexes Prepared with NaSS Comonomer in 30% Methanol
(Styrene = 3.15 mole/l; $K_2S_2O_8$ = 2.1×10^{-2} mole/l; Temperature = 60°C)

Latex Code	NaSS mole/l	Diameter nm	Strong Acid charge density $\mu C/cm^{-2}$
LNSS - 1	8×10^{-3}	441	12.1
LNSS - 2	1.6×10^{-2}	342	13.8
LNSS - 3	3.2×10^{-2}	275	18.2
LNSS - 5	6.4×10^{-2}	237	31.9

TABLE IV

Properties of Latexes Prepared with NaSS
and Itaconic Acid Comonomers in 30% Methanol
(Styrene = 3.15 mole/1; $K_2S_2O_8 = 2.1 \times 10^{-2}$; Temperature = 60°C)

Latex Code	NaSS mole/1	Itaconic Acid mole/1	Diameter nm	Strong Acid $\mu C/cm^2$	Weak Acid $\mu C/cm^2$
LNSS - 3	3.20×10^{-2}	-	275	18.2	-
LSIT - 1	"	5×10^{-3}	315	19.2	6.8
LSIT - 2	"	1.5×10^{-2}	276	15.8	17.0
LSIT - 3	"	2.55×10^{-2}	248	12.9	24.5
LSIT - 4	"	7.5×10^{-2}	255	11.7	57.7
L 28	1.60×10^{-2}	2.55×10^{-2}	286	9.0	24.5
L 40	2.55×10^{-2}	"	285	12.8	26.1
LSIT - 3	3.20×10^{-2}	"	248	12.8	24.5

The particle size is generally reduced by increasing amounts of ionic comonomer as shown for NaSS (Fig. 3), for itaconic acid in the presence of a constant amount of NaSS (Fig. 4), and for itaconic acid (Fig. 5).

The surface charges measured by conductometric titrations failed to show weak acid in the absence of itaconic acid (Fig. 1a and Table III).

The surface charge densities ($\mu C/cm^2$) are plotted in Fig. 3 for strong-acid groups (NaSS added) and in Fig. 4 for weak acid-groups (itaconic acid added in the presence of a constant amount of NaSS).

The amounts of surface charge (moles/mole of styrene) are listed in Table V and the efficiency--the ratio of surface functional groups detected by titration to functional groups added as comonomers--has been calculated. The efficiency drops off gradually for both comonomers with the amount added, but then appears to level off (Figs. 6 and 7). The surface charge densities achieved can be extremely high as the amount of comonomer is increased (Tables III and IV).

It was experimentally determined that extensive continuous diafiltration of cleaned latexes prepared by the above method does not change the electrophoretic mobilities. This result demonstrates that the surface groups are well integrated into the polymer particles and not desorbable by continuous diafiltration or dilution procedures as was the case with homopolymer latexes (13).

DISCUSSION

The preparation of emulsifier-free homopolymer latexes has confirmed the predictability of particle sizes according to the recipes and polymerization

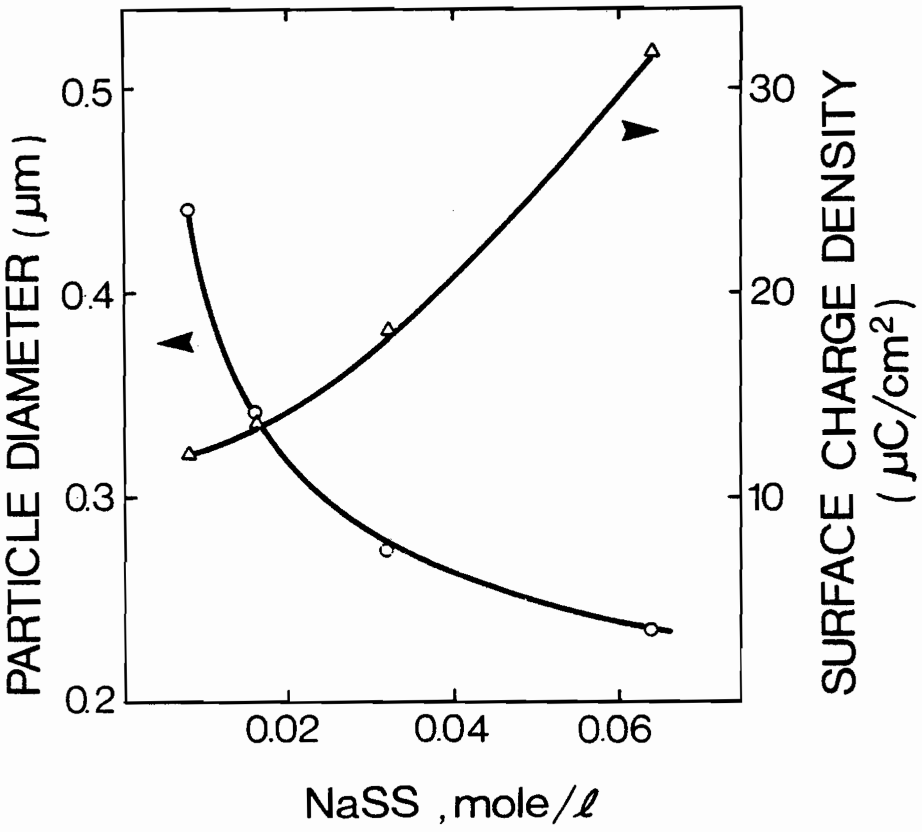

Figure 3: Effect of NaSS concentration on the particle size and the surface charge density of the copolymer latex produced in the H_2O - CH_3OH system.

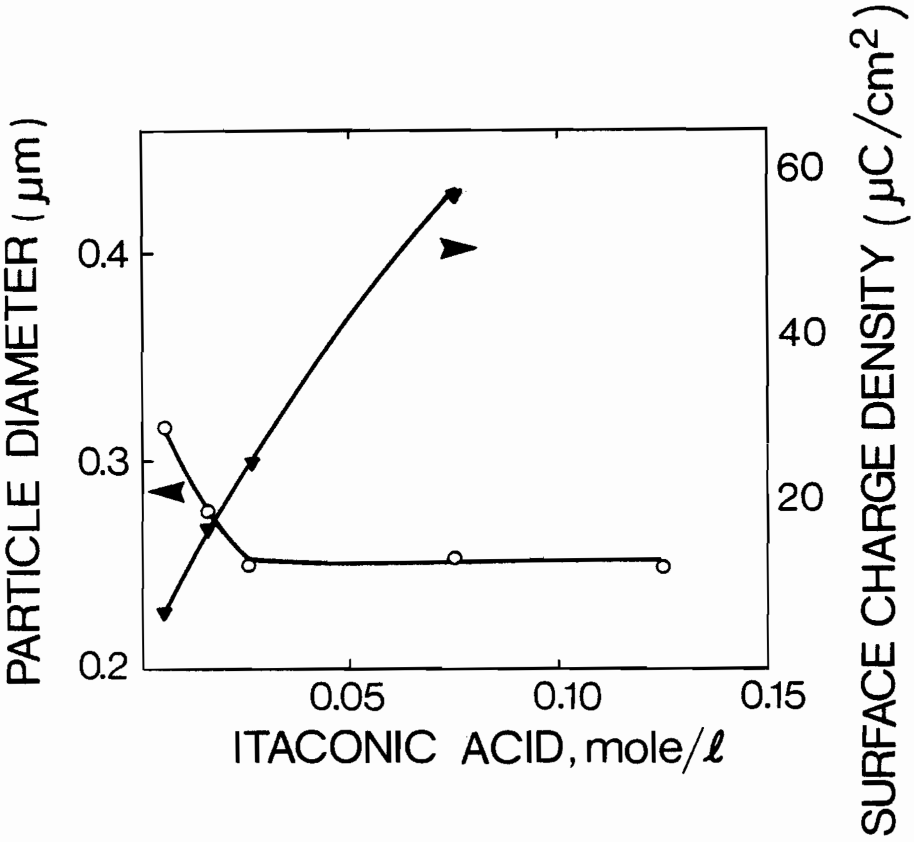

Figure 4: Effect of itaconic acid on the particle size and the weak-acid surface charge densities of latexes prepared in the H_2O - CH_3OH system in the presence of another comonomer (NaSS).

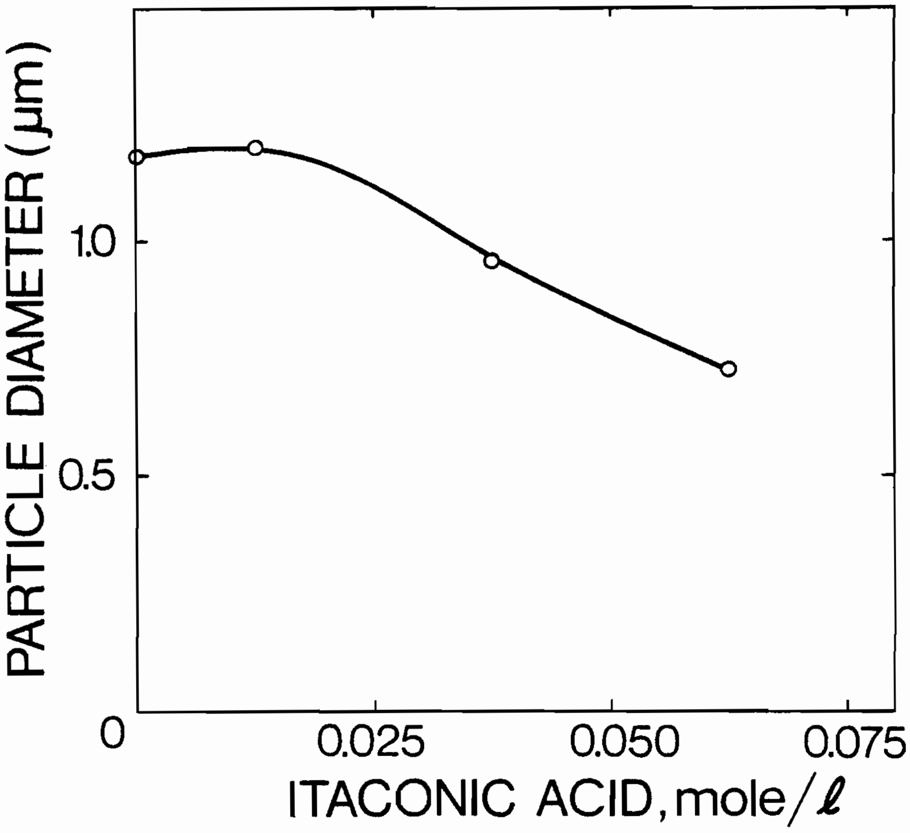

Figure 5: Effect of itaconic acid on the particle size of latexes prepared in the H_2O - CH_3OH system.

TABLE V

Surface Functional Groups in Relation to Amount of Comonomer

($K_2S_2O_8$ = 6.67 x 10^{-3} mole/mole styrene; Temperature = 60°C)

Latex Code	NaSS mole/mole styrene x 10^3	Itaconic Acid equiv./mole styrene x 10^3	Surface Charges mole/mole styrene		Efficiency of Introducing Surface Groups (%)	
			Strong Acid x 10^3	Weak Acid x 10^3	Strong Acid	Weak Acid
L 37 (Blank)	-	-	Nil	Nil	-	-
LNSS - 1	2.54	-	1.69	-	66.4	-
LNSS - 2	5.08	-	2.48	-	49.0	-
LNSS - 3	10.2	-	4.10	-	40.1	-
LNSS - 5	20.1	-	8.30	-	41.1	-
LNSS - 3	10.2	-	4.10	-	40.1	-
LSIT - 1	"	3.2	3.74	1.32	36.8	41.6
LSIT - 2	"	9.5	3.52	3.80	34.6	39.8
LSIT - 3	"	16.2	3.18	6.07	31.4	37.5
LSIT - 4	"	47.6	2.82	13.90	27.8	29.2
L 28	5.08	16.2	1.94	5.40	38.1	33.3
L 40	8.10	"	2.73	5.63	34.0	34.7
LSIT - 3	10.2	"	3.18	6.07	31.4	37.5

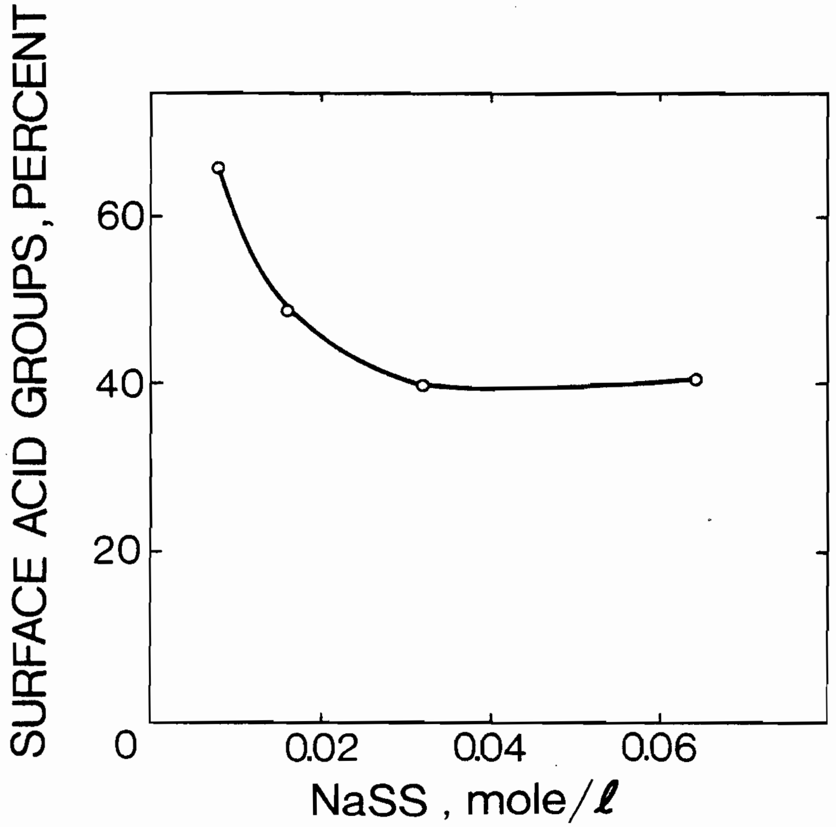

Figure 6: Percentage of sulfonate groups appearing on the surface as a function of the NaSS added to the polymerization media in the H_2O - CH_3OH system.

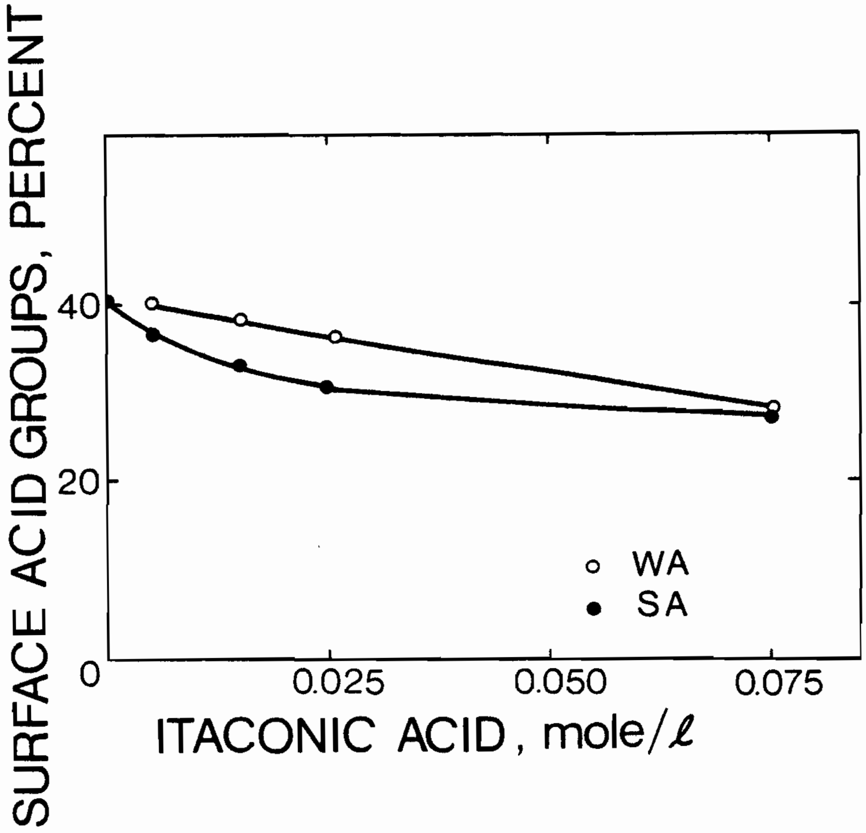

Figure 7: Percentage of weak- and strong-acid groups appearing on the surface of latexes as a function of itaconic acid added to the polymerization media containing a constant amount of NaSS.

conditions (Fig. 2). The presence of variable amounts of weak-acid groups has also been verified and attributed to sulfate group hydrolysis and oxidation (Table I). The latter characteristic renders these latexes unsuitable as model colloids when control of surface charges is required. The incorporation of ionic comonomers in the latex prepared in the aqueous medium does not appear to improve the control of surface charges and the amount of sulfate group hydrolysis appears to be increased (Table II). In the comonomer recipes (Table II), the particle size is substantially reduced. This can be explained by the production of a large number of highly charged stable nuclei which are converted to primary growing particles. The electrostatic stability of such nuclei may be due to the incorporation of the comonomer into the polymer forming the nuclei and to a stabilizing effect introduced by polyelectrolytes which may be produced in situ.

The particle-size decrease observed in preparations with itaconic acid (Table II and Fig. 5) is small or absent and this can be attributed to the lack of weak-acid dissociation during the polymerization.

The presence of 30% methanol appears to alter the process in some fundamental way. It may have several effects:

(a) solubilization of monomers, comonomers, and oligomers;

(b) change in the copolymerization mechanism since the sparingly soluble monomer (styrene) becomes more soluble in the medium;

(c) change in the chain length characteristics of the oligomers formed;

(d) modification of the aggregation of oligomers by affecting their lyophobic-lyophilic characteristics with respect to the bulk medium (8);

(e) effect on the rate of initiation reaction;

(f) possible participation of methanol in the free radical reaction to modify the products;

(g) changes in the dielectric constant, density, surface tension, and viscosity of the bulk medium and the effect of these on diffusion and stability.

Because of some or all of these possible effects, the initiation process may be basically altered and the process of nucleation and particle interaction may be changed. This may explain why (1) these latexes can be prepared at high solid contents, (2) they have no detectable hydrolyzable strong-acid groups, and (3) they demonstrate high efficiency in introducing surface groups from functional comonomers (Table V and Figs. 6 and 7).

The limited experiments do not provide a basis for any description of the changes in the polymerization processes which, in any event, are not well understood even when methanol is not present.

The results obtained provide a basis for the expectation that stable monodisperse latexes having controlled amounts and types of surface charges can be synthesized at high volume fraction and that variation of the polymerization conditions will permit independent control of particle size.

CONCLUDING REMARKS

The particle sizes of emulsifier-free homopolymer latexes prepared under varied conditions agreed with literature values and were in conformity with proposed mechanisms. The control of production of carboxyl groups in the persulfate initiated polymerizations in the aqueous phase was difficult. The copolymerization in the presence of 30% methanol produced monodisperse latexes with controllable amounts and types of surface charges and with high solid contents. No complications from sulfate group hydrolysis during polymerization or from desorption of surface charges upon dilution or washing were observed with these latexes.

REFERENCES

1. Bradford, E.B. and Vanderhoff, J.W., J. Appl. Phys. 26, 864 (1955); Vanderhoff, J.W., Bradford, E.G., Trakowski, H.L. and Wilkinson, B.W., J. Polym. Sci. 50, 265 (1961).
2. Ottewill, R.H. and Shaw, J.N., Kolloid Z.u.Z. Polymere 215, 161 (1967).
3. Kotera, A., Furusawa, K. and Takeda, Y., Kolloid Z.u.Z. Polymere 239, 677 (1970).
4. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Brit. Polymer J. 5, 347 (1973).
5. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Colloid Polymer Sci. 252, 464 (1974).
6. Kolthoff, I.M. and Miller, I.K., J. Am. Chem. Soc. 73, 3055 (1951).
7. Juang, M. S-D. and Krieger, I.M., J. Polymer Sci. (Polymer Chemistry Ed.) 14, 2089 (1976).
8. Homola, A.M., Inoue, M. and Robertson, A.A., J. Appl. Polym. Sci. 19, 3077 (1975).
9. Labib, M.E. and Robertson, A.A., J. Colloid Interface Sci. 67, 543 (1978).
10. van den Hul, H.J. and Vanderhoff, J.W., J. Colloid Interface Sci. 28, 336 (1968).
11. Labib, M.E., This Thesis, Chapter IV.
12. Furusawa, K., Norde, W. and Lyklema, J., Kolloid Z.u.Z. Polymere 250, 908 (1972).
13. Labib, M.E., This Thesis, Chapter VII.

CHAPTER III[*]

APPLICATION OF A DIAFILTRATION TECHNIQUE IN LATEX STUDIES

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ABSTRACT

Diafiltration is presented as an alternative technique to conventional dialysis or ion exchange in cleaning latexes for use as model colloids. Savings of time and effort are combined with the ability to provide equivalent or better removal of impurities. The technique also affords means to equilibrate the latex with a known solution, to concentrate the latex or to fractionate a bimodal latex. Non-integrated surface charges are effectively removed by the diafiltration technique. The rate of solute removal or replacement occurs in conformity with theoretical predictions.

The use of polymer latexes as model colloid systems requires that adequate cleaning methods be available to effect the removal of emulsifiers, electrolytes, and oligomeric materials that remain after latex preparation.

Conventionally, this has been done by dialysis (1), or ion exchange (2), or a combination of the two (3). However, both have been shown to have limitations. On the one hand, dialysis can be ineffective in removing emulsifiers with strong-acid groups (4). The transfer through the membrane may be limited by the size of the impurities either as molecules or aggregates or by their interaction with the membrane (5). On the other hand, the ion-exchange technique fails to remove neutral impurities. Either method can contaminate the latex if the membrane or the resin respectively is improperly or insufficiently cleaned (3, 6).

A cleaning method that avoids some of these disadvantages is provided by diafiltration. The technique can be based on commercial equipment (Amicon TCF10) and the principles of operation may be seen in Fig. 1. In this apparatus a membrane effects the filtration of latex particles by the combined action of pressure and tangential flow over the filter membrane surface. The flow is maintained by continuous recirculation of the suspension by a peristaltic pump through a thin spiral channel above the filter at a rate that prevents both coagulation of the latex and clogging of the membrane.

The apparatus may be used in various modes:

(a) A latex may be concentrated by filtration.

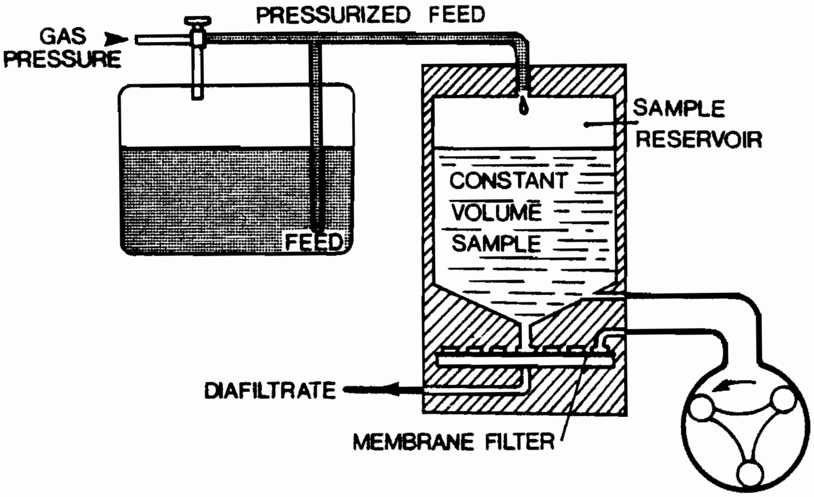


Figure 1: Schematic illustration of fluid flow in the TCF10 diafiltration apparatus.

(b) A latex may be cleaned by introducing distilled water at the rate of filtration while the filtrate purity is being monitored.

(c) A latex may be equilibrated to other solutions or solvents by introducing these to the apparatus at the rate of filtration while the filtrate composition is being monitored.

(d) A bimodal latex may be fractionated by introducing distilled water at the rate of filtration when the smaller latex particles are significantly smaller than the average pore size of the filter.

The apparatus permits the control of several operating variables. The pressure across the membrane and the recirculation rate can be adjusted to provide optimum performance. The membranes may be selected from a range of materials, structures, and pore sizes (Sartorius, Amicon Diaflo, Microporous, etc.) and can be freed of extractives by prior soaking and by prolonged operation of the filter with distilled water.

The operation of the apparatus may be improved by increasing the number of rollers in the peristaltic pump from three to six.

The basic characteristics of the diafiltration process are shown in Figs. 2 and 3. In Fig. 2 the logarithm of the difference between the specific conductance of the filtrate and the feed in a cleaning experiment is shown to decrease linearly with the volume of distilled water washed through the cell. In Fig. 3 a similar asymptotic approach to equilibrium is shown for an equilibration of a latex sample to 7.4×10^{-4}M KCl.

When change of concentration of dissolved species is involved, as in cleaning (Fig. 2) or equilibration (Fig. 3), the efficiency of the

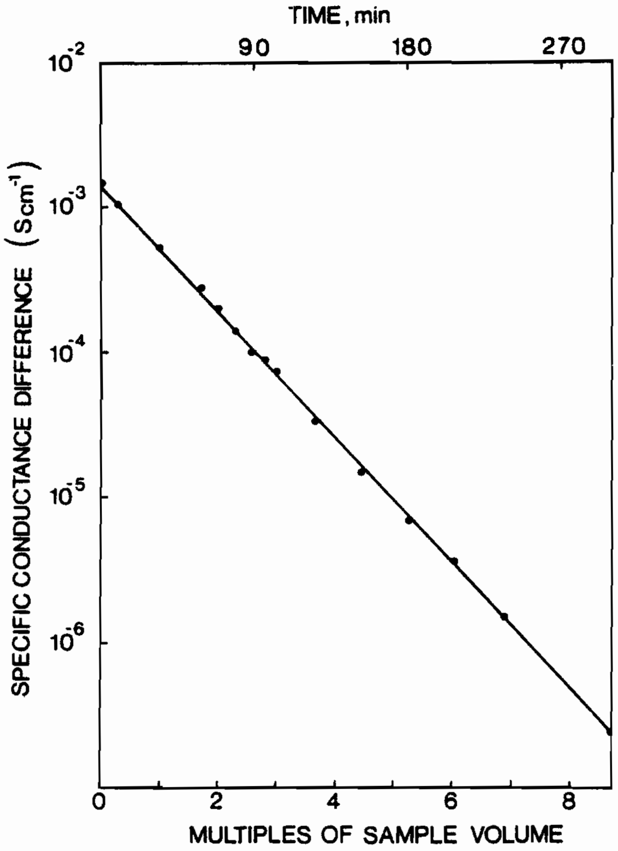


Figure 2: Decrease of specific conductance of filtrate measure as $[K_{sp}(\text{filtrate})-K_{sp}(H_2O)]$ for the constant volume cleaning of latex L25 (10). Sample volume, 0.4ℓ; $K_{sp}(H_2O)$, $2.6 \times 10^{-6} Scm^{-1}$; Sartorius filter, pore diameter 0.2 µm.

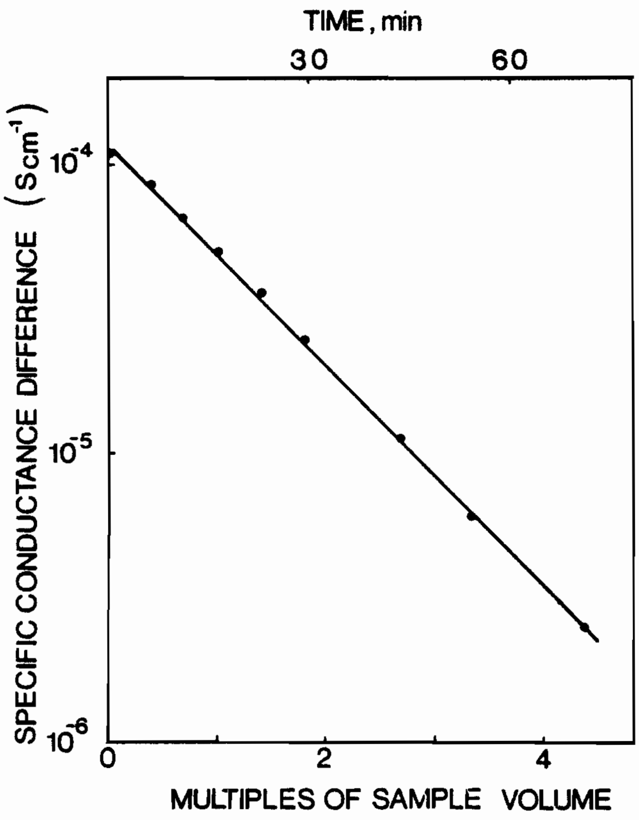


Figure 3: Equilibration of latex with 7.5 x 10^{-4}M KCl as followed by measuring the specific conductance difference $[K_{sp}(\text{electrolyte})-K_{sp}(\text{filtrate})]$. Latex L25 (10).

diafiltration process is close to that of an ideal continuous mixing chamber. Under these conditions,

$$\log \frac{C_1 - C_o}{C_1 - C} = \frac{\nu}{2.3V} \quad ,$$

where C, the concentration of solute in the chamber and the filtrate, has an initial value of C_o, and C_1 is the concentration of the inlet feed. V is the volume of the sample and ν is the volume of the filtrate or feed. A 10-fold reduction of the concentration difference between inlet feed and filtrate should be accomplished by a volume throughput of 2.303 times the volume of latex in the chamber. The plots in Figs. 2 and 3 show factors of 2.4 and 2.7, respectively.

The progress and effectiveness of cleaning may be monitored in several ways:

(a) In the case of latexes that contain small particulate materials, the separation process can be followed by measuring the turbidity of the filtrate or may be revealed directly by electron microscopy. This is illustrated in Figs. 4 and 5 for the separation of gel-like material and small latex particles respectively.

(b) The removal or addition of electrolytes may be monitored by conductance or by using specific ion electrodes to test the filtrate.

(c) Dye interaction can be used to detect the presence in the filtrate of acid groups (7) characteristic of dissolved oligomeric species that may be produced during polymerization.

(d) The presence of cationic or anionic surfactants or oligomeric species in the filtrate can be detected and estimated by their effect on electrophoretic mobility when the filtrate is added to

Figure 4: Electron micrographs showing the removal of gel-like material from an emulsifier-free latex; before cleaning (top) and after cleaning (bottom).

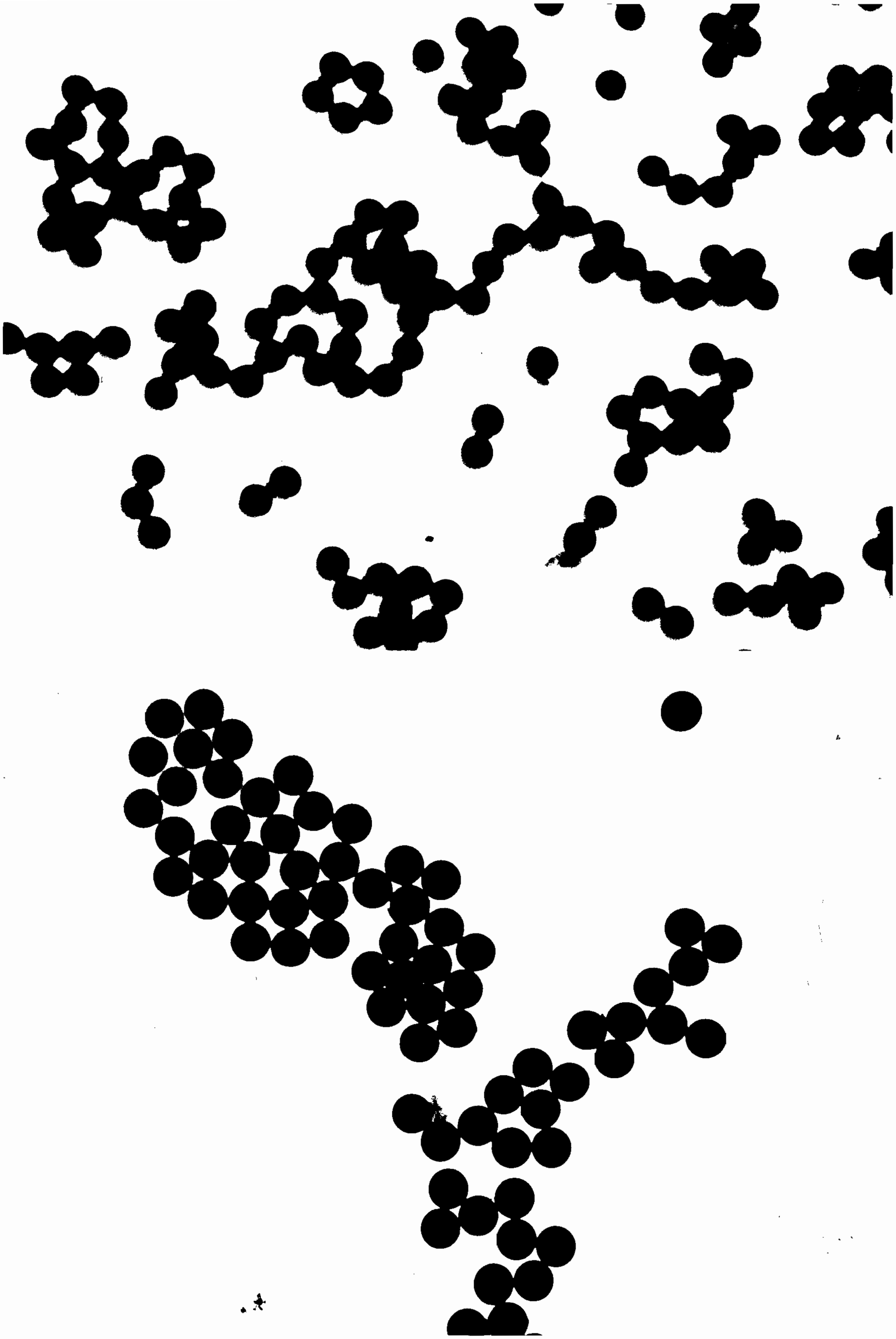
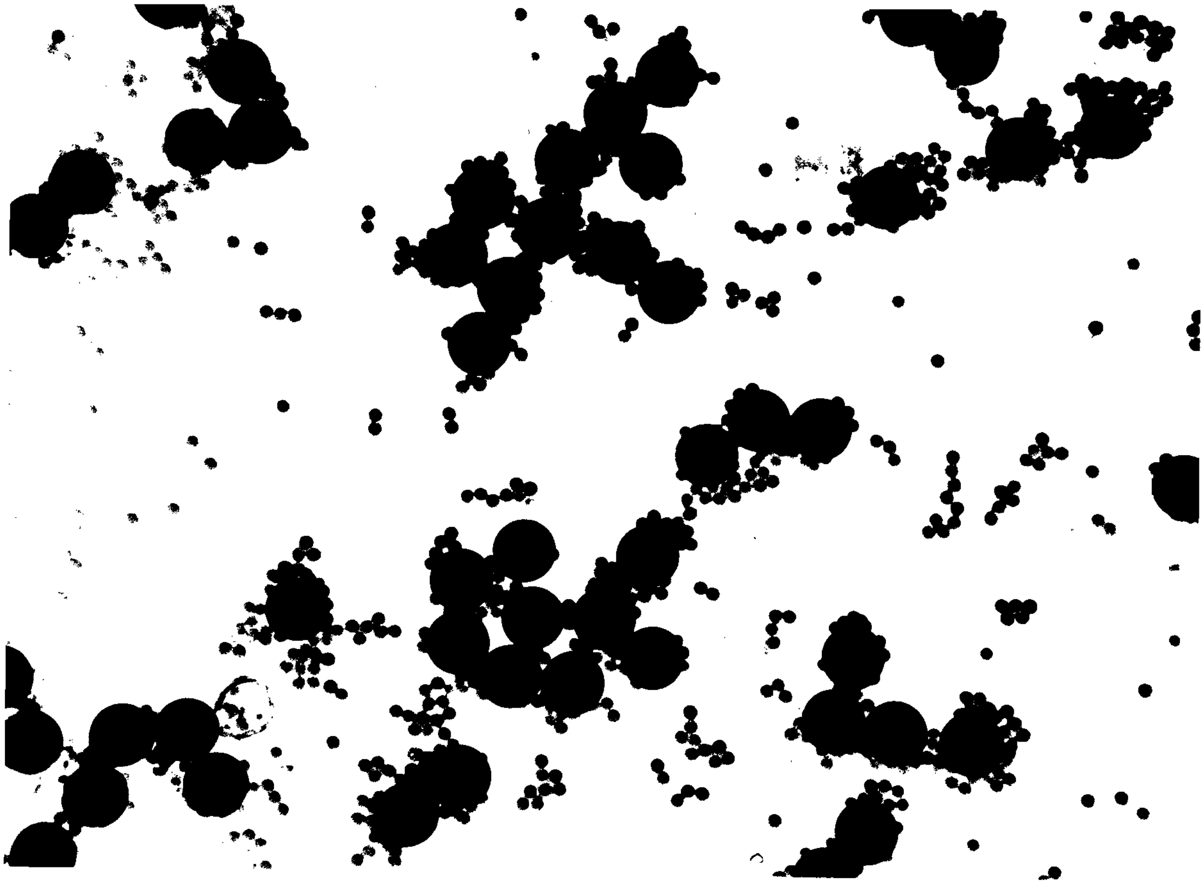
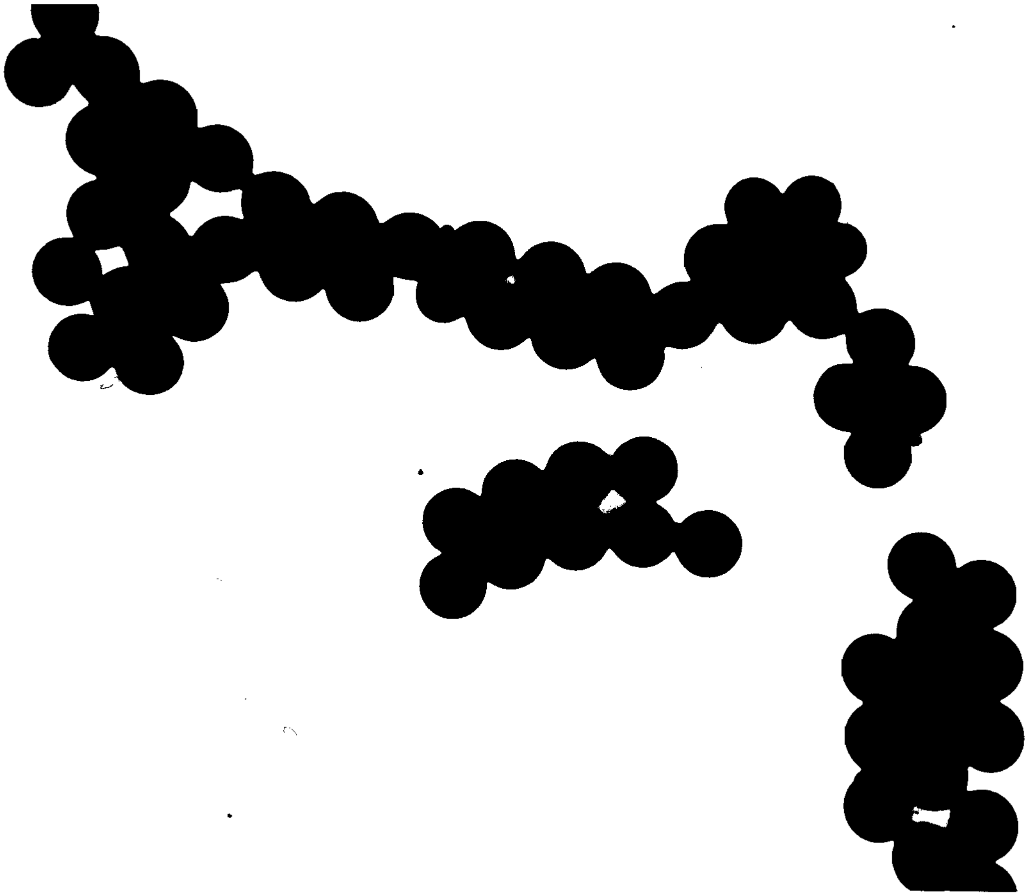


Figure 5: Electron micrographs showing the possibility of separating particulate components of a mixture of latexes (460 nm and 109 nm respectively). The separation shown was effected by the passage of 5 volumes of distilled water and using a Sartorius filter of 200 nm nominal pore size; before (top) and after (bottom).





an oppositely charged latex.

The removal of adsorbed surfactants or oligomeric materials from the surface of the latex particles may be much slower than the removal of dissolved species. In this case,the measurements of the filtrate properties become less sensitive as cleaning proceeds. This desorption may be followed by conductometric titrations of the latex to reveal the functional groups on the surface or by measuring electrophoretic mobilities that reflect the surface charge density.

Thus, conductometric titration has shown that the surface charge densities of an emulsifier-free polystyrene latex cleaned by four alternative methods are equivalent:

(a) prolonged dialysis against distilled water (15 days)-5.14 $\mu C/cm^2$.

(b) dialysis against HCl, then distilled water (30 days)-4.89 $\mu C/cm^2$.

(c) mixed-bed ion exchange (prepared according to Ref.8)-5.25 $\mu C/cm^2$.

(d) diafiltration (6-8 hours)-5.39 $\mu C/cm^2$.

The diafiltration thus effected equivalent cleaning with savings of time and effort.

The further diafiltration of several polystyrene latexes produced by emulsifier-free recipes (9), however, produced further changes revealed by measuring electrophoretic mobilities (Fig. 6). It should be noted that latex L25 (10), prepared with copolymer functionality, did not show this effect. Decreasing mobilities with further washing (distilled water) or by equilibration procedures with KCl solutions suggest a desorption of molecules with functional groups from the surface to an extent not attained with conventional cleaning procedures. Thus, diafiltration offers the possibility for removing non-integrated surface components that are not

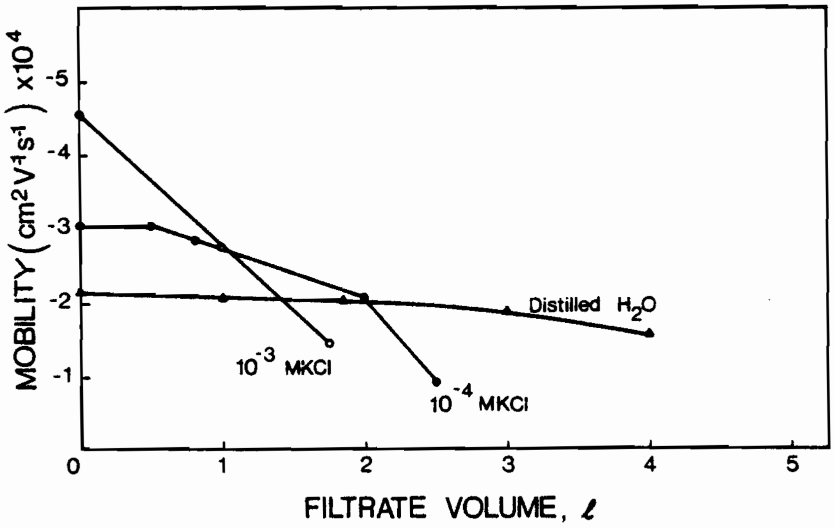


Figure 6: Electrophoretic mobility of an emulsifier-free latex washed in the diafiltration apparatus (constant volume) with electrolyte solutions of different concentrations.

readily removed by conventional techniques, but which could complicate the picture if they are present when such latexes are subjected to dilution or other operations (11).

In summary, it has been found that diafiltration provides a facility for cleaning or equilibrating latexes that is rapid and can be continuously monitored. Further, the cleaning is more complete in that particulate matter can be separated and adsorbed surfactants and other molecular species can be removed. The mode of operation suggests that it would be of particular advantage in removing soluble nonionic or polyelectrolyte contaminants that diffuse slowly and are difficult to remove by dialysis or ion exchange.

REFERENCES

1. Ottewill, R.H. and Shaw, J.N., Kolloid Z.u.Z. Polymere 250, 161 (1967).
2. Vanderhoff, J.W., van den Hul, H.J., Tuask, R.J.M. and Overbeek,J.Th.G. in 'Clean Surfaces', (G. Goldfinger, ed.), Marcel Dekker, New York, (1970).
3. Yates, D.E., Ottewill, R.H. and Goodwin, J.W., J. Colloid Interface Sci. 62, 356 (1977).
4. Brodnyan, H.A. and Kelley, I.L., J. Colloid Sci. 20, 7 (1965).
5. Edelhauser, H.A., Polymer Preprints 7, 843 (1966); Hearn, J., Ottewill, R.H., and Shaw, J.N., Brit. Polymer J. 2, 116 (1970).
6. Shenkel, J.H. and Kitchener, J.A., Nature 182, 131 (1958).
7. Palit, S.R., Anal. Chem. 33, 1441 (1961); Palit, S.R., and Ghosh, P. in 'Microchemical Techniques' (N.D. Cheronis, ed.), p. 663, Interscience, New York (1961).
8. van den Hul, H.J. and Vanderhoff, J.W., J. Colloid Interface Sci. 28, 336 (1968).
9. Furusawa, K., Norde, W. and Lyklema, J., Kolloid Z.u.Z. Polymere 250, 908 (1972).
10. Labib, M.E., This thesis, Chapter II.
11. Labib, M.E., This thesis, Chapter VII.

CHAPTER IV

THE CONDUCTOMETRIC TITRATION OF LATEXES

ABSTRACT

The conductometric titration of latexes as a means for distinguishing and evaluating the various surface groups contributing to electrical stability and electrokinetic properties has been examined in some detail. The extension of the procedure to include back titrations indicates that the conventional identification of weak-acid endpoints is often wrong or misleading. The stoichiometric endpoints are obscured by the changing distribution of ions between bulk and surface during titration by concurrent dissociation and double-layer effects. It is proposed that a practicable identification of the weak-acid endpoint in conductometric titrations is obtained by the extrapolation of the curve for excess alkali back to its intersection with a horizontal line drawn through the strong-acid endpoint conductivity. A similar extrapolation procedure is proposed to determine the stoichiometric endpoints of weak acids from the back titrations.

INTRODUCTION

Polystyrene latexes are potentially model colloids. Emulsifier-free polymerization and copolymerization procedures can produce latexes of different sizes and with different kinds and amounts of functional groups on the surface (1-4). Surface-charge characterization of these systems, however, is required.

Conductometric titration of latexes is considered a basic technique for surface-charge determination (5, 6). Stone-Masui and Watillon (7) have described the conductometric and potentiometric titrations of several polystyrene latexes. Yates (8) and Everett and Gültepe (9) have studied the effect of neutral electrolytes on potentiometric and conductometric titrations of carboxylated and emulsifier-free latexes respectively. Wu (10) has studied the effect of various neutral electrolytes, added to the latex, on the conductometric titrations of strong-acid latexes.

Recently, there have appeared several theoretical and review articles attempting to explain the potentiometric and conductometric titrations of latexes and other colloids (11-13). The authors have considered the nature of the surface and the structure of the double layer.

It is noted in the recorded work that conductometric titrations of latexes are more difficult to interpret than those of free acids. For example, the plots are frequently curved so that conventional extrapolation methods may be inappropriate or impossible.

It is our purpose to examine the conductometric titrations of a number of latexes and to determine how stoichiometric endpoints can be established in an appropriate and reliable manner.

MATERIALS AND METHODS

Latexes

All the latexes used in this study were made by emulsifier-free polymerizations (4). After removing the excess monomer and methanol, the cleaning was achieved by diafiltration (14) followed by ion exchange (15). The removal of monomers, oligomers, polyelectrolytes and neutral electrolytes was monitored by criteria discussed elsewhere (16). The number-average particle diameters of the latexes were determined from the analysis of their transmission electronmicrographs. The characteristics of the latexes used in this study are summarized in Table I.

Titration Procedure

Conductometric titrations were performed on 100-ml samples of cleaned latexes or model mixtures, except for latex LS 1-2 (200 ml), at 25°C. The titrations were done in a stirred vessel with continuous bubbling of N_2 using a conductivity dip-cell and a 'Radiometer' Model CDM3 conductivity meter.

Reagents

All the reagents used in this study were 'analytical grade'. NaOH, $Ba(OH)_2$ and HCl solutions were freshly prepared and standardized a short time before the titrations.

RESULTS

The conductometric titrations of a mixture of strong and weak acids are shown in Fig. 1 . The slopes of the titration curve are compared in Table II with predicted slopes calculated from the algebraic sum of the equivalent conductances of the ions involved in the reactions. The

TABLE I

Latex Data

Latex	Monomers	Temperature °C	Particle Diameter nm	Method of Cleaning
LS 1-2	Styrene	70	342	Ion exchange (15)
L 27	Styrene, Itaconic acid	60	1003	Diafiltration (14) + Ion exchange (15)
L 28	Styrene, Itaconic acid, NaSS *	60	283	Difiltration (14) + Ion exchange (15)

All polymerizations were initiated by $K_2S_2O_8$.

* Styrene p-sulfonic acid sodium salt.

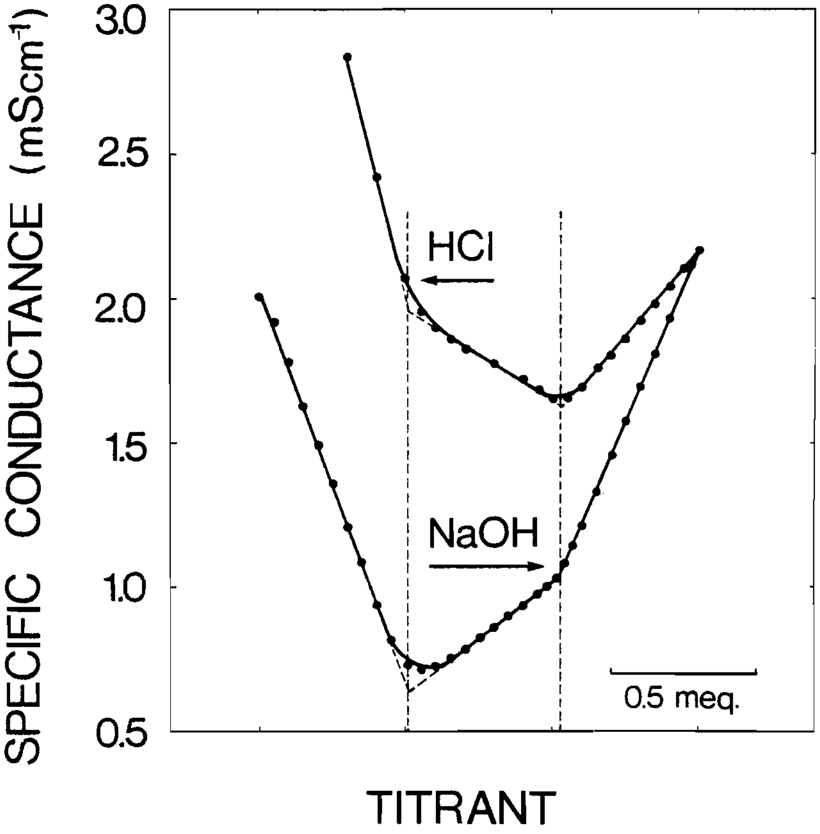


Figure 1. Forward and back conductometric titrations of a 0.5 meq. HCl - 0.5 meq. crotonic acid mixture.

TABLE II

Comparison of the Predicted and Observed Slopes of the Conductometric Titration Plots of HCl-Crotonic Acid* Mixture at 25° C. (Fig.1)

Titration	Slope Code	Ions Involved	Predicted Slope (cm^2 S $equiv.^{-1}$)	Observed Slope (cm^2 S $equiv.^{-1}$)
Against NaOH (Forward)	Strong Acid (SA)	$(-)H^+$, $(+)Na^+$	-295	-282
	Weak Acid $(WA)_f$	$(+)Na^+$, $(+)C_4H_5O_2^-$	+ 83	+ 78
	Excess NaOH	$(+)Na^+$, $(+)OH^-$	+240	+237
Against HCl (Back)	-Excess NaOH	$(-)OH^-$, $(+)Cl^-$	-121	-121
	Weak Acid $(WA)_b$	$(-)C_4H_5O_2^-$, $(+)Cl^-$	+ 44	+ 63
	Excess HCl	$(+)H^+$, $(+)Cl^-$	+416	+418

* Crotonic acid has a dissociation constant $K = 2.03 \times 10^{-5}$ (17) and the crotonate ion ($CH_3-CH = CH - COO^-$) is assumed to have the same equivalent conductance as the butyrate ion, 32.6 cm^2 S $equiv.^{-1}$ (17).

initial, endpoint, and final conductivities obtained during the titrations are compared with predicted values (Table III). The conductivity at each point is calculated from the sum of the products of the concentrations of all ions and their equivalent conductances (17).

The conductometric titrations of cleaned latexes show features different from those of free acids. Figs. 2,3, and 4 show the following titrations:

(a) a high surface charge copolymer latex (L28) with both strong-acid (SA) and weak-acid (WA) functional groups,

(b) WA high surface charge copolymer latex (L27), and

(c) SA-WA homopolymer latex (LS1-2)

respectively. The titrations of latexes compared with those of free acids show the following characteristics: smaller SA slopes, lower initial WA slopes, non-linear WA slopes, and indistinct WA-NaOH endpoints.

The conductometric titrations of latexes can be modified by the addition of neutral electrolytes (KCl) (Fig.5) and strong acids (HCl) (Fig.6). The nature of the base used has been found to affect the features of conductometric titrations of latexes; $Ba(OH)_2$ changed the features of the SA slope significantly (Fig. 7).

The surface conductance (λs) of latexes was obtained from Street's equation (18),

$$K_1 = \frac{K_o}{F} + \frac{\lambda_s S_s}{F} \frac{\phi}{1 - \phi} \qquad (1)$$

where K_1 = latex conductance,

K_o = serum conductance,

F = formation factor; for sphere $F = \frac{2 + \phi}{2 - 2\phi}$

S_s = specific surface area (cm^2/cm^3), and

ϕ = volume fraction of latex.

TABLE III

Comparison of the Observed Conductances with those Calculated from the Concentrations and Equivalent Conductances (17) of the Ions Present

		Conductance	
Point Symbol	Basis of Calculation	Calculated ($mS\ cm^{-1}$)	Observed ($mS\ cm^{-1}$)
Initial Point	$[H^+] = [Cl^-]$	2.075	2.070
SA - WA	$[Na^+] = [Cl^-]$, $[H^+] = [C_4H_5O_2^-]$*	0.745	0.730
WA - NaOH	$[Na^+] = [Cl^-] + [C_4H_5O_2^-]$	1.019	1.020
NaOH - WA	$[Na^+] = [Cl^-] + [C_4H_5O_2^-]$	1.677	1.650
WA - HCl	$[Na^+] = [Cl^-]$, $[H^+] = [C_4H_5O_2^-]$*	1.920	2.030

* Concentrations calculated on the basis of a dissociation constant of crotonic acid of 2.03×10^{-5}. Crotonate ion has an equivalent conductance estimated to be 32.6 cm^2 S $equiv.^{-1}$ (17).

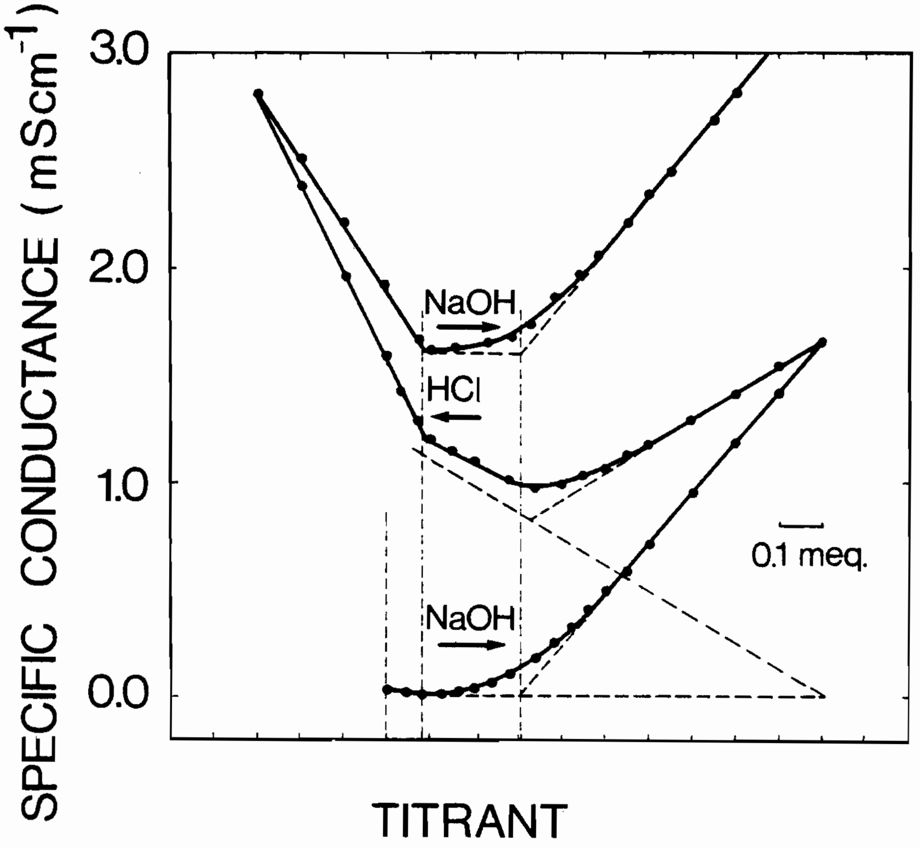


Figure 2. Conductometric titrations of a cleaned SA-WA functional copolymer latex (L28); successive forward and back titrations with NaOH and HCl respectively are shown.

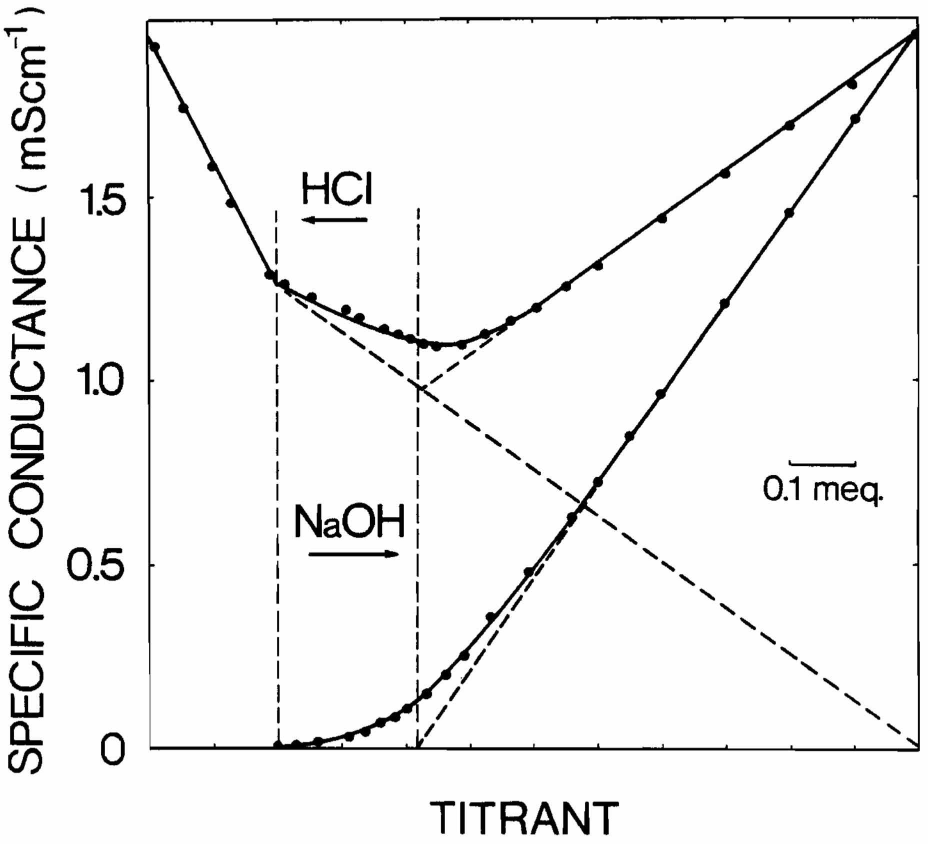


Figure 3. Conductometric titrations of a weak acid functional copolymer latex (L27).

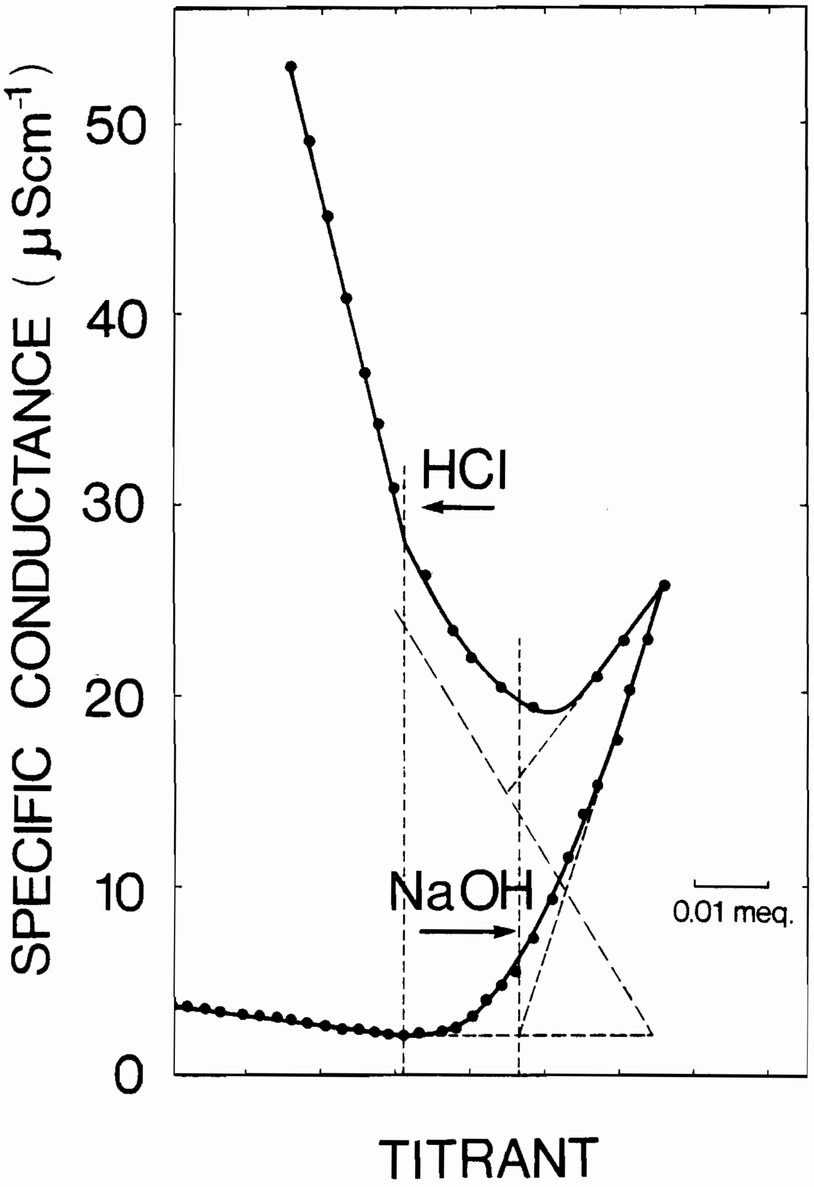


Figure 4. Conductometric titrations of a SA-WA emulsifier-free homopolymer latex (LS 1-2).

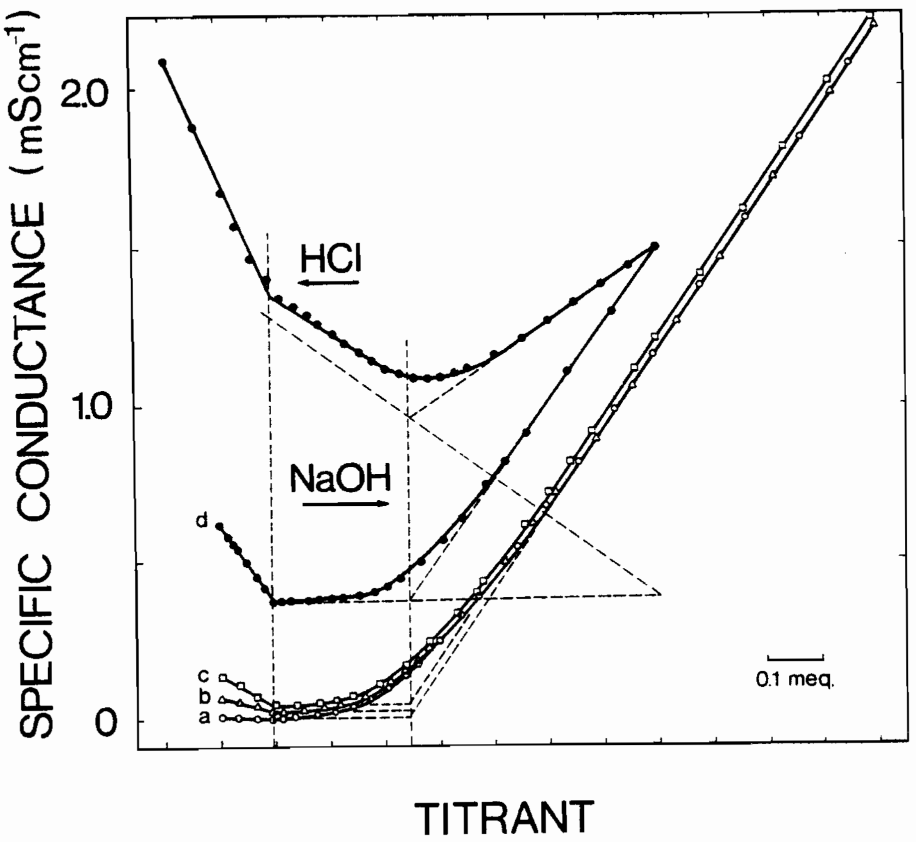


Figure 5. Conductometric titrations of a SA-WA functional copolymer latex (L28) at different KCl concentrations: (a) no electrolyte, (b) 1.50 x 10^{-4}M, (c) 3.00 x 10^{-4}M, and (d) 2.60 x 10^{-3}M.

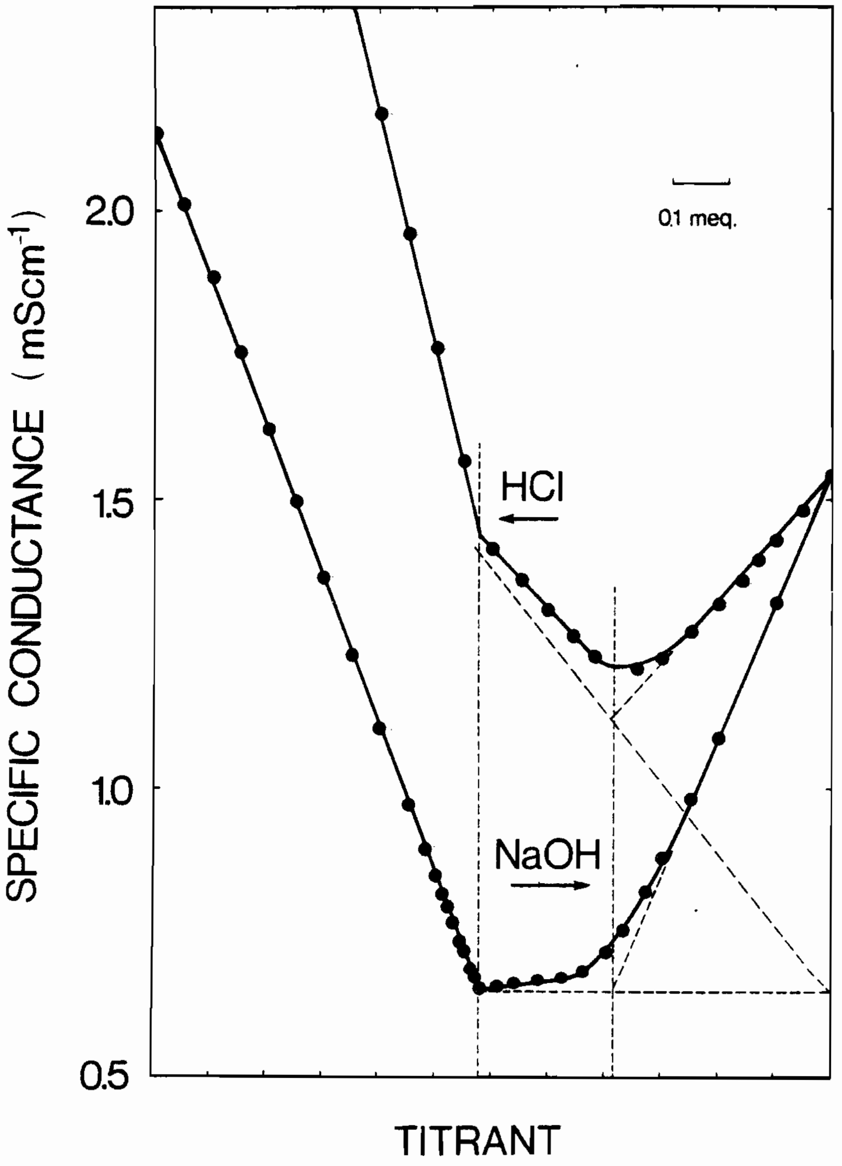


Figure 6. Conductometric titration of a SA-WA functional copolymer latex (L28) with 0.5 meq. HCl added.

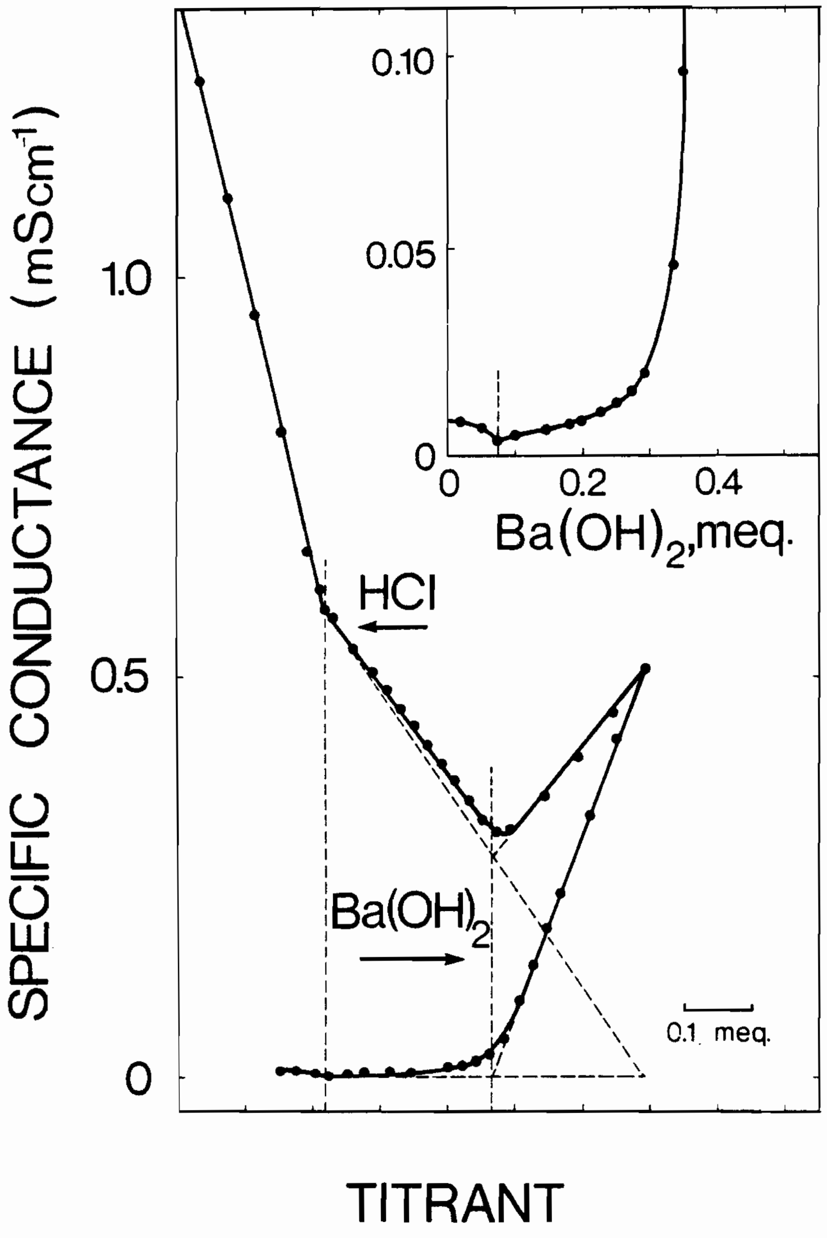


Figure 7. Conductometric titration of a SA-WA functional copolymer latex (L28) and Ba(OH)$_2$; the inset is an enlargement of a part of the forward titration.

The measurement of surface conductance of polystyrene latexes at different ionic strengths has been carried out in this study and elsewhere (19). The data are summarized in Table IV.

DISCUSSION

The differences between the titrations of latexes and of free acids (compare e.g. Fig. 2 or 4 with Fig. 1) are due to the immobility of the functional groups on the surface of the latex particles and to the reduced mobility of counter-ions in the double layer. A comparison between the slopes of conductometric titrations of free acids and of latexes is shown in Table V.

The slopes corresponding to excess reagent in the latex titrations are the same as those for the free acids. It is, however, apparent that the stoichiometric determination of strong-acid (SA) and weak-acid (WA) groups on the latex is different from that of free acids. In the case of free acids, the extrapolation of the titration branches gives the expected endpoints. The SA and WA titrations of latexes are discussed separately.

Strong Acid Titrations

(a) The following features of SA titrations have been observed: very small SA slopes in the absence of electrolytes (Figs. 2 and 4),

(b) increase of SA slopes with electrolyte concentration (Fig. 5),

(c) increase of SA slopes with the addition of free strong acid (HCl) prior to the titrations (Fig. 6),

(d) the SA slopes become non-linear when the titration is performed with $Ba(OH)_2$ (Fig. 7), and

TABLE IV

The contribution of surface conductance, as expressed by $\frac{\lambda_s S_s}{F} \frac{\phi}{1 - \phi}$ eq. (1), to the latex conductance at different pHs and ionic strengths assuming a latex of 0.28 μm particle diameter (L28) and a volume fraction of 0.04.

KCl Concentration	K_o (mS cm^{-1})	pH	λ_s (S) x 10^9	$\frac{\lambda_s S_s}{F} \frac{\phi}{1 - \phi}$ (mS cm^{-1})	Latex	Reference
5×10^{-5}	0.0075	6.0	1.09	0.0086	WA	(19)
5×10^{-4}	0.0149	6.0	0.86	0.0071	WA	(19)
2×10^{-4}	0.0298	6.0	0.89	0.0070	WA	(19)
2×10^{-4} ($HClO_4$)	0.0410	4.0	1.07	0.0085	WA	(19)
2×10^{-4} (NaOH)	0.025	10.0	0.93	0.0073	WA	(19)
2×10^{-4}	0.0149	6.0	2.38x	0.0183	SA	(19)
9×10^{-4}	0.1332	4.4	0.81	0.0063	SA-WA	This study
9×10^{-3}	0.1470	5.9	1.28	0.0100	SA-WA	This study
9×10^{-2}	1.4127	5.0	6.9	0.054	SA-WA	This study

TABLE V

Comparison of the Slopes of Titration Plots from Latexes and Free Acids (Figs. 1 & 2)

Titration	Slope	Latex (cm^2 S $equiv.^{-1}$)	Free Acid Mixture (cm^2 S $equiv.^{-1}$)
Forward (vs. NaOH)	SA	-9	-282
	$(WA)_f$	Non-linear	+ 78
	Excess NaOH	+243	+237
Back (vs. HCl)	-Excess NaOH	-119	-121
	$(WA)_b$	Non-linear	+ 63
	Excess HCl	+410	+418

(e) SA is not indicated by a separate slope when back titrated with HCl (Figs. 2,4,5, 6 and 7).

In order to explain the above features, we have assumed that the cleaned latexes are in the acid form i.e., the only cations present are protons and these exist as counter-ions to the surface acid groups. According to these assumptions, the observed initial conductance is ascribed to surface conductance and the slope that is obtained by titration is due to the effect on surface conductance of the replacement of H^+ by Na^+ as the counter-ion in the surface layer. It is noted that the initial conductances measured (Figs. 2 and 4) are of the order of independently measured surface conductances at low electrolyte concentrations (~ 0.01 mS cm^{-1}) (Table IV).

With the addition of neutral electrolyte (KCl) to a cleaned latex in its acid form, the K^+ and Cl^- ions distribute themselves between the surface and the bulk. If we assume a diffuse layer only, this distribution can be explained by Boltzmann's law, i.e.

$$[H^+] = [H^+]_b \; e^{\frac{-e\psi}{KT}} \qquad (2)$$

$$[K^+] = [K^+]_b \; e^{\frac{-e\psi}{KT}} \qquad (3)$$

$$[Cl^-] = [Cl^-]_b \; e^{\frac{+e\psi}{KT}} \qquad (4)$$

where the concentration at a point having an electrical potential ψ in the diffuse layer is related to the concentration in the bulk. The integration of the above forms (from $\psi = \psi_o$ at the surface to $\psi = 0$ in the bulk) gives the total concentration of each species in the double layer. Since for electrical neutrality the sum of ionic charges in the diffuse layer is equal to the surface charge, the presence of other counter-ions (K^+) displaces the more mobile H^+ to the bulk and enhances the bulk conductance.

The displacement of H^+ from the surface by the addition of KCl may be calculated from the slopes of the conductometric titration curve by assuming that the conductance change during titration is due to neutralization of H^+ in the bulk and its replacement by Na^+. Fig. 8 shows the rise in hydrogen-ion concentration in the bulk due to displacement when the KCl concentrations are increased.

The addition of HCl to latex before the titration resulted in a single SA slope; this slope represents the concurrent titration of the added HCl and the SA groups (Fig. 6). With addition of Na^+ and OH^- to the cleaned latex, in the presence of excess HCl, the Boltzmann distribution of Na^+ and H^+ between the bulk and double layer should progressively change producing a slope less than that expected for the titration of HCl alone (295 cm^2 S $equiv.^{-1}$). This has been proven true and a slope of 257 cm^2 S $equiv.^{-1}$ has been observed.

The use of $Ba(OH)_2$ as the titrant has not changed the SA-WA endpoint, but the SA slope becomes non-linear (Fig. 7). There are differences from the NaOH curves previously shown since the higher valence of the barium ion and its probable specific interaction with surface groups can be expected to affect the diffuse layer structure and the distribution of counter-ions between the surface and the bulk.

Examination of the back titrations (vs. HCl) proves the absence of a distinct back SA slope (Figs. 2,4,5, 6 and 7). With excess HCl in the presence of added or accumulated Na^+, the H^+ and Na^+ are expected to be distributed between the bulk and the diffuse layer according to Boltzmann's distribution. This distribution should progressively change as $[H^+]$ increases producing a slope less than that for free acid (426 cm^2 S $equiv.^{-1}$); slopes of 410 have been observed.

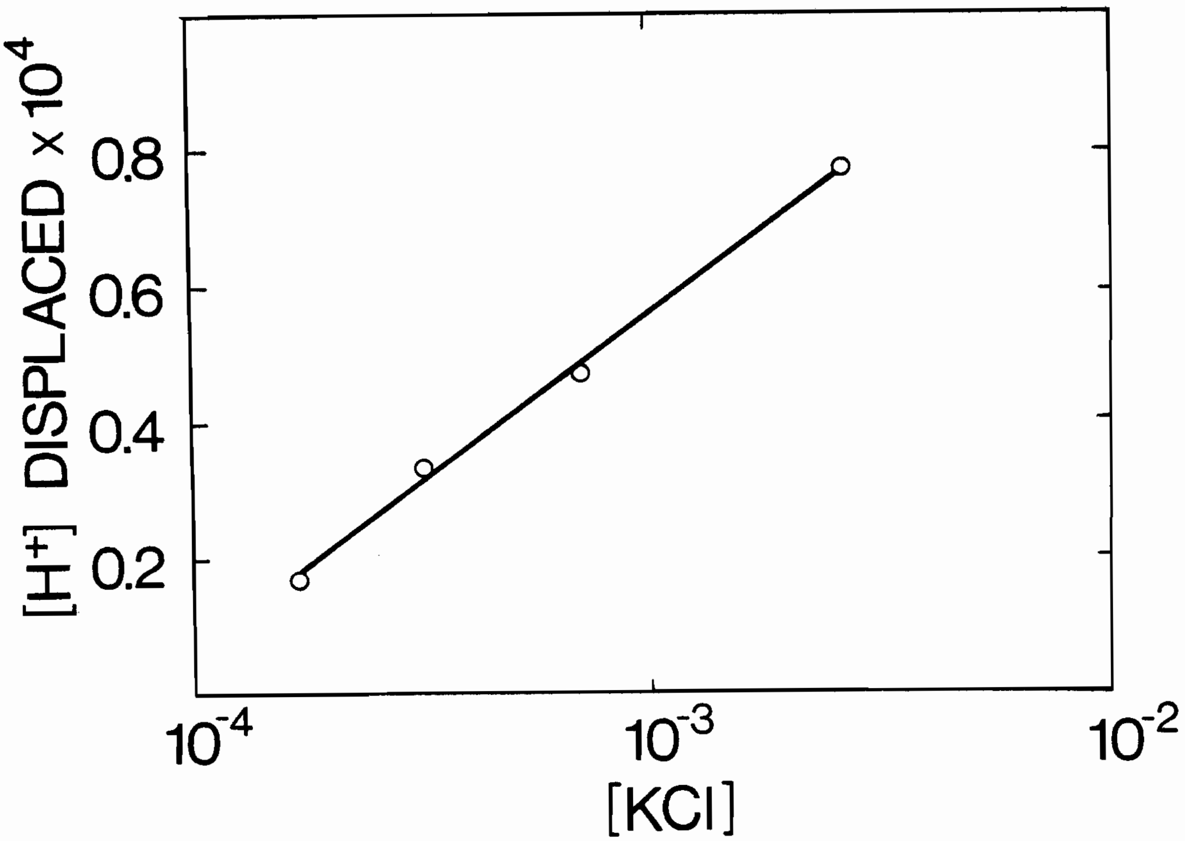


Figure 8. Displacement of double layer protons by KCl added prior to the titration of 9.75 x 10^{-4} mole/l strong acid-groups of a SA-WA functional copolymer latex (L28).

Estimation of the number of titratable SA groups in the latex requires the existence and identification of a valid titration endpoint. In the titration curves related to Latex L28 (Figs. 2,5, 6 and 7), a consistant endpoint is indicated by the end of the initial negative slope. The position of this point is unaffected by the addition of neutral electrolytes (Fig. 5) and can be identified in subsequent back-and-forth titrations (Fig. 2) by a more or less abrupt change in slope. However, the conductance at the indicated point that is calculated from the amount of accumulated or added neutral electrolyte underestimates the measured value by an amount attributable to surface conductance of the latex particles (Table VI).

We suggest that the SA-WA endpoint is identified by the intersection of the extrapolated SA negative slope - preferably in the presence of neutral electrolytes - with the initial low WA slope.

Since the WA titration curve is not linear, it is not possible to carry out extrapolations similar to those used for mixtures of free acids (Fig. 1). Attempts to do so could result in wrong conclusions.

Weak Acid Titrations

In the titration of free weak acid (Fig. 1), the ions formed during neutralization contribute fully to the conductance. In the example studied, the WA slope is equal to the sum of the equivalent conductances of Na^+ and crotonate ion (Table II). In the case of the titration of latex weak acids, the situation is different since the WA groups are immobile (fixed to the surface) and the counter-ions are held near the surface.

Hypothetical titration of ideal weak-acid groups on the surface has been based on the following assumptions:

TABLE VI

Comparison of the observed conductance (K_1) with the predicted contribution of bulk conductance (K_O/F, Eq. 1) measured at the SA-WA endpoint (forward titrations) and at the WA-HCl endpoint (back titrations).

Latex	Electrolyte (Equiv./l)	Predicted Conductance (mS cm^{-1}) $\frac{K_o}{F}$	Observed Conductance (mS cm^{-1}) K_1	Difference $K_1 - \frac{K_o}{F}$	Figure
a) SA-WA Endpoint					
L28	1.50×10^{-4} (KCl)	0.022	0.026	0.004	5
L28	3.00×10^{-4} (KCl)	0.043	0.049	0.006	5
L28	2.60×10^{-3} (KCl)	0.372	0.382	0.010	5
L28	5.00×10^{-3} (KCl)	0.600	0.650	0.050	6
b) WA-HCl Endpoint					
L28	9.25×10^{-3} (NaCl)	1.081	1.225	0.144	6
L27	1.00×10^{-2} (NaCl)	1.164	1.271	0.107	3
L27	4.75×10^{-3} ($BaCl_2$)	0.602	0.675	0.073	7

(a) a weak-acid latex,

(b) a very low dissociation constant, and

(c) a negligible contribution by diffuse-layer counter-ions to the conductance.

The behaviour of this model is shown in Fig. 9 and Table VII. A stoichiometric amount of NaOH (OA) is added with negligible change in conductance. The conductances measured thereafter are, in sequence, due to the addition of excess NaOH (AB), the neutralization by HCl of the excess NaOH (BC), the increase in the concentration of NaCl (CD) as the surface weak-acid groups (in the Na^+ form) are converted to their undissociated form, and finally the addition of excess HCl. The behaviour in the absence of latex - the direct titration of an equivalent amount of base by HCl - is also shown by ORD of Fig. 9.

The titration of a latex that is believed to have only weak-acid surface groups (L27) is compared with the idealized behaviour in Fig. 10. Curve 1 shows the experimental data. Curve 2 shows the conductivity obtained for additions of base in the absence of latex. The difference, Curve 3, (Curve 2 - Curve 1) is identified with the NaOH that is consumed in neutralizing the weak-acid groups if weak-acid dissociation and counter-ions are assumed to contribute negligibly to the conductance.

The surface conductances of polystyrene latexes have been measured both here and elsewhere (19) (Table IV) and are typically of the order of 10^{-9} S and, at least for the weak-acid latexes, vary little with pH or electrolyte concentration. Under the conditions of our titrations ($\phi = 0.04$), the surface-conductance contribution to conductivity is typically 0.008 mS cm^{-1}. This magnitude is significant in the absence of added electrolyte and we have used its variation to titrate strong acids. We have, however, assumed that

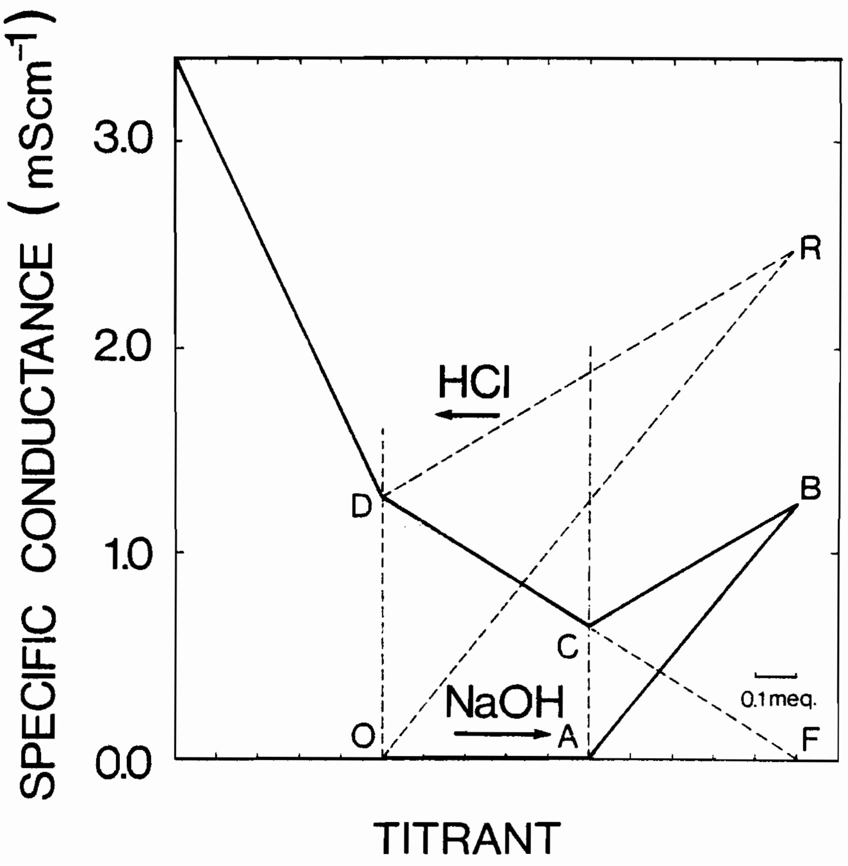


Figure 9. Hypothetical titration of an idealized weak-acid latex.

TABLE VII

Hypothetical Weak-Acid Latex

Titration	Slope Code	Slope Magnitude (cm^2 S $equiv.^{-1}$)
Forward (vs. NaOH)	$(WA)_f$	0
	+Excess NaOH	+248
Back (vs. HCl)	-Excess NaOH	-122
	$(WA)_b$, (+NaCl)	+126
	Excess HCl	+426

any variation in surface conductance during the weak-acid titration is negligible and the shape of the titration curve is unaffected.

In Fig. 10, OA is believed to measure the stoichiometric amount of NaOH and WA. Curve 3 follows the neutralization of weak acid through the titration. The final amount of NaOH consumed can be estimated from the constant value of conductance of Curve 3, i.e., the magnitude OC which, when converted to [NaOH], is equivalent to OA -- the stoichiometric amount of surface WA groups.

The degree of neutralization (α) at any point is calculated from the ratio of the specific conductance at this point (K_{sp}) and the maximum constant specific conductance ($K_{sp_{max}}$) of Curve 3, i.e. $\alpha = \frac{K_{sp}}{K_{sp_{max}}}$. The graph showing the degree of neutralization thus has the shape of Curve 3.

Unlike the case of free WA, α of surface WA is a non-linear function of the NaOH added and complete neutralization ($\alpha = 1$) is not attained until there is a large excess of base present. As can be seen from Fig. 10, the stoichiometric WA cannot be identified with the total amount of NaOH added to $\alpha = 1$.

The determination of the WA from the forward titration follows the method shown in Figs. 2-7. This procedure involves the extrapolation of the excess NaOH slope (250 cm^2 S $equiv.^{-1}$) to intersect a horizontal line passing through the SA-WA endpoint (Figs. 2,4,5, 6 and 7). This method is simply equivalent to the estimation of NaOH consumed upon the addition of the WA latex to excess base.

The conductance increase (Curve 1 of Fig. 10) is assumed to be due to Na^+ and OH^- in the bulk and any change in the conductance attributable to the latex or its counter-ions is assumed negligible. This has been discussed in connection with Table IV.

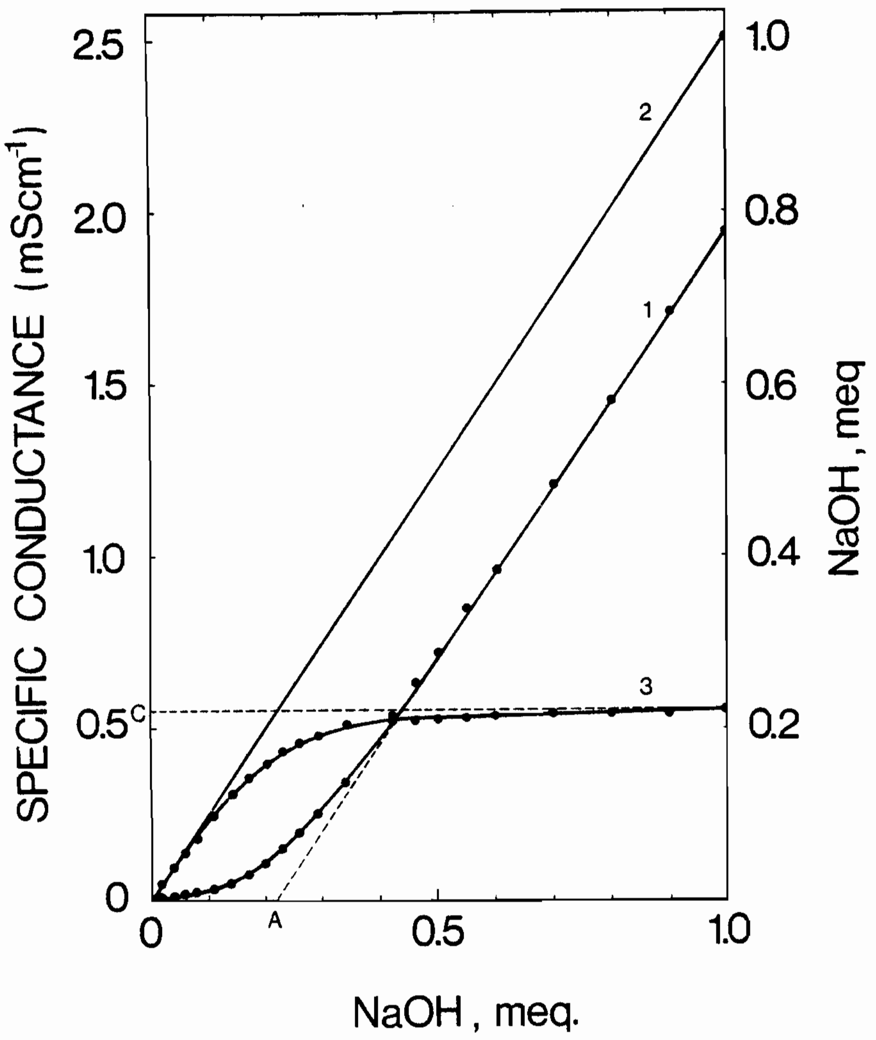


Figure 10. Analysis of the forward titration of a weak-acid latex (L27). Curve 1 is in the presence of latex, Curve 2 is in the absence of latex, and Curve 3 is the conductance difference 2 - 1. Curve 3 shows the conductance of NaOH consumed in the neutralization of WA. The extrapolation method for the determination of the stoichiometric amount of WA(OA) is shown.

Back Titrations

The back titrations can similarly be idealized and compared with experimental curves with similar identities (Fig. 11):

Curve 1 - experimental WA latex,
Curve 2 - without latex, and
Curve 3 - difference of (2) and (1).

As excess NaOH is titrated, Curves 1 and 2 are parallel with a predicated slope of 250 cm^2 S $equiv.^{-1}$. As the weak-acid groups are progressively titrated to their undissociated form, the curves converge to the point F and α decreases from 1 to 0 (Curve 3).

The conductance due to accumulating NaCl is calculated from the equivalent conductance of NaCl with corrections for particle volume and dilution where significant, and is represented by the Curve CF.

It is noted that the forward and back titrations bear a mirror-image relationship modified by the conductance of accumulating NaCl as the added base is titrated by the HCl (Curves 3; Figs. 10 and 11).

The stoichiometric endpoints in the back titration are estimated from:

(a) the intersection (E) of the slope corresponding to the titration of excess NaOH and the constructed line (slope = 126 cm^2 S $equiv.^{-1}$) representing conductance due to accumulating NaCl (CF),

(b) the intersection (F) of the NaCl line with the extrapolation of the slope corresponding to excess HCl.

Fig. 3 combines the forward and back titrations and shows the congruence of the endpoints obtained by the methods described for a weak-acid latex.

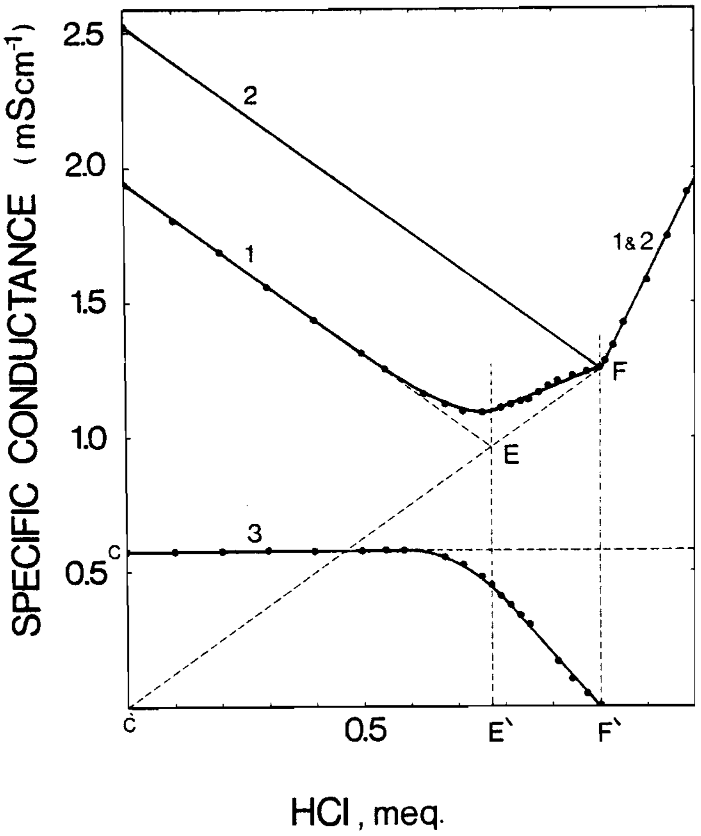


Figure 11. Analysis of the back titration of a weak-acid latex (L27). Curve 1 is in the presence of latex, Curve 2 is without latex, and Curve 3 is the difference 2 - 1. The extrapolation method for the determination of weak-acid amount (E'F') is shown.

The same method, applied to a SA-WA latex (Fig. 2), shows similarly congruent endpoints for repeated forward and back titrations. The base line is now the conductance corresponding to the SA-WA endpoint and the calculated line, representing the accumulated NaCl, is drawn from this level. However, it is now observed that the conductance of the left-hand endpoint (WA-excess HCl) is not fully accounted for by the accumulated NaCl, and other contributions to conductivity must be present. These might include an increased surface conductance at the higher electrolyte concentration as observed by Wright and James (20), or changed distribution of counter-ions between bulk and surface as the ionic composition of the system is changed. The present results do not permit further analysis.

The use of $Ba(OH)_2$ as the standard base results in a conductometric curve that has similar properties and provides identical endpoints (Fig. 7). The slope corresponding to accumulating salt is now calculated from the equivalent conductance of $BaCl_2$.

Effect of Neutral Electrolytes

The effect of neutral electrolytes can be seen from the data of Fig. 5 if the neutral electrolyte conductivity (conductivity at SA-WA endpoint) is subtracted. These data plotted in Fig. 12 show that the stoichiometric endpoints are independent of the amount of neutral electrolytes added.

The differences in the slopes corresponding to the excess alkali are attributed to the equivalent conductance of the ions decreasing with ionic concentration (17).

The titration of surface WA groups involves the approach of OH^- to the charged surface. This approach is inhibited by a potential barrier that is lowered by the presence of neutral electrolytes. Thus the neutralization reaction equilibrium, for a given amount of added

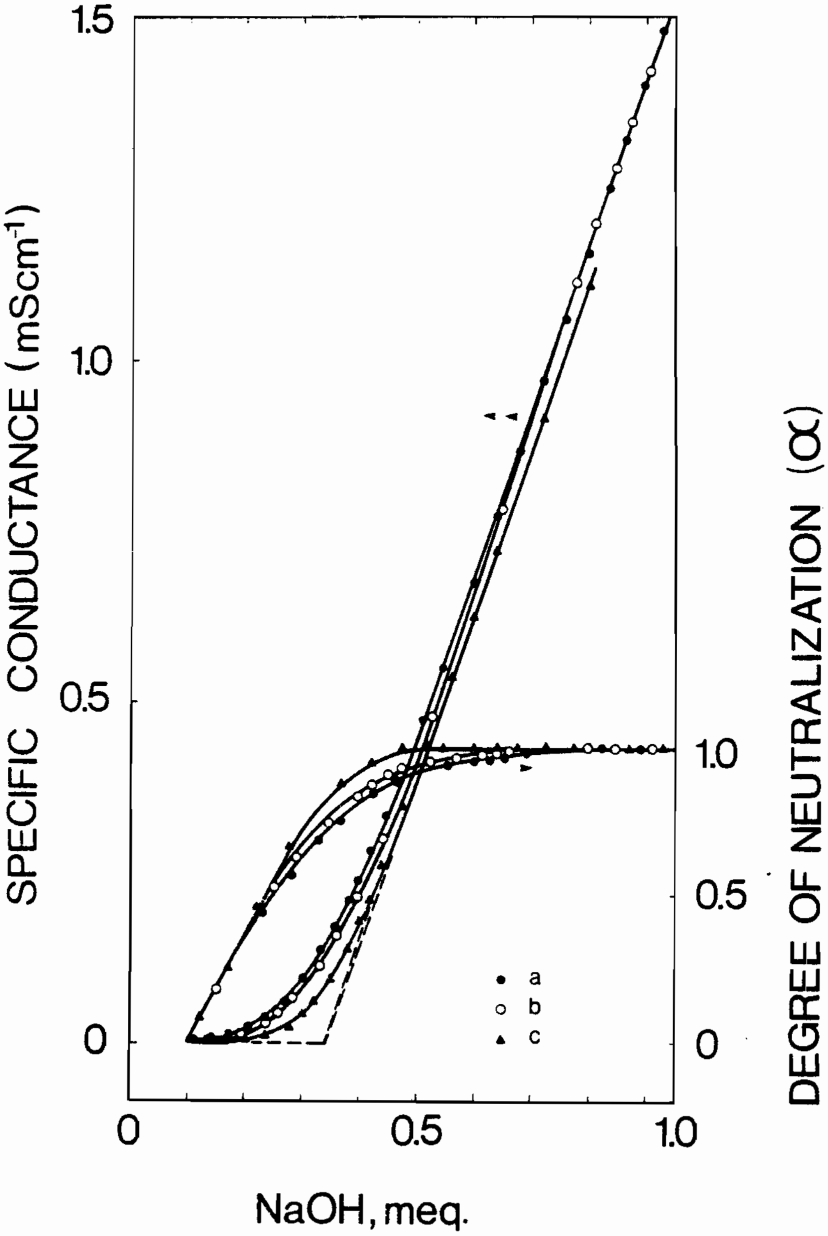


Figure 12. The effect of electrolytes (KCl) on the titration curves and the degree of neutralization (α) of latex weak acids (L28). The titration curves were constructed by subtracting the conductance at the SA-WA endpoint from the observed conductance of Fig. 5. The degrees of neutralization were the result of analysis analogous to Fig. 10. The curves are in order of increasing KCl concentration.

alkali, is shifted towards higher values of the degree of neutralization as the electrolyte concentration increases. The data of Fig. 5 show this effect and Fig. 12 indicates that neutralization is achieved at a lower alkali concentration when the electrolyte concentration is higher.

Effect of SA Groups

A comparison of the titration of WA and SA-WA latexes (Figs. 2, 3 and 4) shows that the weak-acid titrations in both cases have similar properties, and thus similar interpretations are possible. The possible effects of SA groups on the surface potential could in turn affect the dissociation properties of the weak acids, but this has not been investigated (12 and 13).

CONCLUDING REMARKS

The interpretation of conductometric titration curves obtained with latexes has often been uncertain, and the procedures appropriate for free acids in solution cannot generally be applied. The present work demonstrates that for clean latexes stabilized by weak-acid groups or by both weak- and strong-acid groups, the interpretation is improved by:

(a) continuing the titration until excess alkali is indicated by attainment of the theoretical slope,

(b) performing a subsequent back titration with strong acid until excess acid is indicated by the appropriate slope of the titration curve,

(c) adding neutral electrolytes prior to titration to steepen the strong-acid slope and to facilitate the weak-acid neutralization,

(d) estimating the stoichiometric endpoint for the strong-acid component from the end of the initial decreasing slope and confirming it with a back-titration endpoint,

(e) estimating the stoichiometric endpoints for the weak acid by extrapolations of the conductometric slopes obtained with excess titrants to intersect base lines that are derived on the assumption that surface groups and their counter-ions do not contribute significantly to conductivity.

REFERENCES

1. Kotera, A., Furasawa, K., and Takeda, Y., Kolloid-Z.u.Z. Polymere 239, 677 (1970).

2. Goodwin, J.W., Hearn, J., Ho, C.C., and Ottewill, R.H., Brit. Polymer J. 5, 347 (1973): Ibid., Colloid Polymer Sci. 252, 464 (1974).

3. Juang, M.S-d., and Krieger, I.M., J. Polym. Sci.: Polymer Chemistry Ed. 14, 2089 (1976).

4. Labib, M.E., This thesis, Chapter II.

5. Vanderhoff, J., van den Hul, J.J., Tausk, R.J.M., and Overbeek, J.TH.G., in "Clean Surfaces: Their Preparation and Characterization for Interfacial Studies" (G. Goldfinger, Ed.), P.15, Dekker, N.Y. (1970).

6. van de Hul, H.J. and Vanderhoff, J.W., J. Electroanal. Chem. 37, 161 (1972).

7. Stone-Masui, J., and Watillon, A., J. Colloid Interface Sci. 52, 479 (1975).

8. Everett, D.H., and Gultepe, M.E., in "NATO Advanced Study Institute-Polymer Colloid Reprints", The Norwegian Institute of Technology, Trondheim, Norway, 1975.

9. Yates, D.E., in "NATO Advanced Study Institute-Polymer Colloid Reprints", The Norweigian Institute of Technology, Trondheim, Norway, 1975.

10. Wu, W.D., Ph.D. Thesis, Lehigh University, 1977.

11. Davis, J.A., James R.O., and Leckie J.O., J. Colloid Interface Sci. 63 480 (1978).

12. Davis, J.A., Leckie, J.O., J. Colloid Interface Sci. 65, 331 (1978).

13. Healy, T.W., and White, L.R., Advances in Colloid and Interface Sci. 9 303 (1978).

14. Labib, M.E. and Robertson, A.A., J. Colloid Interface Sci. 67, 543 (1978).

15. van den Hul, H.J., and Vanderhoff, J.W., J. Colloid Interface Sci. 28, 336 (1968).

16. Labib, M.E., This thesis, Chapter V.

17. CRC 'Handbook of Chemistry and Physics' 51st Ed., The Chemical Rubber Co., Ohio, 1970-1971; and, Robison, R.A., and Stokes, R.H.,"Electrolyte Solutions", Butterworth, London, 1959.

18. Street, M., Aust. J. Chem. 9, 333 (1956); 10, 207 (1957).

19. Watillon, A., and Stone-Masui, J., J. Electroanal. Chem. 37, 143 (1972).

20. Wright, M.H., and James, A.M., Kolloid-Z.u.Z. Polymere 251, 745 (1973).

CHAPTER V

APPLICATION OF CONDUCTOMETRIC TITRATIONS TO LATEX CHARACTERIZATION

ABSTRACT

Conductometric titrations of polystyrene homopolymer and copolymer latexes at various stages of cleaning have been made. The nature of the impurities and the efficiency of their removal have been determined by comparison with the conductivity of model systems. Diafiltration is shown to be an effective cleaning method.

INTRODUCTION

The use of latexes as model colloids requires the complete characterization of surface groups, that is, the type of groups that are present and their number. In general, the analytical techniques require some prior purification of the latex. In particular, the surface group characterization of anionic polystyrene latexes by conductometric titration requires that interfering impurities be removed and that the functional groups on the surface be in the acid form (1).

The impurities present after the preparation of an emulsifier-free latex include the decomposition products of the initiator (usually $K_2S_2O_8$), residual monomers and comonomers, oligomeric species (2), electrolytes or non-electrolytes added in the recipe and their reaction products. The impurities may exist in solution, in the serum, or adsorbed at the polymer interface. The recognition and assessment of the effects of impurities on the course of the conductometric titration curves are essential in establishing the cleanness of the surface and the performance of a meaningful characterization.

The titration of strong acid groups requires the prior removal of all counter-ions that reduce the acidity. Ahmed (3) claims that ion-exchange cleaning or serum replacement by the sequence H_2O, HCl, H_2O can effect better cleaning of a strong-acid latex than dialysis or serum replacement vs. H_2O. Shenkel and Kitchener (4) showed the possibility of the contamination of latexes by polyelectrolytes leached from the ion-exchange resins used to clean them. Yates et al (5) found that oxidized cellulose products are desorbed from dialysis membranes and re-adsorbed on the latex surface to give rise to a weak-acid inflexion in the conductometric titration curve. McCarvill and Fitch (6) noted that the amount of base consumed in the titration of sulfonated polystyrene latexes depends on the quality of the water used in a holo-fiber dialysis cleaning process.

In current work (7), the procedure for conductometric titrations has been improved by including a back titration and the method for establishing endpoints has been revised. These conductometry procedures have been used to establish the amount and the nature of the contaminants of emulsifier-free latexes as they are formed and after various amounts and kinds of cleaning.

MATERIALS AND METHODS

Latex Preparation

The latexes used in this study were either polystyrene homopolymer or copolymer latexes prepared without emulsifiers. The latexes used are listed in Table I. The details of the polymerization conditions and the recipes can be found elsewhere (8).

Method of Titration

Conductometric titrations were performed at 25°C as described in Ref. 7. The measured specific conductances were corrected for volume increase during the titrations. The data were plotted as specific conductances against the number of milliequivalents of NaOH or HCl.

TABLE I

The Characteristics of the Latexes Used in this Study (cf. Ref. (8))

Latex Code	Type of Latex	Monomers Used	Particle Diameter nm
L27	Copolymer	Styrene, itaconic acid	1003
L28	Copolymer	Styrene, itaconic acid, NaSS*	286
LS 1-2	Homopolymer	Styrene	342

* NaSS denotes sodium salt of styrene p-sulfonic acid.

Interpretation of Titration Curves

The strong-acid surface charge was calculated directly from the amount of NaOH consumed up to the strong acid (SA) - weak acid (WA) endpoint, defined to the criteria given by Ref. 7. Weak-acid surface charge is determined in the forward titration by the extrapolation of the excess NaOH slope to a horizontal line drawn through the SA-WA endpoint. In the back titration, the WA surface charge is determined by the extrapolation of the '-excess NaOH slope' to a line with a slope of 125 cm^2 S $equiv.^{-1}$ drawn to represent the conductance contribution of accumulating NaCl as HCl is added. Further details are given by Ref. 7.

The interpretation of the titration curves of uncleaned latexes is based on the information supplied from the study of the titration of model mixtures described in this work and elsewhere (7,9,10).

Cleaning Methods

Diafiltration (11) and ion-exchange (12) cleaning techniques were used. Diafiltration was continued until the filtrate conductivity equalled that of distilled water (8.0×10^{-7} S cm^{-1}). Two ion-exchange resins were used. Resin (A) was a research grade mixed-bed commercial resin and was used as received; the other resin (B) was that recommended by van den Hul and Vanderhoff (12) and was purified according to their procedure. The ion-exchange process was continued until no further conductance decrease was observed upon adding more resin.

RESULTS

Model experiments were made in which a strong acid or a weak acid was added in a known quantity to a cleaned latex to determine the effect of these known contaminants on the conductometric titration curve. Fig. 1 compares the titration of the clean latex with the same latex after addition of 0.5 meq. HCl. The effect is to extend and steepen the slope of the part of the titration curve attributed to the strong-acid titration curve attributed to the strong-acid titration and to raise the conductivity at the SA-WA endpoint by an amount corresponding to the amount of NaCl that results from the neutralization.

Fig. 2 records the conductometric titration of itaconic acid alone and Fig. 3 shows the results when 0.43 meq. of itaconic acid is added to the clean latex (L28).

The model systems described (Figs. 1-3) are intended to aid in the interpretation of conductometric titrations of crude or incompletely cleaned latexes in which free or adsorbed, strong or weak acid contaminants or residues may be present.

Fig. 4 compares the conductometric titrations of crude and cleaned copolymer (styrene, itaconic acid) Latex (L27). The initial slope is attributed to strong acid (cf. Fig. 1) and the subsequent linear rising region is attributable to a free weak acid (cf. Fig. 3). Both disappear on cleaning leaving a titration curve typical of latexes having only weak acid surface groups (7).

A similar behaviour is observed in the comparison of latex L28 after incomplete and after adequate cleaning (Fig. 5). The titration curve for the incompletely cleaned latex (curve a) shows, in the forward titration with NaOH, an initial linear decrease in conductance attributed to the titration of strong acid followed by increasing conductance in which three regions can be seen corresponding, by analogy to the model experiments, to

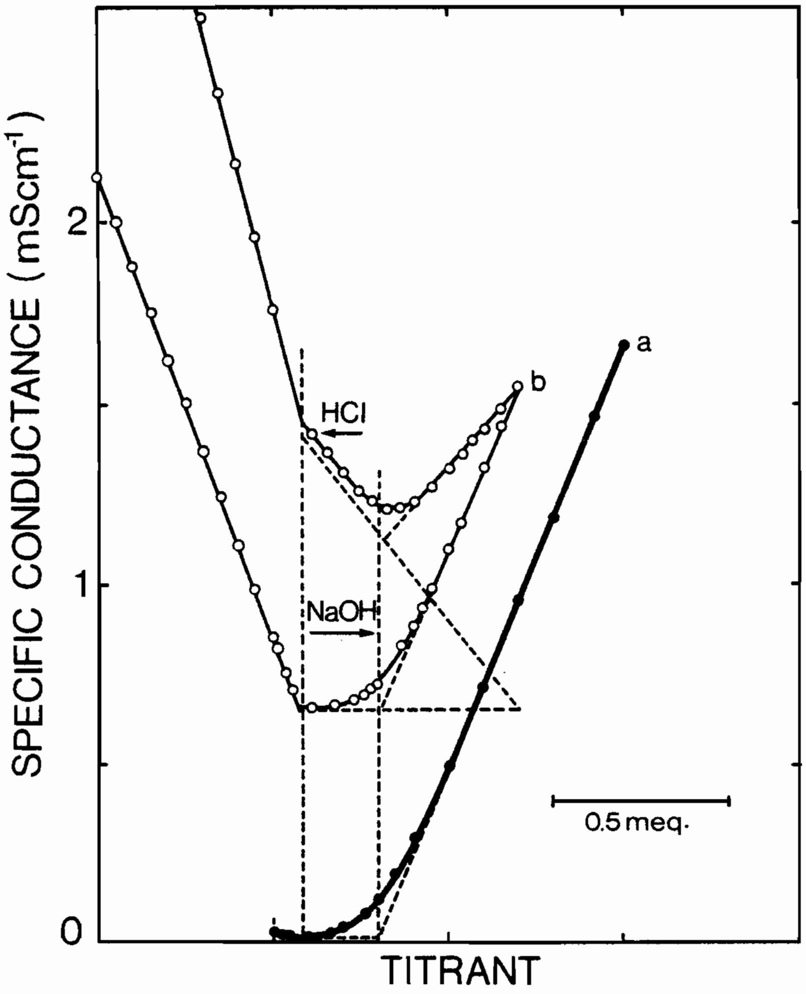


Figure 1: The conductometric titrations of cleaned latex L28 (curve a) and of the same latex plus 0.5 meq. HCl added (curve b). The latter shows both forward and back titrations.

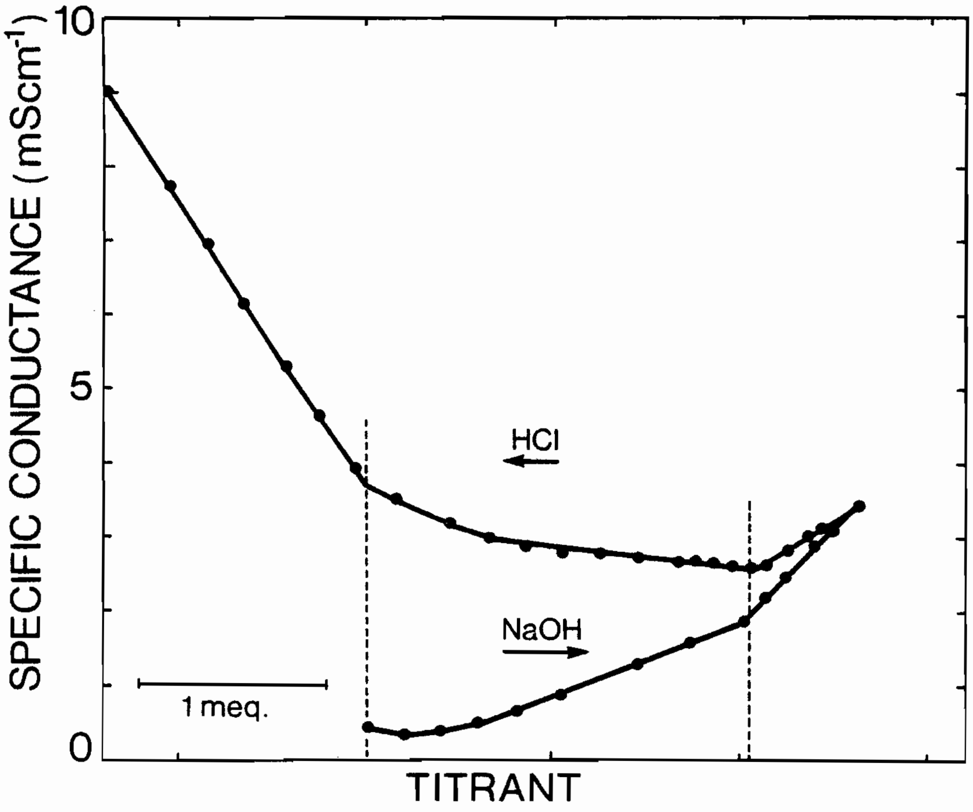


Figure 2: The forward and back conductometric titrations of 2.05 meq. of itaconic acid.

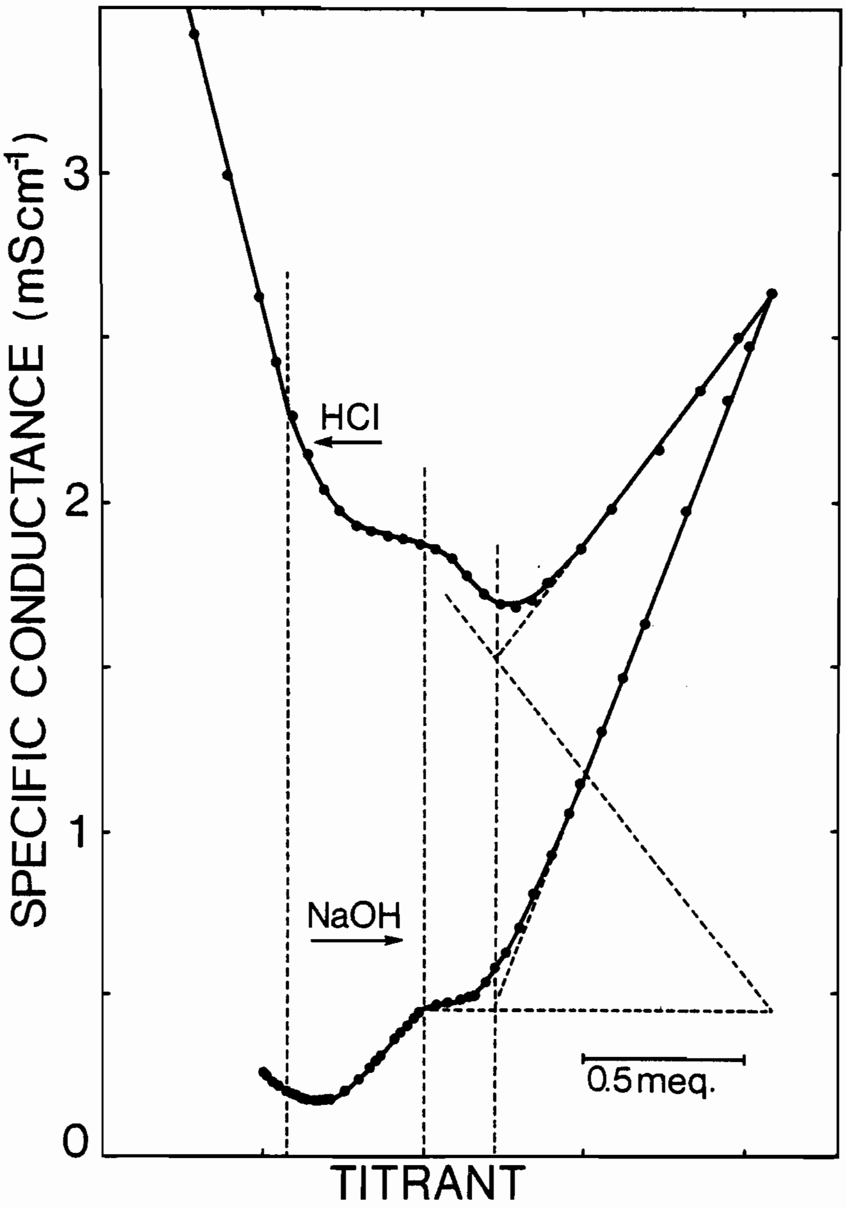


Figure 3: The conductometric titrations of cleaned latex L28 after the addition of 0.22 meq. itaconic acid.

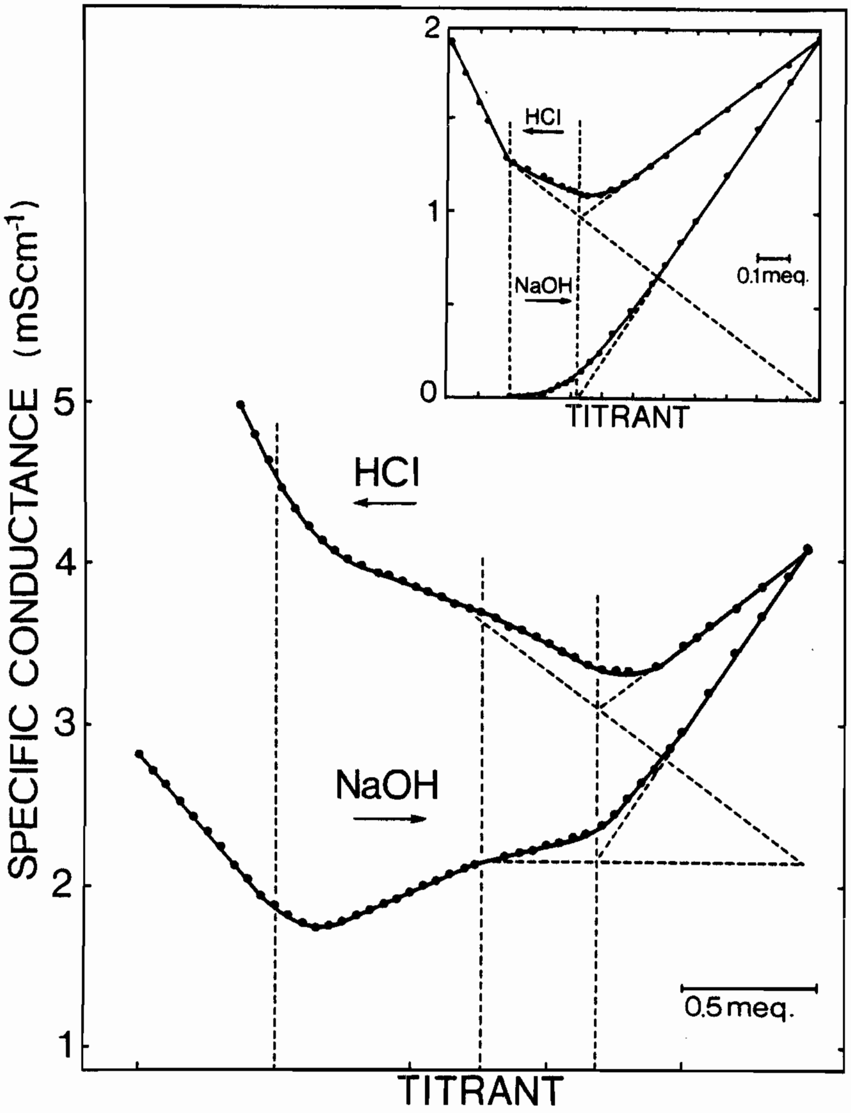


Figure 4: The forward and back conductometric titrations of uncleaned carboxylated latex L27. The inset shows the titration of the same latex after diafiltration (11) followed by ion-exchange cleaning (12).

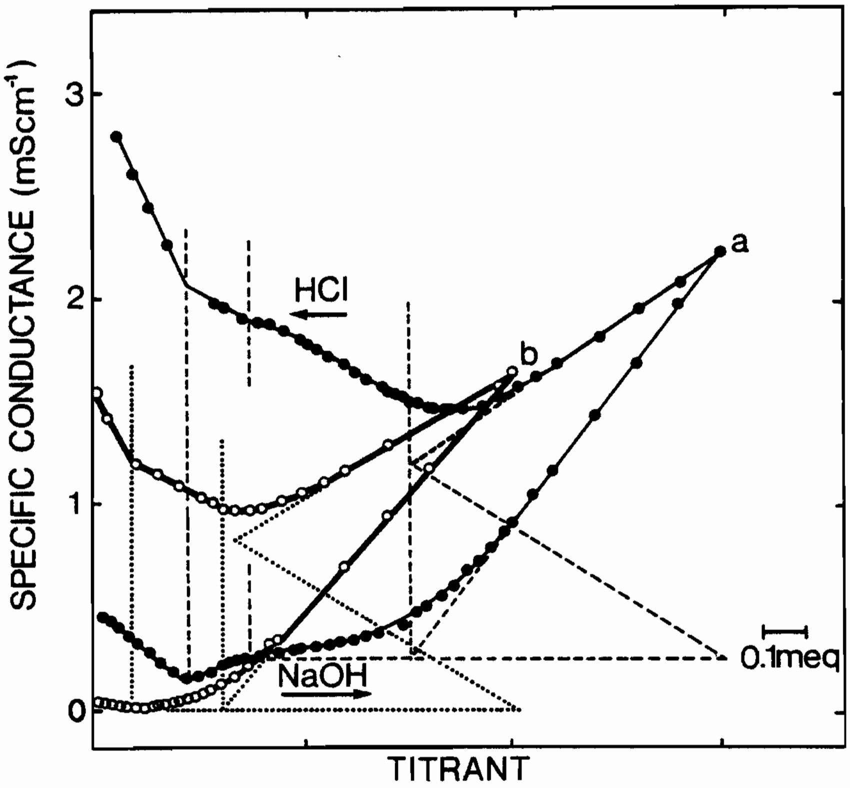


Figure 5: The conductometric titration of (1) inadequately cleaned latex L28 (curve a) of volume fraction ϕ = 0.065, and of (2) adequately cleaned latex L28 of volume fraction ϕ = 0.044.

the successive titration of free weak acid, adsorbed or surface weak acid and to addition of excess NaOH. The same sequence is reflected in the back titration.

The cleaned latex (curve b), which was titrated at different solid contents, shows a shorter, less steep, strong acid titration; a lower conductance at the SA-WA endpoint; no slope attributable to free weak acid and a slightly shorter fixed weak acid titration. The characteristics of various slopes are shown in Table II. The analysis of the titration curves provides the results shown in Table III.

Similar conductometric titrations were made to compare the following methods of cleaning:

(a) Ion exchange until no further conductance decrease can be observed,

(b) Diafiltration against distilled water,

(c) Further diafiltration of (b) against the sequence H_2O, HCl, H_2O,

(d) Further diafiltration of (b) against H_2O followed by ion exchange.

The results of the analysis appear in Table III. Table III also contains data on the cleaning of emulsifier-free homopolymer latex (LS 1-2) by different methods.

DISCUSSION

Free and bound strong acids, titrated together, are not differentiated in the conductivity plot (Fig. 1). The distributions of H^+ and Na^+ between the surface and the bulk are governed by Boltzmann distributions and the

TABLE II

The slopes corresponding to various components in the forward and back titrations of model mixtures, uncleaned, and cleaned latexes.

	Forward Titration				Back Titration				
Latex	SA	Free WA	Surface $(WA)_f$	Excess NaOH	-Excess NaOH	Surface $(WA)_b$	Free WA	Excess HCl	Figure
L28 (cleaned)	- 9	-	nonlinear	239	-120	nonlinear	-	424	1 and 5
L28 +0.5 meq. HCl	-257	-	nonlinear	230	-120	nonlinear	-	410	1
L27 (crude)	-197	+70	nonlinear	246	-125	nonlinear	+60	350	4a
L27 (cleaned)	-	-	nonlinear	250	-122	nonlinear	-	416	4b
L28 (incompletely cleaned)	-146	+100	nonlinear	250	-122	nonlinear	+46	400	5

TABLE III

Endpoints Analysis of Copolymer (L27 and L28) and Homopolymer (LS 1-2) Latexes with Various Degrees and Methods of Cleaning.

Latex Code	Latex Identification	SA $\mu C/cm^2$	Bound Weak Acid $(WA)_{fb}$* $\mu C/cm^2$	Free WA (meq./l)	Conductance at SA-WA Endpoint mS cm^{-1}	Figure
L27	Crude	137.8	113.6	7.50	1.690	4a
L27	Ion-exchanged (resin B)	15.7	107.0	0.20	0.008	-
L27	Diafiltered and ion-exchanged (resin B)	00.0	103.8	0.00	0.003	4b
L28	Ion-exchanged (Resin A) (incompletely cleaned)	16.4	28.6	1.30	0.116	5a
L28	Diafiltered vs. H_2O	9.1	25.5	0.35	0.013	-
L28	Diafiltered vs. HCl, H_2O	8.7	24.6	0.25	0.013	-
L28	Diafiltered vs. H_2O and ion-exchanged (resin B)	9.2	25.2	0.00	0.004	5b
LS 1-2	Partially cleaned (resin B)	6.7	1.3	0.00	0.038	-
LS 1-2	Ion-exchanged (resin B)	3.3	1.3	0.00	0.002	-
LS 1-2	Dialyzed vs. H_2O	2.7	1.5	0.00	0.006	-
LS 1-2	Diafiltered vs. H_2O	2.4	1.5	0.00	0.004	-

* $(WA)_{fb}$ is the average of the forward and back titrations of surface weak-acid charge determined according to (7).

neutralization reduces the number of both bulk and counter-ion protons simultaneously. The strong acid part of the titration curve is found to be linear and its slope is determined largely by the concentration of the free H^+ which has a high equivalent conductivity in the bulk. The slope is steep if the ratio of bulk H^+ to surface H^+ is high and is low if the H^+ exists only as counter-ions in the diffuse layer.

The slope has a minimum value if the latex is clean (Fig. 5b), i.e., when all the protons are associated with surface as counter-ions (Table II). The slope is increased if free strong acid is present (Fig. 1 and Table II) or in the presence of neutral electrolyte (cf. Ref. 7). Thus cleaning a latex of electrolyte should decrease the slope of SA titration,and the removal of strong acid contaminants should decrease both the slope and the titer (Figs. 4 and 5).

When both free and bound weak acid are present,they are distinguishable in the conductometric titration curve (Figs. 3,4,5); the free acid is titrated first. The bound weak acid has a lower effective dissociation constant than the free acid because of the potential that develops at the particle surface due to the concentration of anionic groups (5,7,13).

The free weak acid titration shown in Fig. 3 is similar to the one obtained in the absence of latex (Fig. 2) and its course has been described and accounted for elsewhere (7,10). The initial conductivity is due to partial dissociation of the weak acid. As the titration proceeds,the conductance decreases as the protons are neutralized and replaced by less conductive cations (Na^+). Past the minimum of the titration curve, the slope tends to become constant and equal to the sum of the equivalent conductances of Na^+ and the weak acid anion.

The course of the titration of bound weak acid alone is shown in Fig. 4 (inset) and has been discussed elsewhere (7). When both free and bound weak acids exist, they are readily differentiated by an abrupt change of slope (Figs. 3, 4, 5 and Table II).

It is clear by comparison with the model systems that the crude latexes titrated here show strong acid, weak acid, and neutral electrolyte impurities that are removed to varying degrees by various cleaning procedures. The comparison made in Fig. 4 has shown that diafiltration followed by ion exchange removes both strong and weak acid impurities as well as neutral electrolyte so that only bound weak acid is titrated in the cleaned sample (cf. Table III).

The incomplete removal of impurities by ion exchange alone (resin A) is demonstrated in Fig. 5. An ion-exchanged latex subjected to cleaning by diafiltration and further ion-exchange treatment has shown reduced strong acid and weak acid functionality and no evidence of free weak acids. It is noted from the data in Table III that diafiltration alone, either with distilled water or by a water-acid-water sequence,was inadequate in removing free weak acid impurities completely.

The data of Table III and Figs. 4 and 5 indicate that the number of bound weak-acid groups indicated in the case of crude or incompletely cleaned latex decreases with diafiltration or diafiltration followed by ion-exchange cleaning. This indicates the presence of adsorbed weak acid impurities, appearing as bound WA, which are removed upon adequate cleaning. This observation confirms that adsorbed and bound weak acids are not differentiated by conductometric titration (9).

Ion-exchange cleaning has shown limitations in removing all the impurities, especially in the case of copolymer latexes (L27 and L28,

Table III). The commercial resin "A" has limitations in achieving lower conductances.

It should be noted that the conductance at the SA-WA endpoint is a measure of the amount of neutral electrolyte contaminants and provides a convenient assessment of the completeness of the cleaning (Table III).

Furthermore, the cleaning of a homopolymer latex (LS 1-2) using various methods shows a varying amount of the strong-acid charge with the method of cleaning (Table III). This result indicates that strong-acid impurities are removed more effectively by diafiltration (11). The weak-acid charge, however, has increased slightly with prolonged cleaning procedures (dialysis and diafiltration) indicating the possibility of hydrolysis and oxidation of sulfate groups during cleaning.

CONCLUDING REMARKS

The cleaning of latexes may be attempted by a variety of means with varying degrees of effectiveness. Conductometry can provide considerable information on the extent of success achieved although there may be some degree of uncertainty if the impurities desorb very slowly or there are ongoing chemical changes in the system. The criteria of cleanness that have been suggested by this work are that (a) the number of strong- or weak-acid groups is constant with prolonged application of the cleaning method, (b) the conductance at the strong acid - weak acid endpoint is below 4×10^{-6} S cm^{-1} and (c) there is no evidence in the titration curve of the presence of free weak acids.

REFERENCES

1. Vanderhoff, J.W., van den Hul, H.J., Tuask, R.J.M., and Overbeek, J.Th.G., in "Clean Surfaces", (G. Goldfinger, Ed.). Marcel Dekker, New York, (1970).
2. Goodall, A.R., Wilkinson, M.C., and Hearn, J., J. Poly. Sci. (Polymer Chemistry Edition) 15, 2193 (1977).
3. Ahmed, S.M., Ph.D. Thesis, Lehigh University, (1979).
4. Shenkel, J.H., and Kitchener, J.A., Nature (London) 182, 131 (1958).
5. Yates, E.E., Ottewill, R.H., and Goodwin, J.W., J. Colloid Interface Sci. 62, 356 (1977).
6. McCarvill, W.T., and Fitch, R.M., J. Colloid Interface Sci. 64, 403 (1978).
7. Labib, M.E., This thesis, Chapter IV.
8. Labib, M.E., This thesis, Chapter II.
9. Hen, J., J. Colloid Interface Sci. 49, 425 (1974).
10. Gilbert, J., Bull. Soc. Chim. France, 663 (1957).
11. Labib, M.E., and Robertson, A.A., J. Colloid Interface Sci. 67, 543 (1978).
12. van den Hul, H.J., and Vanderhoff, J.W., J. Colloid Interface Sci. 28, 336 (1968).
13. Stone-Masui, J., and Watillon, A., J. Colloid Interface Sci. 52, 479 (1975).

CHAPTER VI

THE OSCILLOMETRIC TITRATION OF LATEXES

ABSTRACT

Oscillometry and conductometry have been shown to provide equivalent results when used to follow the titrations of mixtures of strong and weak acids. On this basis, the use of oscillometry has been extended to the surface charge characterization of anionic and cationic polystyrene latexes. The assessment of functional groups is again equivalent to that obtained by conventional conductometry.

INTRODUCTION

Conductometric titrations have frequently been used in the characterization of the surfaces of synthetic latexes (1-3). These titrations provide the basis for distinguishing and evaluating strongly and weakly acidic or basic groups.

A variation of the conductometric technique is provided by oscillometry which effectively measures the conductivity of a suspension or solution at high frequency (4). This is achieved in the 'Sargent Model V' oscillometer by incorporating a cell (with external electrodes) containing the suspension or solution in an oscillatory circuit. As the suspension is titrated, the capacitance changes and a variable capacitor is adjusted to maintain the frequency at 5 MHz as indicated by a null point (5).

The capacitance of the cell and its contents is given (5) by

$$C_p = \frac{C_g K_{sp}^2 + 2\Pi f \ (C_g C_s^2 + C_g^2 C_s)}{K_{sp}^2 + (2\Pi f)^2 \ (C_g + C_s)^2} \qquad (1)$$

in which it is seen that the total capacitance, C_p, is a function primarily of the specific conductance of the cell contents, K_{sp}, since the capacitance of the empty cell, C_g, and the frequency, f, are constants and the capacitance of solution, C_s, that reflects changes in the dielectric constant, does not change significantly.

The relationship between C_p and K_{sp} permits the construction of an empirical 'transfer plot' by determining the instrument reading for a series of solutions of known conductance. This 'transfer plot' can provide the basis for comparing conductometric and oscillometric titration in aqueous solutions (6).

There are potential advantages of oscillometry over conventional conductometry. These are: (1) the greater sensitivity of the measurement resulting from the use of a capacitance bridge (7); (2) the use of external electrodes out of contact with the solution that is possible in capacitance measurements; and (3) the possibility of the detection of any components of conductance that are frequency dependent (8) by comparison of the results with conventional conductometry.

EXPERIMENTAL

Conductometric titrations were performed on 100 ml samples of cleaned latexes or model acid mixtures. The titrations were done in a stirred vessel with continuous bubbling of N_2 using a conductivity dip-cell and a 'Radiometer' Model CDM3 conductivity meter operating at 1 KHz. The conductivity procedure is similar to that used in Ref. 3.

Oscillometric titrations were made with the 'Sargent' Model V oscillometer using the prescribed procedure (4), again using a 100 ml - stirred cell but without N_2 bubbling.

The titrations were made with 0.1N NaOH and HCl. For the comparison, the effect of temperature and the volume increase during the titrations were taken into account.

Details of latex characteristics can be found elsewhere (9).

RESULTS AND DISCUSSION

The transfer plot shown in Fig. 1 was obtained by recording the instrument reading for solutions of KCl and NaOH of known conductance.

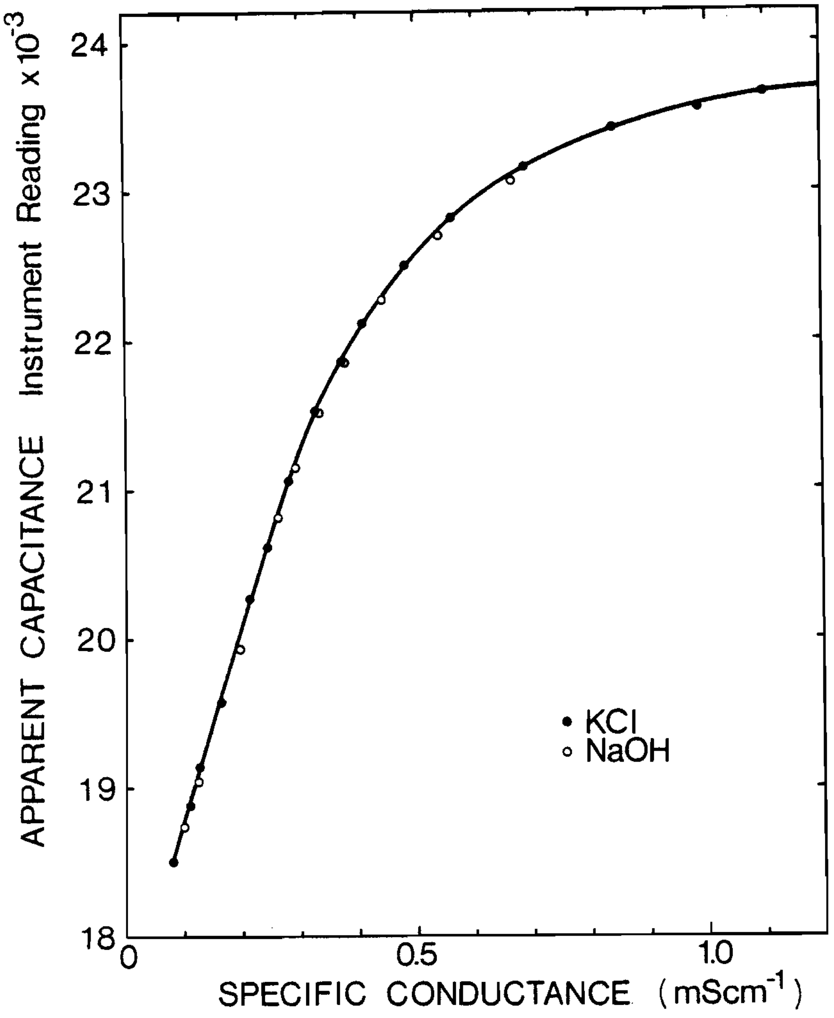


Figure 1: Transfer plot obtained by plotting oscillometric response to increasing specific conductance of KCl and NaOH solutions.

The plot indicates that the apparent capacitance observed is independent of the electrolyte used and that there is a range of conductivity over which the transfer plot is linear and where the response is most sensitive. In this range, 10^{-4} Scm^{-1} (20 divisions on the conductivity meter) is equivalent to 1,266 ± 2 divisions on the oscillometric scale; this is more sensitive than conventional precision conductivity bridges.

A comparison of oscillometry and conductometry is provided by the titration of a mixture of a strong acid (HCl) and a weak acid (crotonic acid) by a strong base (NaOH). The oscillometric titration curve, the oscillometric curve transformed into a conductivity curve by the use of the transfer plot (Fig. 1), and the conductivity curve are shown in Figs. 2a, 2b, and 2c respectively.

The endpoints of the titration indicating the amounts of strong and weak acid present are provided by the intersections of the successive branches of the plot or of their extrapolations. The complete interpretation of the curve depends also on the slopes of different branches that are determined by the equivalent conductances of the contributing ions. The slopes obtained by the two techniques are compared in Table I.

It is seen that the two titrations are equivalent in all the basic aspects. The transformed oscillometric curve is virtually identical to the conductometric curve and the endpoints and slopes are in agreement (Fig. 2 and Table I). The transfer plot thus retains its validity through an acid-base titration.

The comparison of oscillometric titrations of latexes is provided by Figs. 3 and 4:

(a) A diafiltered (10) and-ion exchanged (11) copolymer latex with titrations indicating both strong- and weak-acid groups.

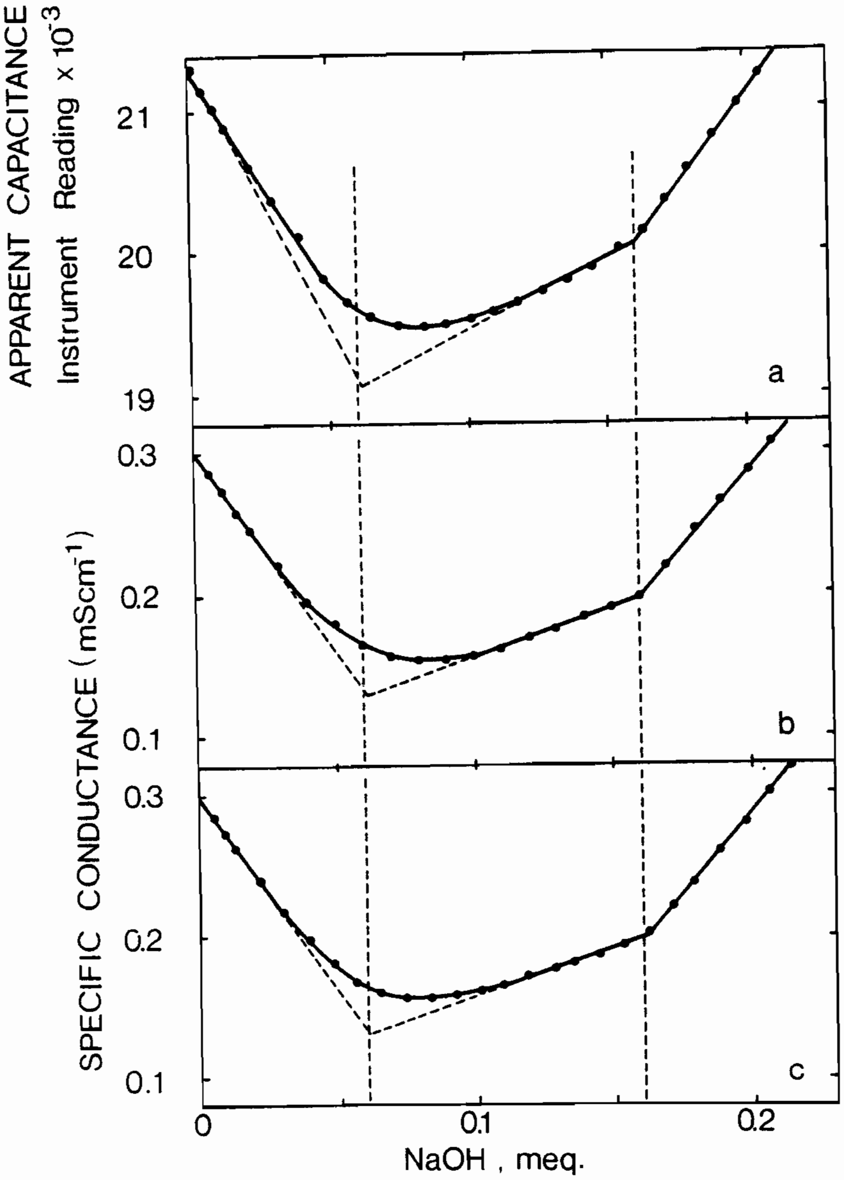


Figure 2: Comparison of oscillometric and conductometric titrations of 0.06 meq. HCl - 0.1 meq. crotonic acid mixture with NaOH. (a) Oscillometric titration curve, (b) Oscillometric curve transformed into a conductometric curve by the use of the transfer plot (Fig. 1), (c) Conductometric titration curve.

TABLE I

Comparison of branch slopes (corrected to 25°C) of the conductometric and oscillometric titrations of 0.06 meq. HCl - 0.1 meq. crotonic acid (Fig. 2).

Slope	Conductivity (cm^2 S $equiv.^{-1}$)	Oscillometry (cm^2 S $equiv.^{-1}$)	Predicted (cm^2 S $equiv.^{-1}$)
Strong Acid (SA)	-299	-299	-300
Weak Acid (WA)	+ 73	+ 72	+ 83
Excess NaOH	+245	+247	+250

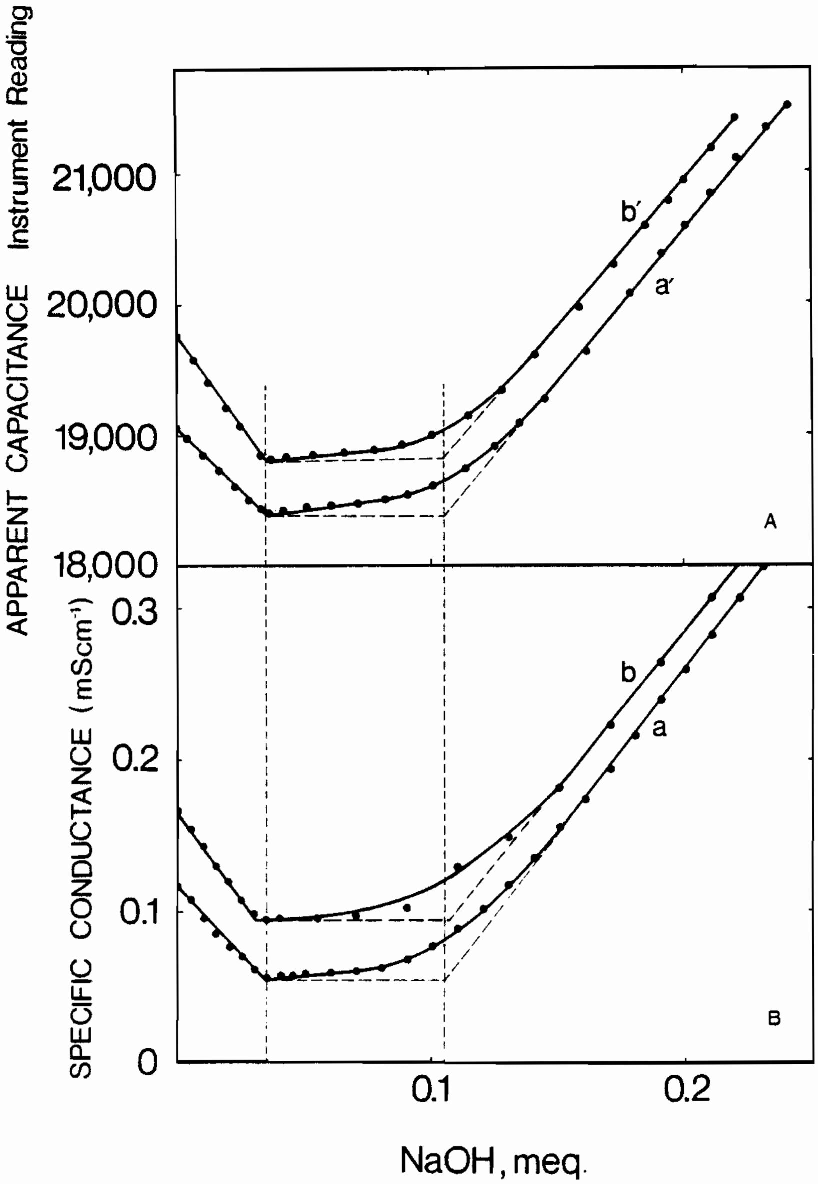


Figure 3: Comparison of oscillometric and conductometric titration of latex L28 containing both strong-acid and weak-acid groups (a) at 3.75 x 10^{-4} MKCl and (b) at 6.4 x 10^{-4} MKCl.

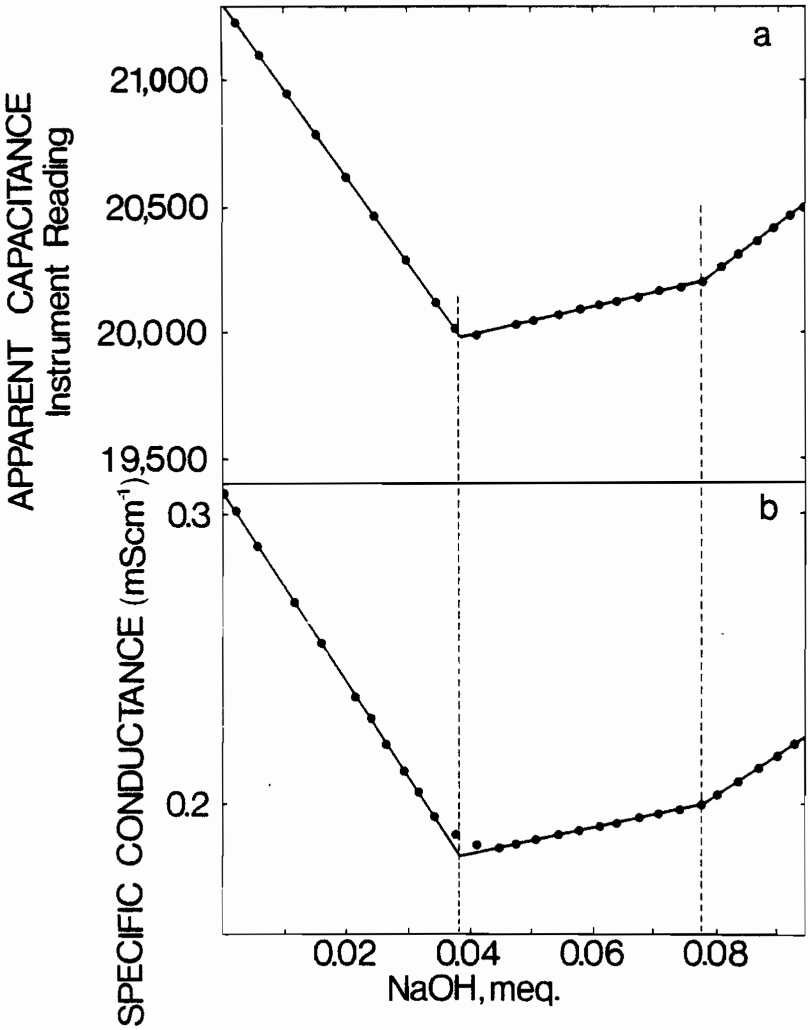


Figure 4: Comparison of oscillometric and conductometric titrations of latex L5207 containing cationic tertiary amine groups; excess HCl was added to the latex prior to the titration.

(b) A diafiltered (10) cationic latex with excess HCl titrated with NaOH.

In both sets the curves for oscillometry and conductometry show similar properties. In the first (Fig. 3), the strong-acid and weak-acid endpoints are readily identified according to the method described in (3). In the second (Fig. 4), the tertiary base endpoints are identical.

The electrolyte concentration in the latex is expected to affect the shape of the oscillometric titration curve if the conductance does not correspond to the linear portion of the transfer plot (6).

Within the linear range of the transfer plot, equivalent titrations are obtained independent of the electrolyte level (Figs. 3a and b).

At higher electrolyte concentrations, the titration is carried out under conditions corresponding to the curved transfer plot and the oscillometric titration curve is distorted (Fig. 5a). Its equivalence to the conventional conductometric curve of the same latex (Fig. 5c) is shown by replotting the oscillometric data using the transfer plot (Fig. 5b).

The determination of endpoints in the above case by the procedure described in (3) shows equivalent amounts of strong acid and weak acid from conductivity and the transformed oscillometric curves (Figs. 5b and c).

The extent of the agreement obtained in following the titrations by the two methods suggests that oscillometry is a valid alternative to conductometry in latex characterization studies with the advantage of greater sensitivity in the linear region of the transfer plot.

It should be mentioned that in order to perform successful oscillometric titrations with the 'Sargent Model V' oscillometer, a neutral electrolyte must be added to the clean latex prior to the titration. The level of electrolyte should be selected so that the titration curve

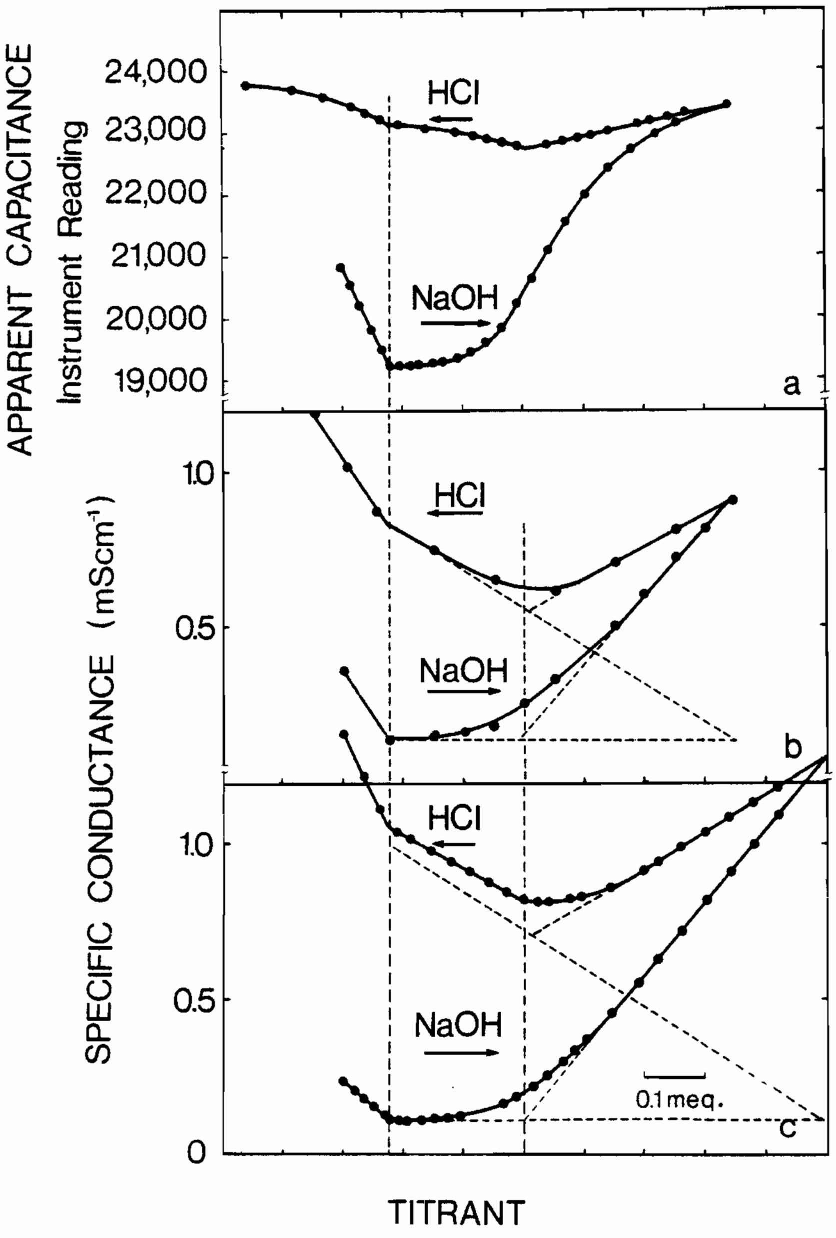


Figure 5: Titration of latex L28 at an electrolyte (KCl) concentration corresponding to the curved transfer plot. (a) Oscillometric titration at 9 x 10^{-4} MKCl, (b) Oscillometric curve transformed to conductance units by the transfer plot (Fig. 1), (c) Conductometric titration.

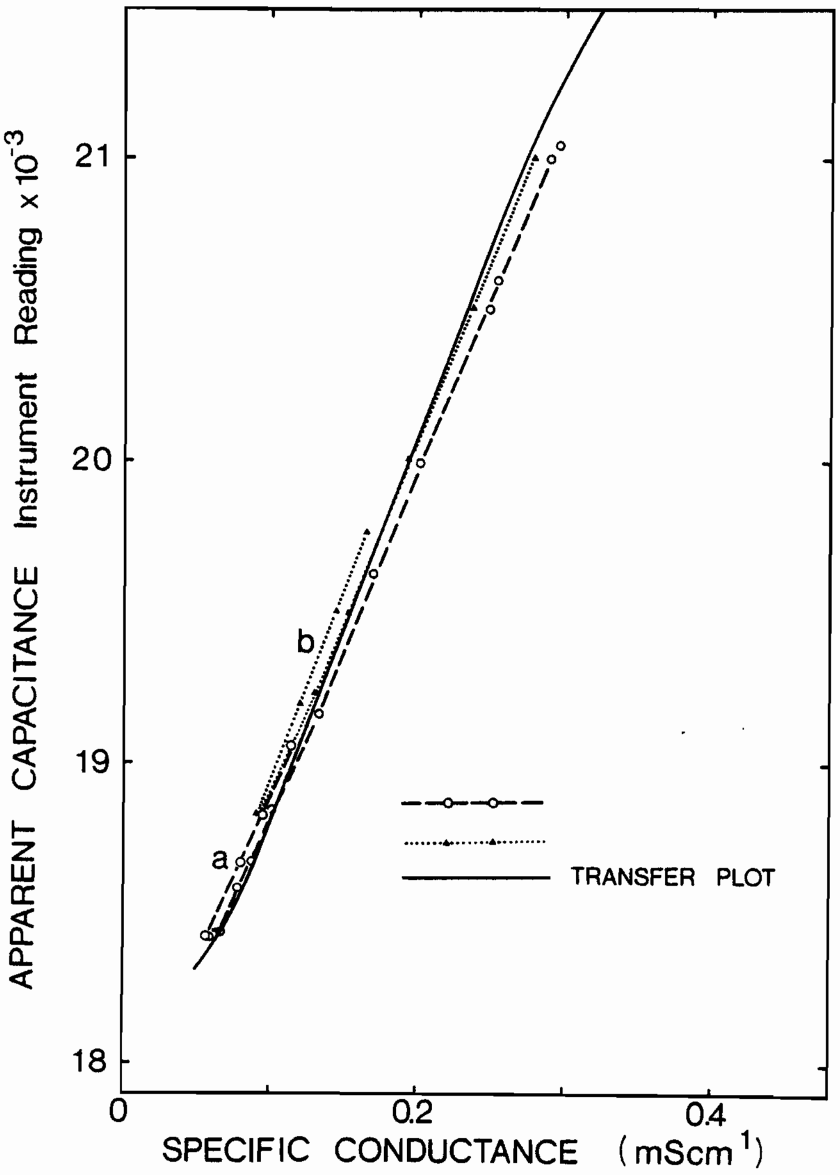


Figure 6: Transformation of the oscillometric and conductometric curves of Figs. 3a and b of latex L28 on the transfer plot of Fig. 1. The oscillometric strong-acid curve is higher than the transfer plot indicating a frequency-dependent component in latex titration.

falls in the linear region of the transfer plot (Fig. 1).

When the same latex is titrated by both oscillometry and conductometry at the same neutral electrolyte concentration, cross-plotting permits the construction of a transfer plot for the latex which may be compared with the transfer plot obtained with a simple electrolyte (Fig. 1). Comparisons are made in Fig. 6 for latex L28 (Figs. 3a and b).

The ratio of oscillometric readings to conductometric readings is higher for the latexes than for the simple electrolytes for the part of the titration curve in which strong acids or weak acids are titrated, but is similar or lower with excess titrant. The results suggest that the conductance of surface acid groups is frequency dependent with higher conductance at the higher frequency used in oscillometry. The anomalously low oscillometer readings at higher conductances has been attributed to carbon dioxide absorption during the oscillometric titrations. No further investigation relating to the frequency dependence has been carried out but the role of surface conductance is discussed elsewhere (3).

CONCLUDING REMARKS

The use of oscillometry at 5 MHz in latex characterization provides an alternative to conventional conductometry over a limited range of suspension conductivities. The use of oscillometry could be considered when additional sensitivity is required, when the presence of electrodes exposed to the latex would cause complications, or when the titrations are required in non-aqueous media.

REFERENCES

1. Vanderhoff, J.W., van den Hal, H.J., Tausle, R.J.M., and Overbeek, J. Th. G. in "Clean Surfaces: Their Preparation and Characterization for Interfacial Studies", (G. Goldfinger, Ed.), Marcel Dekker, New York, (1970).
2. Stone-Masui, J., and Watillion, A., J. Colloid Interface Sci., 52, 479 (1975).
3. Labib, M.E., This thesis, Chapter IV.
4. Shedlovsky, T., and Shedlovsky, L., in "Physical Methods of Chemistry", Vol. I, Part IIA, Chapter III, (A. Weissberger and B.W. Rossiter, Eds.), Interscience, New York, (1971).
5. Sherrick, P.H., Dawe, G.A., Karr, R., and Ewen, E.F., Manual of Chemical Oscillometry, E.H. Sargent & Co., Chicago, (1954).
6. Reilly, C.N., and McCurdy, W.H., Anal. Chem., 25, 86 (1953).
7. Pungor, E., "Oscillometry and Conductometry", Pergamon Press, London and New York, (1965).
8. Debye, P., and Flakenhangen, H., Physik. Z., 29, 121, 401 (1928); Arnold, O.M., and Williams, J.W., J. Am. Chem. Soc., 58, 2613, 2616 (1936); (see also reference (4)).
9. Labib, M.E., This thesis, Chapter II.
10. Labib, M.E., and Robertson, A.A., J. Colloid Interface Sci., 67, 543 (1978).
11. van den Hul, H.J., and Vanderhoff, J.W., J. Colloid Interface Sci., 28, 336 (1968).

CHAPTER VII

NATURE OF SURFACE CHARGES OF EMULSIFIER-FREE LATEXES

ABSTRACT

A decrease in the electrophoretic mobility of emulsifier-free polystyrene latexes upon dilution or washing has been observed and is attributed to desorption of oligomeric species from the particles. The consequences of the presence of oligomers on the electrokinetic and other properties of emulsifier-free latexes have been examined. Functional copolymer latexes do not show the same effects.

INTRODUCTION

Polystyrene latexes prepared without emulsifiers have been proposed as model colloids. Interest in these latexes has increased since they can be prepared in different sizes with high monodispersity (1-3). The absence of emulsifiers in the preparation of such latexes presumably makes them easier to clean than conventional latexes. The stability of emulsifier-free latexes has been attributed to acidic endgroups derived from the initiator and covalently attached to the polymer.

Emulsifier-free latexes have some drawbacks, however. There are difficulties in their characterization (4). It is sometimes uncertain in persulfate initiated polymerization, whether or not carboxyl groups are produced (4,5,6) and, in any event, there seems to be no reliable control of the amount of carboxyl groups obtained by various recipes or polymerization conditions (6 and 7). Cox et al (8) reported anomalous particle formation during emulsifier-free polymerization of styrene. Goodall et al (9) have also reported the formation of oligomeric species during such polymerization and these have been verified by GPC analysis after steam stripping and iso-octane extraction of the particles. Labib (10) observed anomalous electrophoretic behaviour of emulsifier-free polystyrene latexes with electrolyte concentration and also noted the presence of extraneous material in electron micrographs of these latexes (see Ref. 11).

The purpose of this paper is to investigate some of the properties of emulsifier-free latexes that affect their suitability as model colloids.

MATERIALS AND METHODS

Latexes

The characteristics of the latexes used in this study are summarized in Table I. Emulsifier-free homopolymer (polystyrene) latexes were prepared according to recipes based on Kotera et al (1), Goodwin et al (2,3) and Furusawa et al (7). Functional copolymer latexes were prepared in the absence of emulsifier by procedures following Juang and Krieger (12) and Labib (13).

Mobility Measurements

(a) Mass transport electrophoresis: Electrophoretic mobilities were measured by the transfer of latex under the influence of an electric field between the two chambers of a modified Hittorf cell. Gravimetric and turbidimetric analysis were used to measure the amount of latex transferred. The apparatus was calibrated with human erythrocytes and the mobilities calculated (14,15) were identical with those measured by microelectrophoresis under the same conditions.

(b) Microelectrophoresis: A 'Zeiss Cytopherometer' was used for mobility measurements employing Pd/H_x reversible electrodes (16). Measurements of at least 50 particles were made at the front and back stationary levels as well as at 1/6 and 1/2 depths of the flat cell used. The true mobility (u_t) was calculated from the mobilities at 1/6 ($u_{1/6}$) and 1/2 ($u_{1/2}$) cell depths according to the following equation:

$$u_t = 0.75\, u_{1/6} + 0.25\, u_{1/2}$$

TABLE I

The Characteristics of the Latexes Used in this Study (cf. Refs.(12 and 13).

Latex Code	Type of Latex	Particle Diameter nm
LS 1-2	Homopolymer (Polystyrene)	340
LS 3-4	"	460
L 11	"	362
L 13	"	550
L 17 B	"	1005
L 16	Copolymer (Styrene and NaSS*)	950 (Bimodal)
L 18	"	118

* NaSS denotes sodium salt of styrene p-sulfonic acid.

Methods of Cleaning and Equilibration

(a) Diafiltration: Latexes were cleaned using a 'TCF 10' Amicon diafiltration apparatus (11). Diafiltration was carried out at constant volume against distilled water until the conductance of filtrate equalled that of distilled water (8×10^{-7} S cm^{-1}). Diafiltration stripping was achieved by continued diafiltration of latexes beyond the above criterion. Stripping was effected against distilled water or isoionic solution having the same conductance as the serum. A latex could be concentrated by diafiltration but without serum replacement.

The materials used for cleaning and washing were all analytical grade in order to avoid contamination.

(b) Dialysis: Dialysis was performed in a drum-shaped cell. The two membranes were cellulose nitrate (Sartorius) with a nominal pore diameter of 0.2 μm. Cleaning by dialysis was considered complete when the dialyzate conductance equalled that of distilled water (8×10^{-7} S cm^{-1}) over a long period of time. Equilibration of a latex with KCl solutions was considered complete when the EMF between Ag/AgCl reversible electrodes placed on each side of the membrane reached zero mV.

(c) Ion-exchange cleaning: Ion-exchange cleaning was achieved by a batch process using a mixed-bed resin cleaned and conditioned according to van den Hul and Vanderhoff (18). The cleaning was considered complete when a consistent low latex conductance was unchanged when more resin was added.

(d) Centrifugal Washing: Latexes were centrifugally washed by repeated centrifugation and exchange of the serum by isoionic solution.

Methods of Identification of Oligomeric Species

(a) GPC: 'Waters Liquid Chromatograph' Model 301 with a 'Styrogel' column was calibrated with polystyrene standards dissolved in tetrahydrofuran (THF). The serum of emulsifier-free latexes was separated by filtration (11) using a 0.05 μm pore diameter cellulose nitrate membrane. The serum was concentrated by evaporation under vacuum and the residue was extracted by THF. A concentrate of the latter was used for the GPC analysis. The molecular weight was estimated from the position of the peak produced.

(b) Dye-interaction and dye-partition techniques: The dye-interaction technique used in this work was explained by Palit (19). This technique is based on measuring the change in absorbance of a Rhodamine 6GX reagent in benzene upon its interaction with carboxyl, sulfate, or sulfonate groups. The serum of the latex was separated by the diafiltration apparatus (12), concentrated by evaporation, extracted in benzene, mixed with the Rhodamine reagent, and then analyzed by the above recommended procedure (19). The above technique was sensitive for concentrations above 10^{-6} mole/l of the charged groups.

The dye-partition technique was also employed in the identification of oligomers using the methylene blue reagent and the procedure following Ref. 19. The serum of the latex was concentrated by evaporation and then added to the above reagent. The mixture was extracted in chloroform and then analyzed spectrophotometrically at $\lambda = 655$ nm.

(c) Electrokinetic titrations: The electrokinetic titrations were based on the decrease of the mobility of a latex with tertiary amine surface groups upon its addition to the serum of the anionic emulsifier-free latex to be tested. The number of the tertiary amine surface groups of the latex used was determined by conductometric titrations. A known amount of this tertiary amine latex was added to different volumes of the emulsifier-free latex serum. The number of anionic groups needed to achieve zero electrophoretic mobility was taken to be equal to the number of the tertiary amine surface groups. This method was sensitive to concentrations of oligomers in the range of 10^{-6} - 10^{-8} mole/l.

Methods of Dilution

The latexes were diluted by adding them in different proportions to the appropriate solution (dialyzate, isoionic solution, or centrifugate) and then leaving them overnight to equilibrate. The dilutions were made in volumetric flasks, cleaned with chromic-acid solution and soaked for several days in distilled water.

In measuring the time-dependence of the electrophoretic mobilities of emulsifier-free latexes, the dilutions were made immediately prior to use. Care was taken to eliminate the possibility of latex contamination with electrode products by frequent flushing of the electrophoresis cell with the test suspension.

RESULTS

The electrophoretic mobilities of emulsifier-free polystyrene latexes decreased upon dilution of such latexes with dialyzate (Fig. 1). This decrease was observed when the mobility measurements were followed entirely by microelectrophoresis or by both microelectrophoresis and the mass transport technique. The mobility decreased significantly at high dilutions and then remained constant.

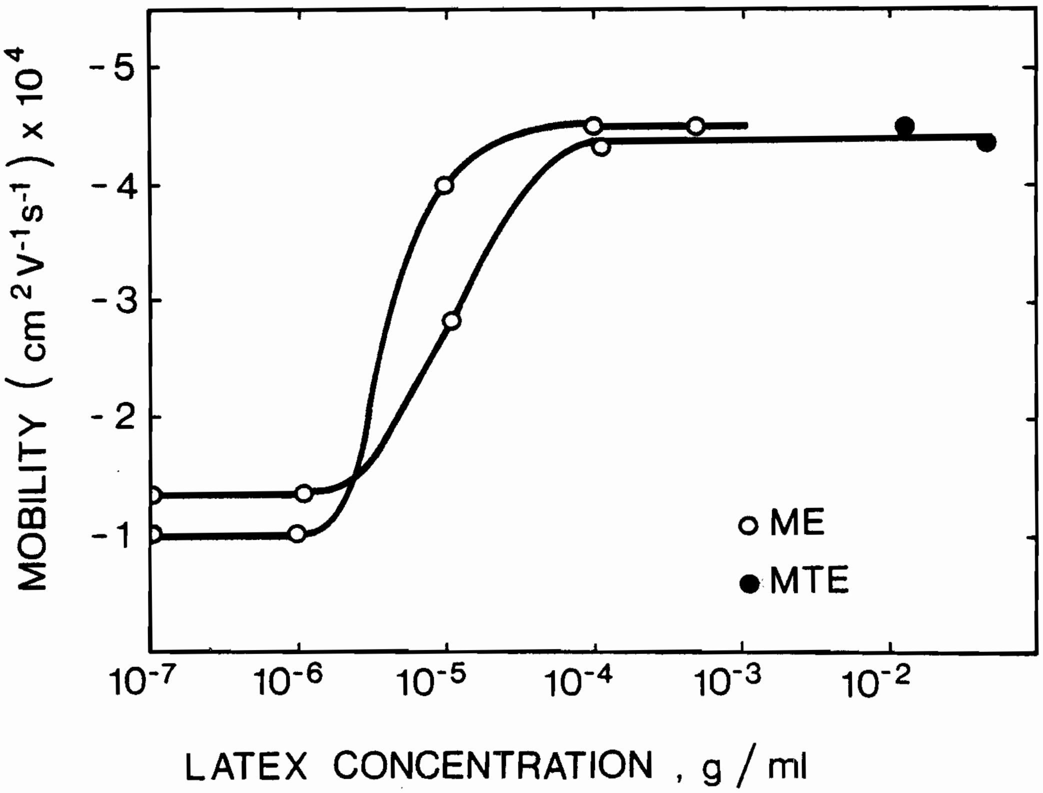


Figure 1: Electrophoretic mobility decrease upon dilution with dialyzate of emulsifier-free polystyrene latexes. The measurements were followed entirely by microelectrophoresis (ME) for latex (L 13) and by microelectrophoresis and mass transport electrophoresis (MTE) for latex (L11).

The dilution effect was extended to include several emulsifier-free polystyrene latexes at different electrolyte concentrations and has shown a significant mobility drop in such cases (Fig. 2A). However, when functional copolymer latexes were subjected to similar dilution treatments, no mobility decrease was observed (Fig. 2B). The decrease in the apparent mobility with latex concentration, in this case, occurs unless a backflow correction (20,21) is made.

The mobility of emulsifier-free polystyrene latexes has been shown to be a time-dependent process (Fig. 3). The mobility decreased rapidly following dilution and then steadily thereafter. When the latex was diluted with isoionic solution, the mobility values were lower than those obtained when the dilution was made with dialyzate (Fig. 3).

The decreased mobility of emulsifier-free polystyrene latexes (dialyzed or ion exchanged) at high dilution has remained constant or decreased slightly when the latexes were concentrated by removing serum by filtration (Fig. 4).

Figure 5 shows the dilution behaviour of an emulsifier-free latex at different KCl concentrations. At high electrolyte concentrations (10^{-3} - 10^{-2} MKCl), a significant decrease in mobility upon dilution occurred at higher latex concentration. However, at lower electrolyte concentration the mobility showed a slight but steady decrease.

When diafiltration of previously cleaned latex was continued at different ionic strengths, a progressive mobility decrease was observed (Fig. 6). Also, continued washing of the same latex by repeated centrifugation achieved a similar mobility decrease (Fig. 5 (inset)).

Dilutions of emulsifier-free polystyrene latex with its centrifugate supernatant and with isoionic solutions are shown in Fig. 7. The

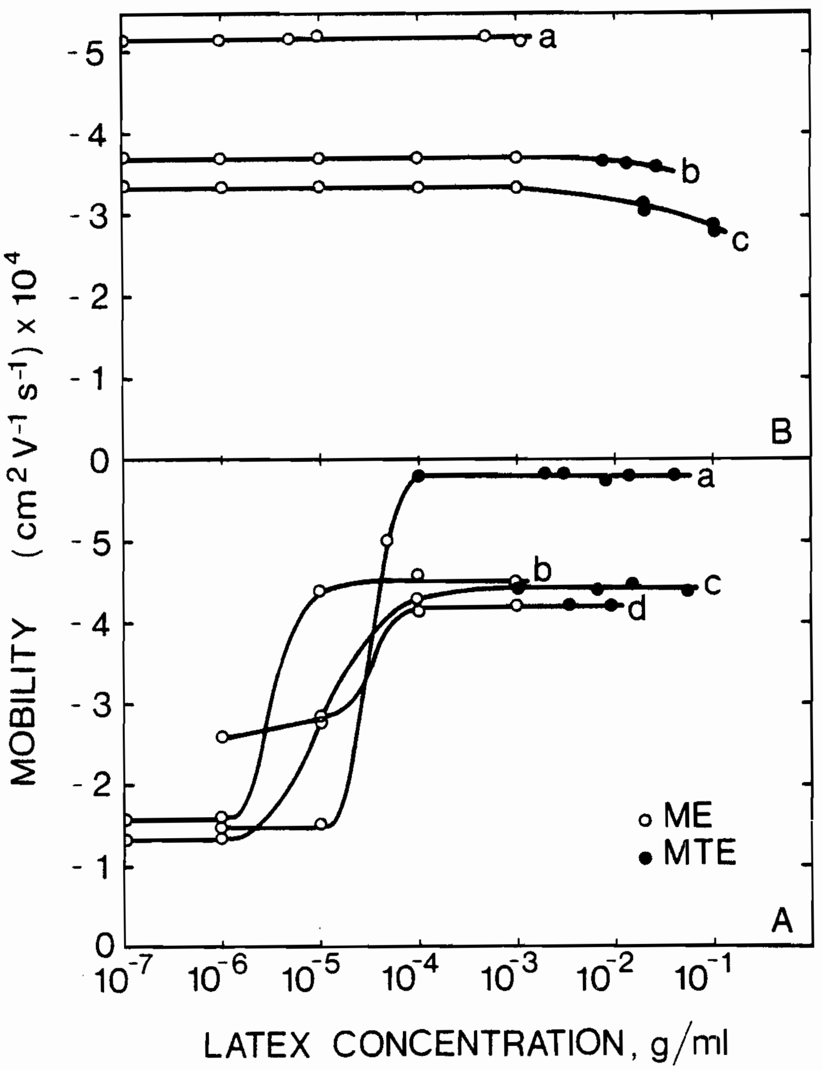


Figure 2: Mobility behaviour upon the dilution of emulsifier-free polystyrene latexes (shown in A) and functional copolymer latexes (shown in B). (A) includes: (a) latex LS(3-4) diafiltered and equilibrated with 10^{-2} MKCl, (b) Latex L 13 diafiltered and equilibrated with 7 x 10^{-4} MKCl, (c) Latex L 11 dialyzed and equilibrated with 7 x 10^{-4} and (d) Latex LS (1-2) ion exchanged and equilibrated with 10^{-3} MKCl. (B) contains: (a) Latex (L 16), (b) Latex (L 18), and (c) Latex L 18 covered with Tween (60).

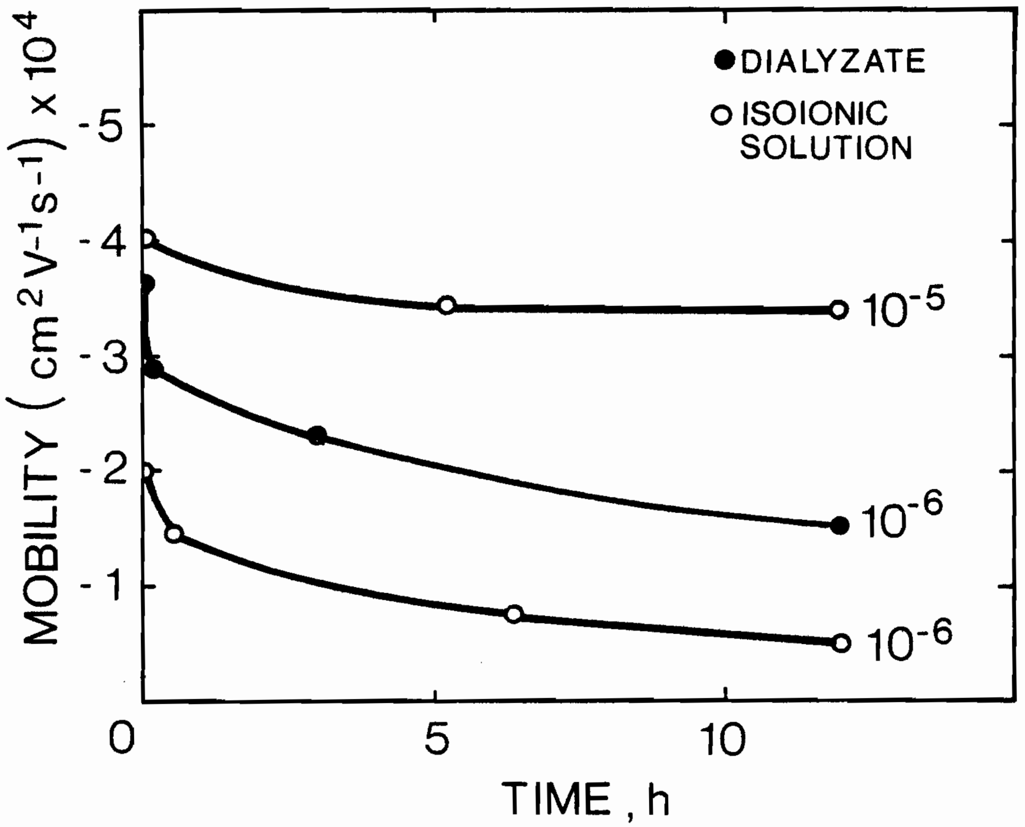


Figure 3: Time dependence of mobility following a dilution of emulsifier-free polystyrene latex L 13. Curves in descending order are at 10^{-5} g/cc diluted with isoionic solution, at 10^{-6} g/cc diluted with dialyzate and at 10^{-6} g/cc diluted with isoionic solution.

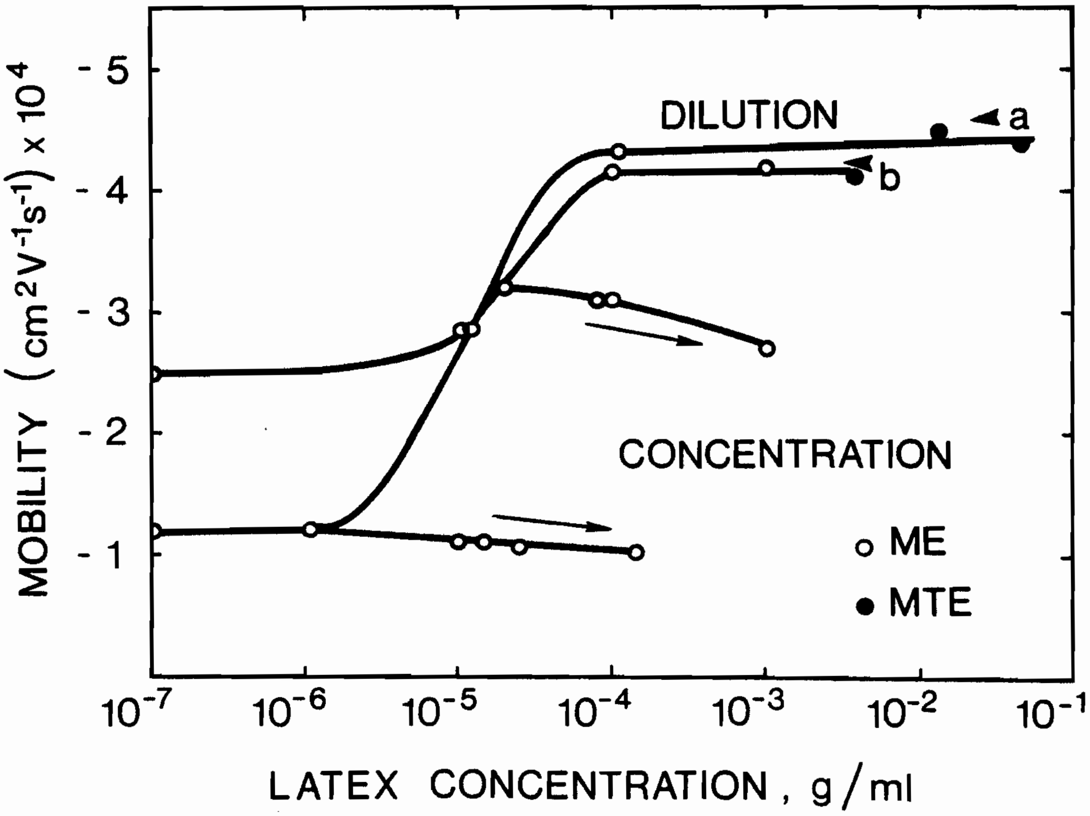


Figure 4: Electrophoretic mobility (measured by ME and MTE) behaviour of emulsifier-free polystyrene latexes upon dilution and reconcentration with dialyzates of (a) dialyzed latex L 11 and (b) ion-exchanged latex LS (1-2).

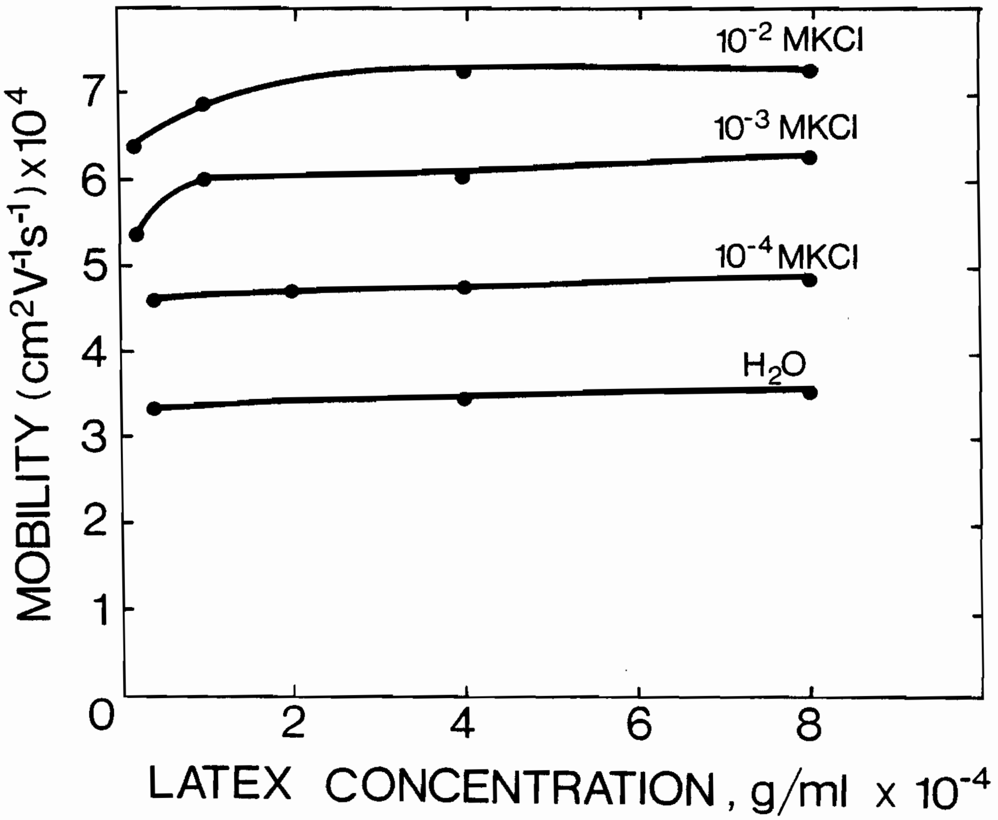


Figure 5: Dilution of emulsifier-free latex (L 17 B) with isoionic KCl solutions of the concentrations shown.

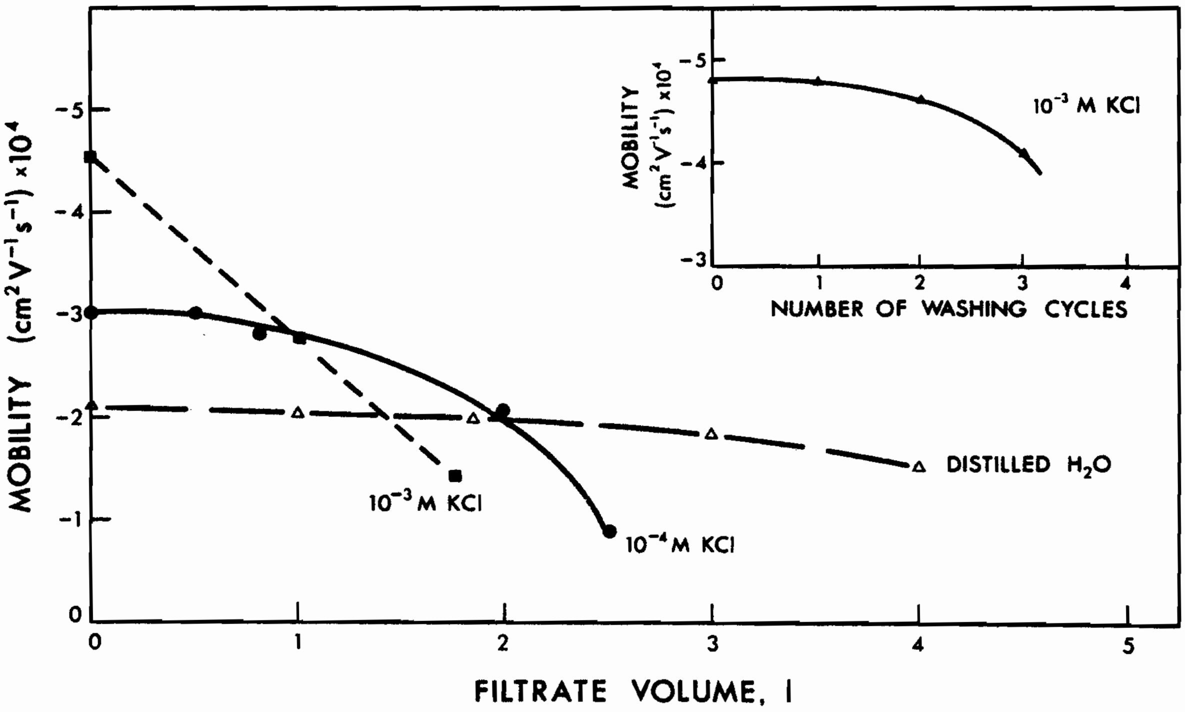


Figure 6: Mobility decrease of emulsifier-free latex L 13 upon diafiltration washing with isoionic solutions at several electrolyte concentrations. The inset shows the change of mobility upon centrifugal washing of the same latex.

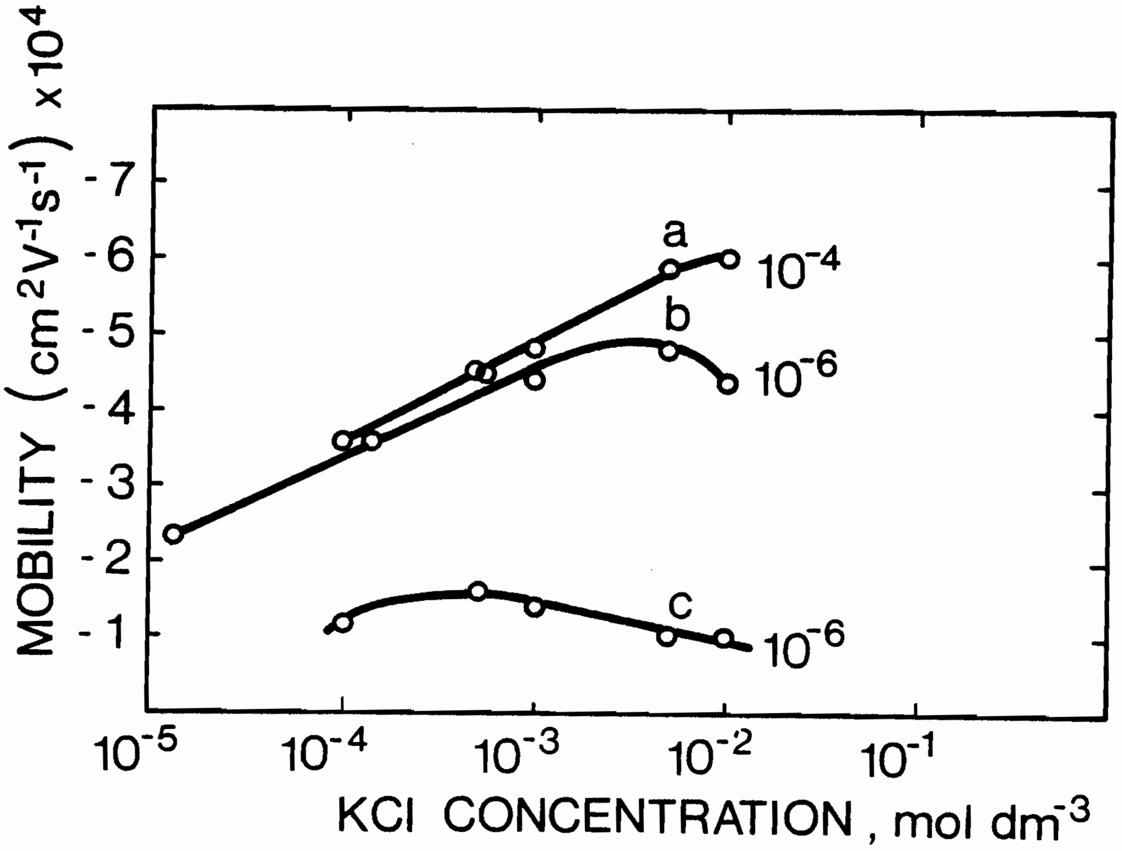


Figure 7: Electrophoretic mobility behaviour of emulsifier-free polystyrene latex L 13 at different ionic strengths: (a) at 10^{-4} g/cc in isoionic solution, (b) diluted with supernatant centrifugate to 10^{-6} g/cc and (c) diluted with isoionic solution to 10^{-6} g/cc.

mobility was shown to be constant or decreased slightly when the latex was diluted with its centrifugate, but decreased drastically when the dilution was made with isoionic solutions.

Detection and identification of desorbed charged material in the serum or with the latex have shown the following results:

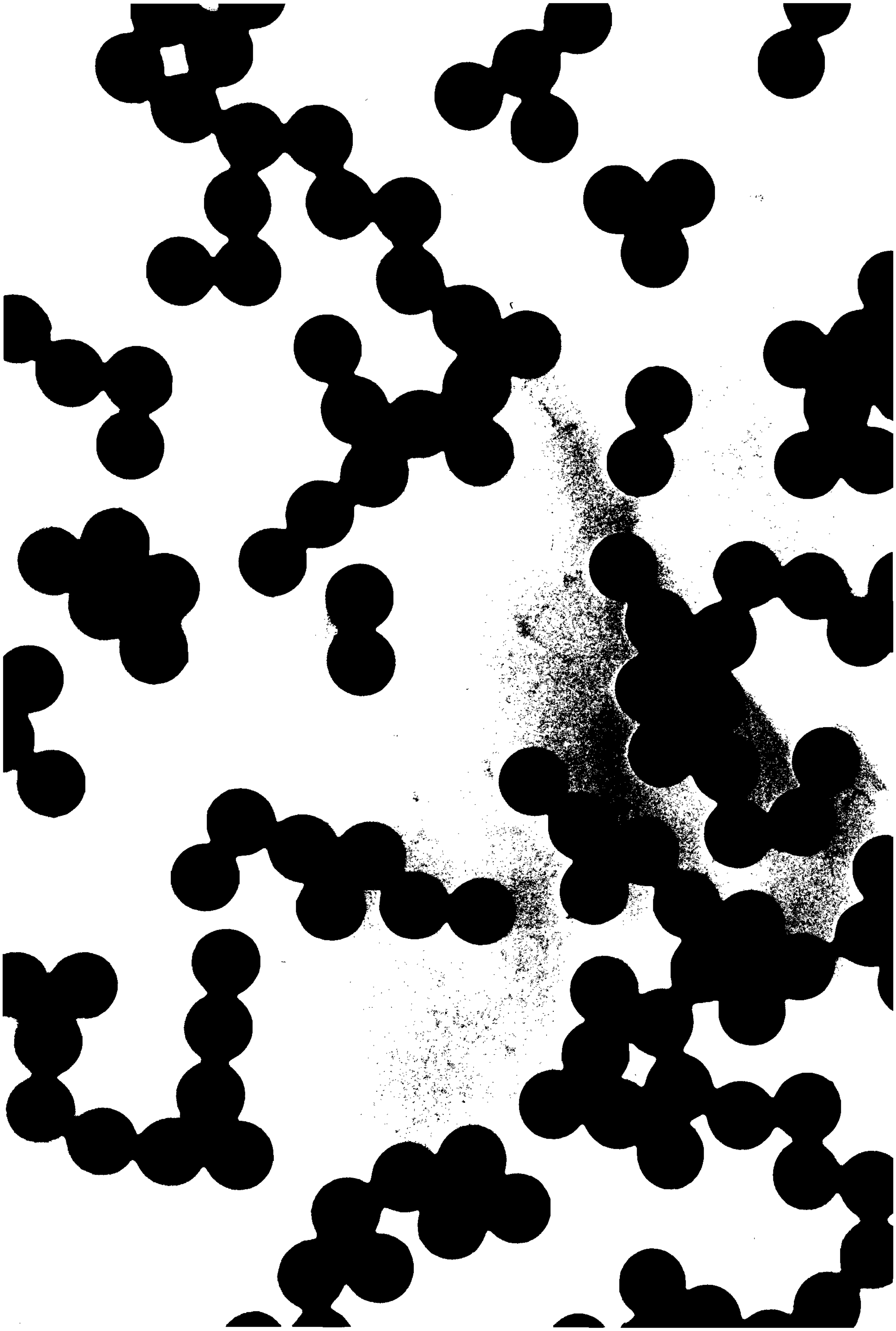
(a) Electron micrographs of emulsifier-free polystyrene latexes have shown the presence of extraneous material in the latex that dries down to membranous or filamental material (Fig. 8).

(b) GPC analysis of a THF extract of a residue prepared by evaporation of a particle-free serum of an emulsifier-free polystyrene latex provided evidence of the presence of a polystyrene material of molecular weight in the range of 1,600 - 16,000. An infrared spectrum of the above residue revealed a typical polystyrene structure.

(c) The dye-interaction technique performed on the serum of emulsifier-free polystyrene latexes has shown the presence of charged species with these latexes. It should be noted that other acidic species (e.g. persulfate decomposition products) do not interfere because of their insolubility in benzene. The dye-partition technique has also shown large amounts of oligomers with uncleaned latexes.

(d) Electrokinetic titrations have shown the presence of anionic species with emulsifier-free latexes in the order of 10^{-6} - 10^{-8} mole/l. The dilutions of a tertiary amine polystyrene latex with an appropriate isoionic solution have produced a more or less constant mobility (Fig. 9, curve a). Dilution of this positively-charged latex with the serum of emulsifier-free polystyrene anionic latexes resulted in a mobility decrease and finally in a sign reversal indicating the presence of charged anionic species (Fig. 9, curve b).

Figure 8: Transmission electron micrograph of emulsifier-free latex LS (3-4) showing the presence of extraneous material in the latex.



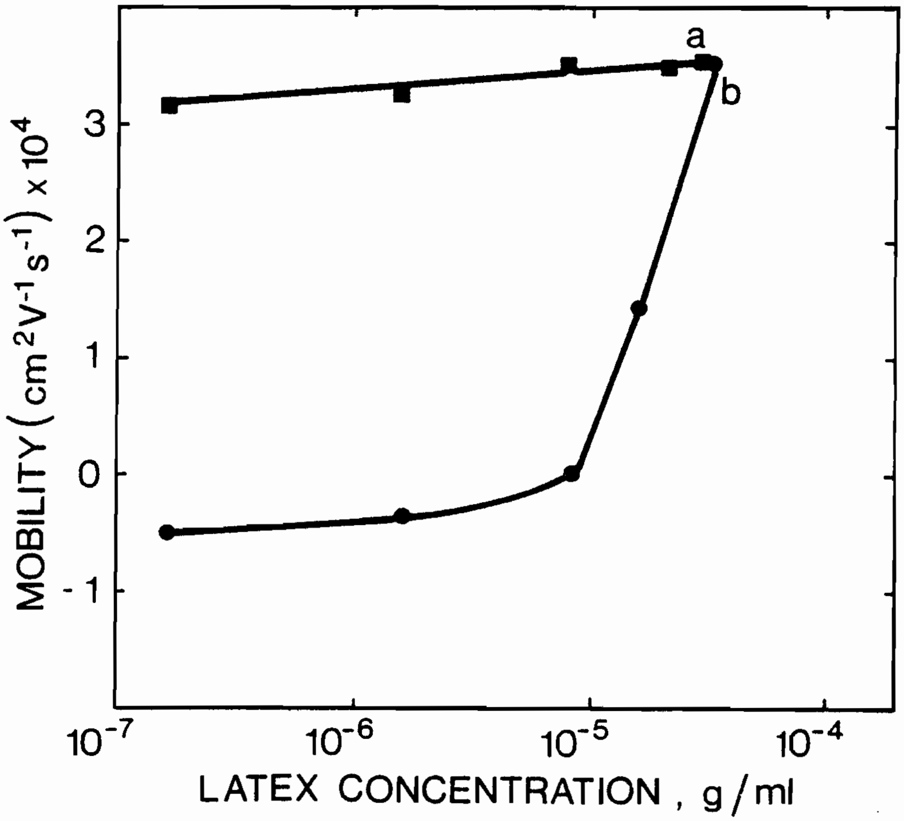


Figure 9: Electrokinetic titration shown as mobility decrease of a tertiary amine latex when diluted with a serum of an emulsifier-free anionic polystyrene latex (curve (b)). Curve (a) shows the constancy of the mobility when the above latex is diluted with an isoionic solution.

DISCUSSION

The decrease in electrophoretic mobility produced by dilution or continuous washing of emulsifier-free latexes is attributed to desorption of charged oligomeric species. This is demonstrated by the following:

(a) Copolymer latexes subjected to similar dilution procedures did not show a mobility decrease (Fig. 2B); this indicates that the mobility decrease that is observed upon dilution of emulsifier-free latexes is not an effect of particle concentration alone, but must be attributed to other causes.

(b) The time-dependence of mobility decrease in the dilution experiment (Fig. 3) is consistent with diffusion processes. When the latex is diluted, surface oligomers desorb from particles causing the observed mobility to decrease.

(c) When the latex was diluted, the mobility decreased; when it was concentrated by diafiltration, the mobility remained more or less constant (Fig. 4). This result indicates that the mobility decrease upon dilution is an irreversible process due to a permanent loss of charged surface oligomers and is not due to particle concentration effects.

(d) When diafiltration of a cleaned emulsifier-free polystyrene latex was continued with isoionic solutions, the mobility decreased with the extent of diafiltration (Fig. 6). The mobility decrease in these experiments is attributed to a decrease in the surface charge resulting from stripping oligomers from the surface of the particles.

In order to explain this desorption behaviour, it is assumed that before dilution, oligomers are distributed with an equilibrium established between oligomers in solution, oligomers adsorbed on the particle surfaces and suspended oligomer aggregates. When dilution initially occurs (Fig. 1), the electrophoretic mobility remains essentially constant and there is thus no indication of change in the amount of oligomers adsorbed. The equilibrium may correspond to the plateau of the adsorption isotherm and thus be insensitive to changes in bulk concentration or the bulk concentration may be maintained by the dissolution of oligomer aggregates. Further dilution results in decreased mobility; this is assumed to correspond to desorption as the bulk concentration is reduced below the plateau region and as any oligomer aggregates disappear. The above view is supported by a lack of mobility decrease at high dilution ($\phi = 10^{-6}$) when the latex was diluted by its centrifugate (Fig. 7), in contrast with the drastic mobility decrease obtained when the latex was diluted with isoionic solution.

The presence of charged oligomers was detected by GPC, dye-interaction and dye-partition techniques, and electrokinetic titrations (see Results section and Fig. 9). The presence of extraneous material with emulsifier-free latexes, as indicated in electron micrographs of these latexes, (Fig. 8) may be associated with the presence of oligomer aggregates in the latex. Moreover, the desorption resulting from dilution with dialyzate (Figs.1 and 2) but not with centrifugate (Fig. 7) suggests that oligomeric material is slow to diffuse through the dialysis membrane and is not readily removed by this means.

When the electrolyte level is increased at high latex concentration, the electrophoretic mobility is increased. The dilution behaviour remains qualitatively the same but the drop in mobility occurs with less dilution (Fig. 5). It is thus evident that the adsorption equilibrium has been changed and this suggests that more oligomers are adsorbed. This can only occur if the adsorption capacity of the surface indicated by the plateau of the adsorption isotherm is increased and this implies a change in the orientation of adsorbed species or in the structure of the adsorbed layer. This possibility is discussed elsewhere (10). The increased mobility indicates a higher ζ-potential, despite the increased ionic strength, which reflects changes in the number and the arrangement of charged species in the adsorbed layer and the position of the shear plane.

The rate of decrease in mobility upon dilution (Fig. 3) is thought to reflect the rate of approach to equilibrium adsorption values. The rate of decrease in mobility in diafiltration washing measures the rate of desorption into a slowly but continuously diluted environment. The mobility behaviour in Fig. 6 is qualitatively similar to that observed in the incremental dilution experiments (Figs. 1 and 2). The response to electrolyte concentration is also similar and less diafiltration is required to reduce the mobility at high electrolyte concentrations (Fig. 5). Although adsorption equilibrium is presumably not maintained during this continuous dilution process, the desorption of oligomers is logically governed by the concentration of the dissolved oligomers in the medium.

The consequences of the presence of non-integrated, adsorbed, and extraneous oligomeric charged material in the emulsifier-free homopolymer latexes are as follows. Firstly, there is a need for cleaning methods that remove desorbed, unadsorbed, and extraneous material by serum replacement rather than by techniques relying on diffusion--that is, diafiltration or centrifugal washing is preferred to dialysis or ion exchange. Secondly, model systems are to be sought using other recipes that produce copolymer and cross-linked latexes whose surface groups are permanently bonded.

CONCLUDING REMARKS

Polystyrene latexes polymerized in the absence of emulsifiers have been shown to be unreliable as model colloids because of the presence of charged oligomers in the system and their desorption from the surface of particles upon dilution or washing. Desorption-adsorption equilibria of such oligomers were found to explain the observed electrophoretic behaviour of these latexes. Copolymer latexes in which the stabilizing charges are provided by a functional comonomer may be more appropriate for use as model colloids since their electrophoretic mobility is unaffected by dilution or diafiltration.

REFERENCES

1. Kotera, A., Furusasa, K. and Takeda, Y., Kolloid Z.u.Z. Polymere 239, 677 (1970).
2. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Brit. Polymer J. 5, 347 (1973).
3. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Colloid Polymer Sci. 252, 464 (1974).
4. Goodall, A.R., Hearn, J. and Wilkinson, M.C., J. Polymer Sci. 17, 1019 (1979).
5. Shaw, J.W., J. Polymer Sci. C27, 237 (1969).
6. Stone-Masui, J. and Watillon, A., J. Colloid Interface Sci. 52, 479 (1975).
7. Furusawa, K., Norde, W. and Lyklema, J., Kolloid Z.u.Z. Polymere 250, 908 (1972).
8. Cox, R.A., Wilkinson, M.C., Creasey, J.M., Goodall, A.R. and Hearn, J., J. Polymer Sci. 15, 2311 (1977).
9. Goodall, A.R., Wilkinson, M.C. and Hearn, J., J. Polymer Sci. 15, 2193 (1977).
10. Labib, M.E., This thesis, Chapter VIII.
11. Labib, M.E. and Robertson, A.A., J. Colloid Interface Sci. 67, 543 (1978).
12. Juang, M.S. and Krieger, I.M., J. Polymer Sci. 14, 2089 (1976).
13. Labib, M.E., This thesis, Chapter II.
14. Shaw, D.J., "Electrophoresis", Acad. Press, London and New York, p. 59-60 (1969).

15. Furchgott, R.F. and Ponder, E., J. Gen. Physiol. 24, 447 (1941).

16. Neihof, R., J. Colloid Interface Sci. 30, 128 (1969).

17. McCarvill, W.T. and Fitch, R.M., J. Colloid Interface Sci. 64, 403 (1978).

18. van den Hul, H.J. and Vanderhoff, J.W., J. Colloid Interface Sci. 28, 336 (1968).

19. Palit, S.R., Anal. Chem. 33, 1441 (1961); Palit, S.R. and Ghosh, P. in "Microchemical Techniques" (N.D. Chernis, Ed.), p. 663. Interscience, New York, (1961).

20. Stigter, P., Rec. Trav. Chim. 73, 771 (1954).

21. Homola, A. and Robertson, A.A., J. Colloid Interface Sci. 51, 202 (1975).

CHAPTER VIII

ELECTROKINETIC PROPERTIES OF EMULSIFIER-FREE LATEXES

ABSTRACT

The electrophoretic mobility of emulsifier-free latexes has been investigated to determine the suitability of these latexes as model colloids. An unexpected ζ-potential increase with electrolyte concentration has been observed and is discussed on the basis of the nature of the surface charge.

INTRODUCTION

Monodisperse emulsifier-free latexes can be prepared in one step and in a wide range of particle sizes (1-4). The ease of their preparation and the absence of emulsifiers suggest their use as model colloids.

Since the investigation of electrokinetic behaviour is often used as an approach to the principles of colloid and surface science (5), it is our purpose in this paper to study such properties for emulsifier-free latexes in order to determine their suitability for use as model colloids.

MATERIALS AND METHODS

Latexes

The characteristics of the latexes used in this study are shown in Table I. Details of their preparation can be found in Ref. (4).

Electrophoresis

A 'Zeiss Cytopherometer' microelectrophoresis apparatus was used to measure mobilities. The apparatus was calibrated with human erythrocytes in a phosphate buffer (6). Measurements of the mobilities of at least 50 particles were made at the front and back stationary levels and at 1/6 and 1/2 depths of the rectangular cell used. The true mobility (u_t) was calculated from the mobilities at 1/6 ($u_{1/6}$) and 1/2 ($u_{1/2}$) cell depths employing the following equation:

$$u_t = 0.25\ u_{1/6} + 0.75\ u_{1/2} \qquad (1)$$

All the mobility measurements were made at 25°C and at particle volume fractions $> 10^{-4}$ where there were no complications from dilution effects (7).

Particle Size Determination

The particle sizes of the latexes used in this study were determined by the analysis of their transmission electron micrographs; at least 50 particles were analyzed for this purpose. The sizes of the latexes used are indicated in Table I.

TABLE I

The Characteristics of Latexes Used in This Study (cf. Ref. 4)

Latex Code	Type of Latex	Particle Radius (a) (m) x 10^6	Surface Charge Density (σ_o) $\mu C/cm^2$
L 14	Homopolymer (Polystyrene)	0.231	3.81
L 17	"	0.234	-
L 16	Copolymer (prepared with NaSS in the absence of methanol)	0.475	-
L 25	Copolymer (prepared with NaSS as comonomer in 30% methanol)	0.189	7.54

Conductometric Titrations

The surface charge densities (σ_o) of the latexes were determined by conductometric titrations following the procedure and the interpretation given by Labib (8). The titrations were made in the absence of electrolyte and in the presence of varying amounts of neutral electrolytes. The surface charge densities determined by titrations were independent of the electrolyte concentration as confirmed by others (9).

Method of Plotting the Mobility Data

The electrophoretic mobilities were plotted against κa - the ratio of the particle diameter (a) to the diffuse layer thickness $1/\kappa$. κ is defined as:

$$\kappa = \left[\frac{2e^2 N_A c Z^2}{\varepsilon K T}\right]^{1/2} \qquad (2)$$

where e is the electronic charge,

N_A is the Avogadro's number,

c is the electrolyte concentration in the bulk,

z is the valence of the counter-ion,

ε is the permittivity of the bulk medium,

K is the Boltzmann constant, and

T is the absolute temperature.

κa is thus proportional to the square root of the electrolyte concentration in a given system.

The mobility values are plotted in this work on graphs showing the mobility predicted by calculations according to Wiersema, Loeb and Overbeek (WLO) (10), as a function of κa for several constant values of ζ-potential. These calculations take into account the retardation and relaxation effects of the diffuse layer on the mobility of the particle assuming a constant ζ-potential and symmetrical 1-1 electrolyte. This manner of plotting the experimental result is convenient in interpreting the mobility data and in following the change in ζ-potential with the electrolyte concentration (expressed as κa).

RESULTS

Examples of electrophoresis results are shown in Fig. 1 for three emulsifier-free latexes. The mobility plot for an emulsifier-free homopolymer latex (L 14) falls across the theoretical plots calculated by the WLO theory for constant ζ-potential in such a way as to indicate an increase in ζ-potential of 50 mV as the concentration of electrolyte (as represented by κa) increases. The copolymer latex (L 25) shows conformity with the WLO plot indicating a constant ζ-potential. The third latex (copolymer) shows a falling ζ-potential at higher electrolyte concentrations.

A decrease in ζ-potential with electrolyte concentration is predicted in simple colloid systems, and the increase or the constancy observed here (Fig. 1) is unexpected. The following experiments were designed to determine what factors could affect the results.

Fig. 2 shows that for the homopolymer latex the increase in ζ-potential is substantially unaffected by the counter-ion of the added electrolyte, and Fig. 3 shows that the effect is independent of the co-ion species.

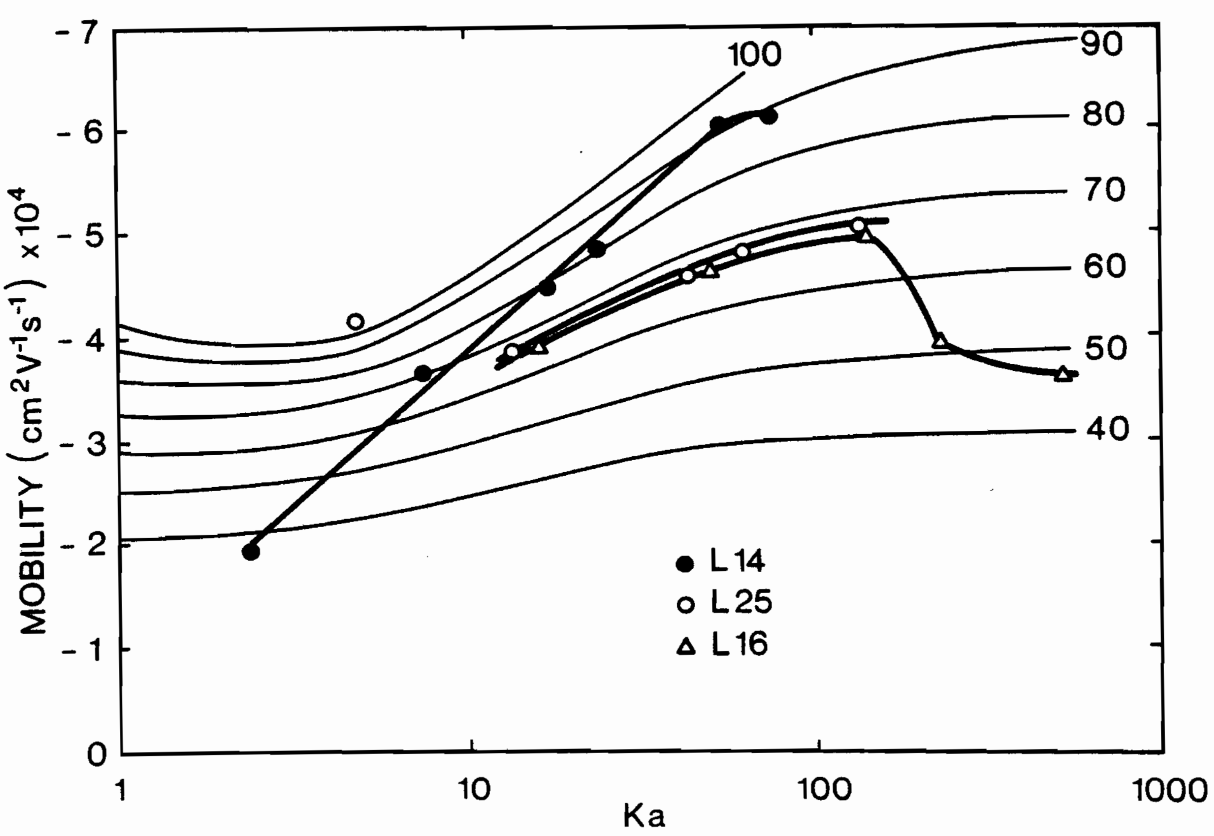


Figure 1: Electrophoretic mobility (u) - κa plots of emulsifier-free homopolymer latex L 14 and copolymer latexes L 25 and L 16. The mobility plot of latex L 14 falls across the predicted WLO mobilities indicating an increase in ζ-potential.

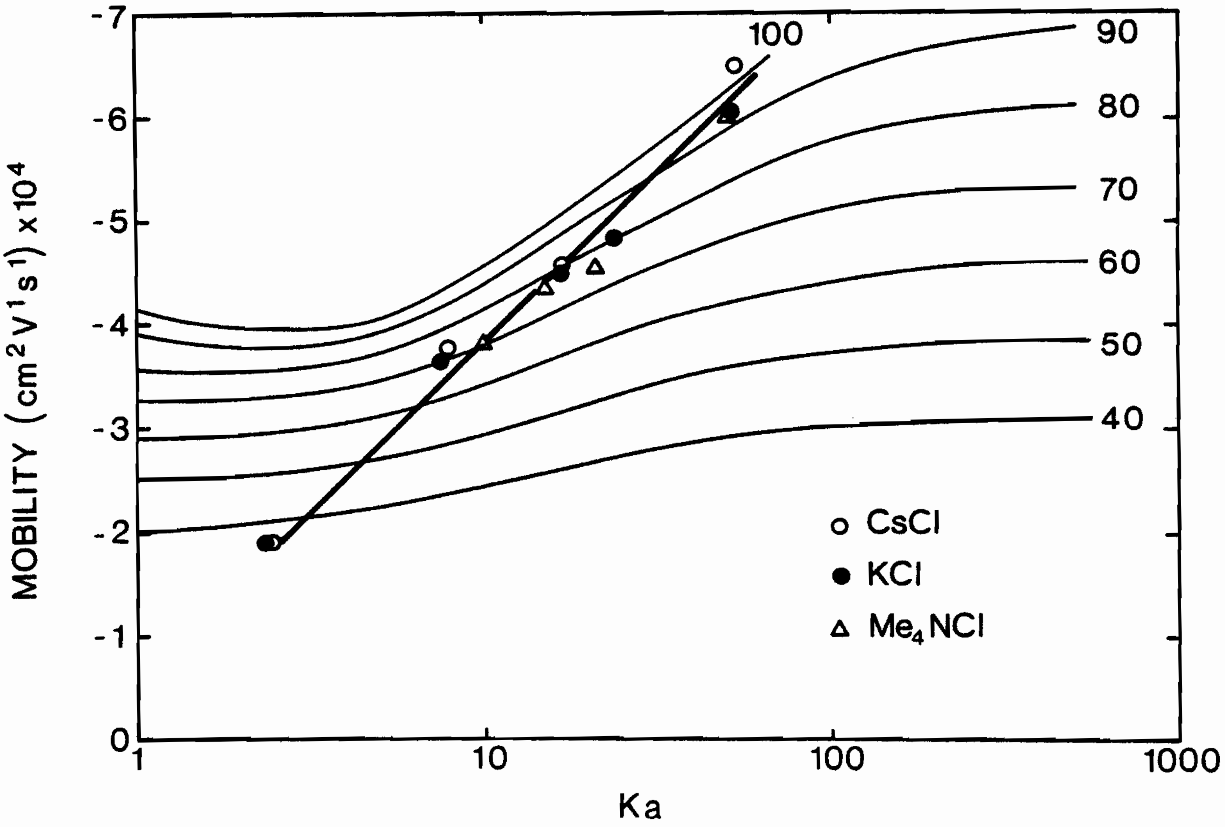


Figure 2: Effect of different monovalent cations on the u-κa plots of emulsifier-free homopolymer latex L 14.

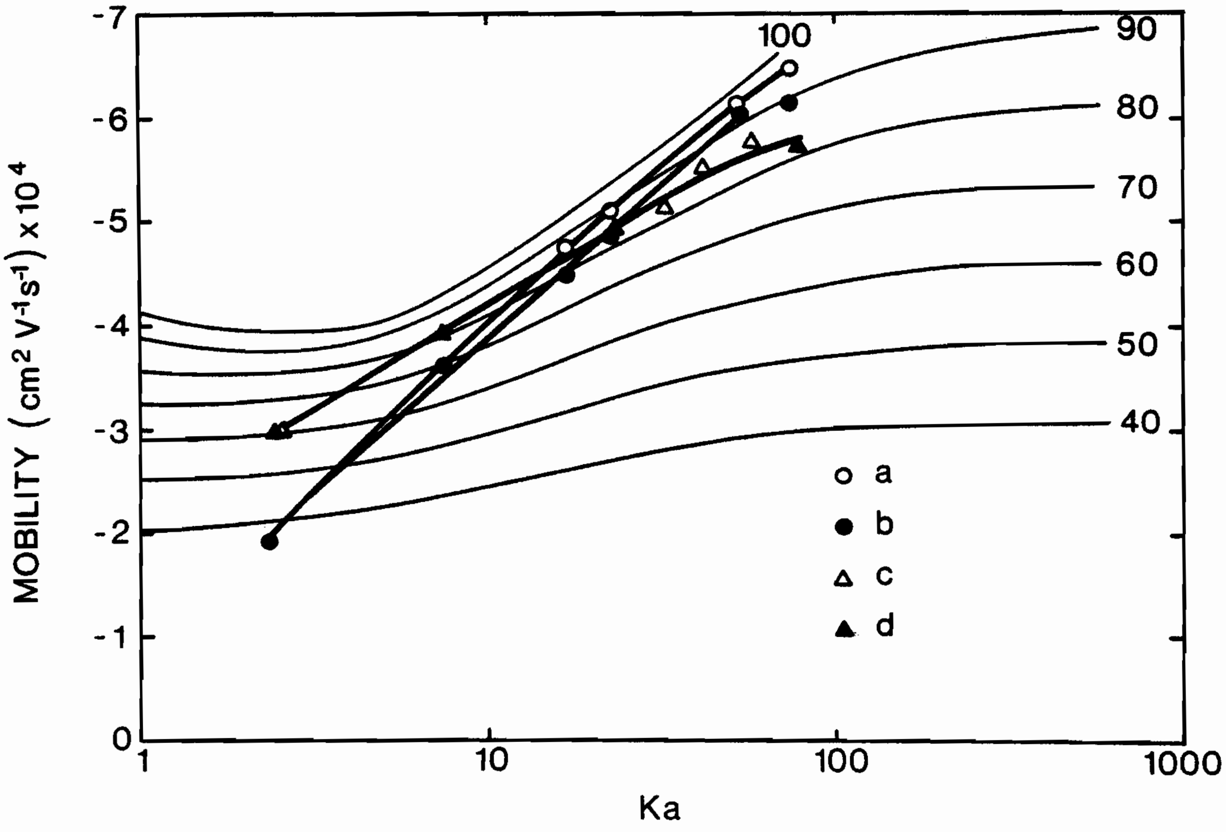


Figure 3: Effect of different anions on the u-κa plots of emulsifier-free homopolymer latexes:

(1) Latex L 14 with (a) KNO_3 and (b) KCl, and

(2) Latex L 17 with (c) K_2SO_4 and (d) KCl.

The ζ-potential increase that is observed with homopolymer latexes was also independent of the pH (Fig. 4). The addition of the electrolyte to the latex in the H^+ or Na^+ form produces the same electrokinetic effect.

Recipes for emulsifier-free homopolymer latexes were varied with respect to initiator concentration, monomer concentration, temperature, and the presence or absence of buffers (4). All the latexes produced, including those with some carboxyl groups, gave, in principle, similar electrokinetic behaviour (i.e., a ζ-potential increase with κa). The results were qualitatively changed (consistently) only when the recipes were basically altered to include functional comonomers (e.g., L 16, Fig. 1) or the latexes were made in a H_2O - CH_3OH medium (e.g., L 25, Fig. 1).

The increase in ζ-potential with electrolyte concentration does not occur, however, if the homopolymer latex is subjected to continued diafiltration washing beyond the criteria usually considered for cleanness (i.e., when the conductivity of the filtrate reaches that of the distilled water used for cleaning). This continued diafiltration washing has been shown elsewhere (7,11) to remove progressively charges from the latex surface. Fig. 5 compares the electrophoretic mobility behaviour of a homopolymer latex (L 14) before and after extensive diafiltration washing. The stripped latex shows a progressive decrease in ζ-potential of the nature expected for conventional simple colloids with increasing electrolyte concentration.

The conductometric titrations of the homopolymer and copolymer latexes are described and recorded elsewhere (8). Both strong- and weak-acid groups are found to be present and their total is considered to

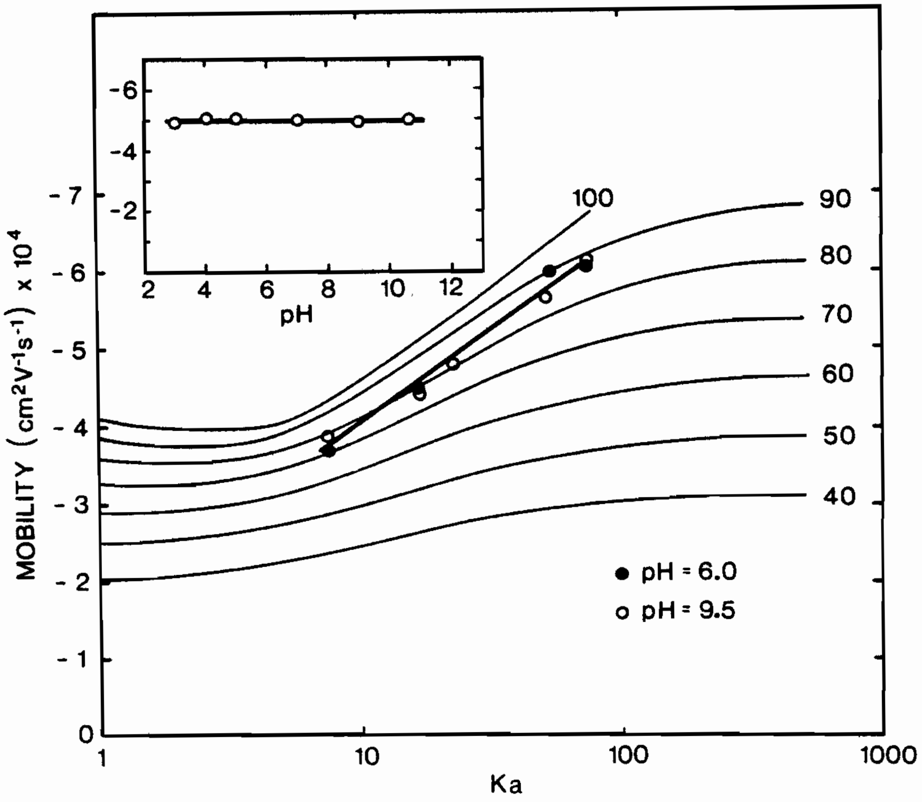


Figure 4: The u-κa plots of emulsifier-free homopolymer latex L 14 at pH values of 6.0 and 9.5. The inset shows the u-pH behaviour of L 14 at 1.1 x 10^{-3} MKCl.

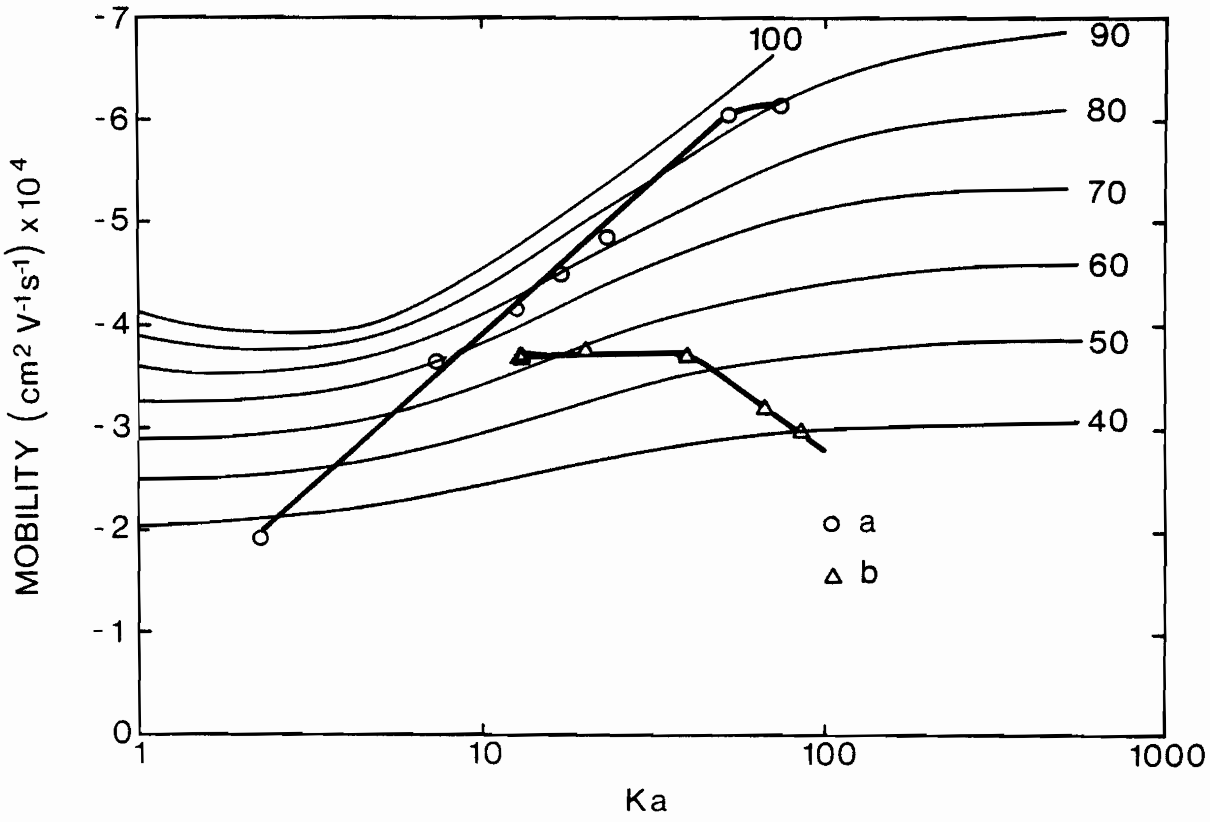


Figure 5: u-κa plots of emulsifier-free homopolymer latex L 14 before (curve (a)) and after (curve (b)) diafiltration stripping at 1.2 x 10^{-4} MKCl.

evaluate the total surface charge from which the surface charge density, σ_o, is calculated. Titrations carried out in the absence of electrolytes and at different electrolyte concentrations were found by Labib and others to give identical results (8,9).

DISCUSSION

The latexes discussed in this paper were prepared by emulsifier-free procedures (4). After cleaning, they were characterized firstly by conductometric titrations (8) and secondly by measuring their electrophoretic mobility at increasing electrolyte concentration.

The conductometric titration provides the basis for calculating the surface charge density (σ_o) from the number of functional groups and the size of the latex particles (Table I).

The simple Gouy-Chapman theory (see Ref. 5) provides a means of calculating a surface potential (ψ_o) from the surface charge density, determined by titration (σ_o), and from the concentration of indifferent electrolyte (c) in the bulk by applying Gouy's equation:

$$\psi_o = \frac{2KT}{ze} \sinh^{-1} \frac{\sigma_o}{\sqrt{8cN_A \varepsilon KT}} \qquad (3)$$

where K, T, z, e, c, N_A, and ε have the same meaning as in equation (2). This idealized surface potential (ψ_o) is greater than the electrokinetic potential (ζ) for a variety of reasons, some general and some specific to given systems. Thus the ζ-potential is less than the ψ_o-potential because of any or all of the following effects:

(a) The surface charge may be less than the titrated value because of a degree of dissociation less than unity, e.g., the presence of carboxyl groups under acidic conditions.

(b) All the titrated groups are not attached to the surface, i.e., unadsorbed charged species exist in the bulk.

(c) The surface charges are hydrophilic terminal groups carried by polymer chains and are distributed through a surface layer or region rather than concentrated on a geometric surface.

(d) Counter-ions may be adsorbed on the particle surface to form a Stern layer.

(e) Counter-ions may be present within the extended charged layer that has been suggested above in (c).

(f) The dielectric constant and the viscosity may differ from the bulk because of the high electric field strengths close to the surface.

There are thus visualized several factors, assumed to be present that act to determine the ζ-potential and to reduce it from its idealized value of ψ_o, either by reducing or modifying the effective surface charge density or by shifting the shear plane, at which the ζ-potential is measured, away from the surface.

The effect of electrolyte concentration on the ζ-potential has two aspects. First, there is the theoretical decrease in the ideal surface potential (ψ_o) calculated by Eq. 3 from the titration surface charge density (σ_o) and plotted as the upper curves in Fig. 6. This is the effect whereby the bulk concentration of ions reduces the field of force of the surface charges by an increasing shielding effect.

The further results of increasing the electrolyte concentration are the effects on the modifying influences listed above. As the electrolyte concentration increases, all may be affected in varying ways and degrees. Arguments can be advanced that the dissociation of acid groups would be increased, the extended charged layer would shrink, Stern layer adsorption would increase, charged oligomers would readsorb, and that rearrangements of counter-ions in a modified surface layer would occur. Consideration of exclusion principles, hydration and dehydration of ions, shielding effects and co-ion adsorption suggests that no analysis of the effect of electrolytes on ζ-potential can be attempted except for simpler systems.

Fig. 6 compares the observed ζ-potentials deduced from the mobility after employing WLO (10) corrections, with the surface potential (ψ_o) calculated from the titration surface charge densities (σ_o). Two results from this work (c) and (e) are compared with the results taken from literature and they are treated in the same way. The results shown in Fig. 6 are as follows:

(a) Ottewill and Shaw (12) for carboxylic polystyrene latex.
(b) Stigter and Mysels (13) for surfactant micelles.
(c) Table I, L 14 for emulsifier-free homopolymer latex.
(d) Meijer et al (14) for emulsifier-free homopolymer latex.
(e) Table I, L 25 for emulsifier-free copolymer latex.
(f) Haydon (15) for stabilized oil droplets.

No general pattern is seen except that there is evidence of convergence of ψ_o and ζ at higher electrolyte concentrations.

The increase in ζ-potential already noted for emulsifier-free homopolymer latexes is replotted for L 14 in (c). Such an increase in

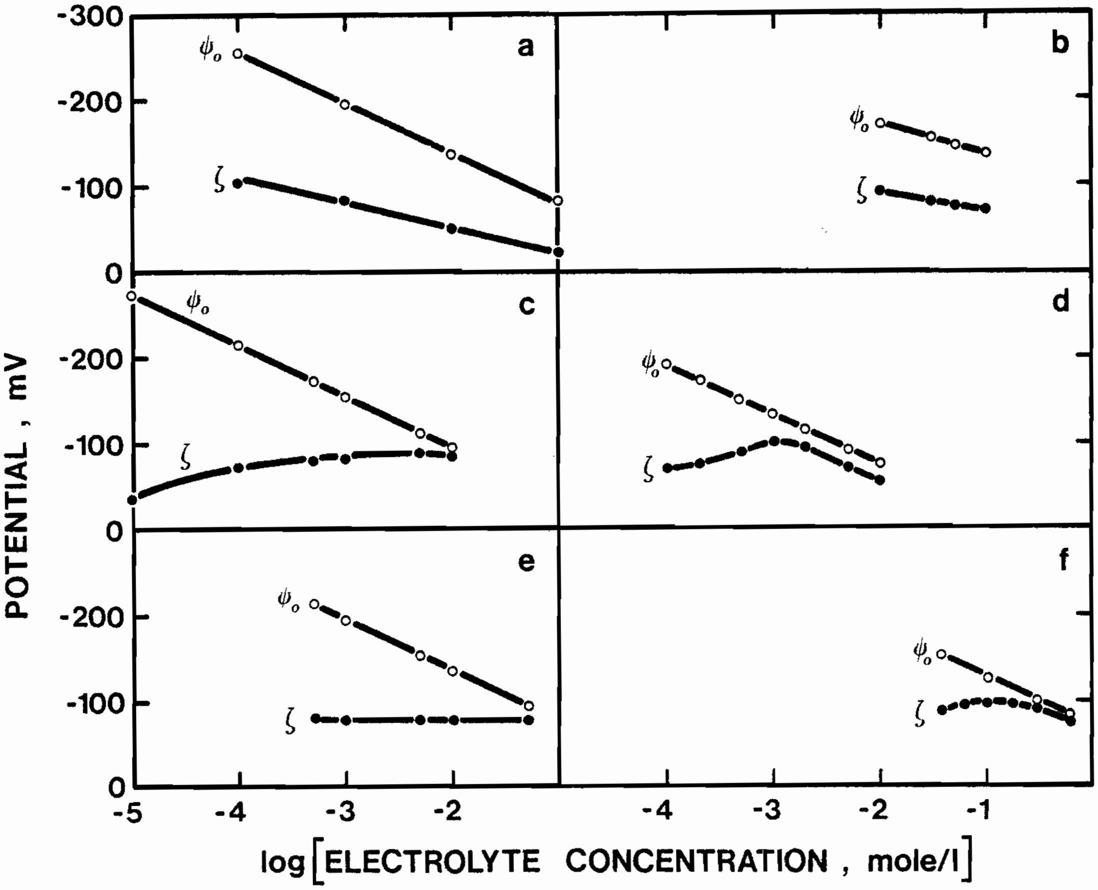


Figure 6: Comparisons between the surface potentials (ψ_o) calculated from titration surface charge densities and the ζ-potentials obtained from mobilities using the WLO (10) corrections. (a) Ottewill and Shaw (12), carboxylic polystyrene latex, (b) Stigter and Mysels (13), surfactant micelles, (c) emulsifier-free homopolymer latex L 14 (Table I), (d) Meijer et al (14), emulsifier-free polystyrene latex, (3) emulsifier-free copolymer latex L 25 (Table I), (f) Haydon (15), stabilized oil droplets.

ζ-potential is also observed for a similar latex reported by Meijer et al (14) (Fig. 6d) and for stabilized oil droplets reported by Haydon (15) (Fig. 6f). These increases in ζ-potential are unpredicted by the elementary theory, and the reasons for them may not be readily assigned in view of the several effects discussed earlier.

The evidence points to a major effect in the case of our latex (case (c)) being related to the structure of the layer formed by functionally terminated polymer chains or by adsorbed oligomers. The thickness is visualized as decreasing due to dehydration effects (salting out), reduction in the force of repulsion between groups, and configurational or conformational changes in an adsorbed layer as the electrolyte concentration increases. The consequence is seen as an increasing concentration of negative charges close to the surface and as a displacement of the shear plane closer to the highly charged surface.

Evidence in favor of this is provided by the recent investigation of the surface of polymer latexes by photon correlation spectroscopy (16). It has been demonstrated that the particle surface layer shrinks by as much as 10 nm by increasing the electrolyte concentration from 10^{-5} to 10^{-2} M$NaNO_3$ while the particle core was found to be unchanged.

A contributing effect can be assigned to increased adsorption of functional oligomers as described in the previous chapter (7). It has been demonstrated that adsorption/desorption equilibrium of these oligomers exists and changes as a function of electrolyte concentration.

The increasing ζ-potential with electrolyte concentration is a characteristic of latexes which were shown to be progressively stripped of charges by continued diafiltration washing (7,11). The suggestion of a surface layer of charged oligomers capable of loose or dense packing or possible desorption is thus possible. When such a latex is partially stripped of charges by diafiltration washing, the electrophoresis behaviour changes and the effect of increasing the electrolyte concentration is to decrease the ζ-potential as conventionally expected (Fig. 5).

The effect of electrolyte concentration on emulsifier-free copolymer latexes is also unexpected. The ζ-potential remains constant despite the anticipated decrease based on the effect of electrolytes on compressing the diffuse layer as shown in the Gouy-Chapman formulation. The explanation of the above observation is not simple as previously discussed because of the number of factors that may be operative in these latexes. It should be mentioned, however, that no desorption of charges was observed when these copolymer latexes were extensively washed by diafiltration and the electrophoretic behaviour was unaltered.

The ζ-potentials in Fig. 6 have been calculated from the electrophoretic mobility measurements by using the WLO method. While no alternative treatment is being suggested, the assumptions implicit in the WLO derivations may not be appropriate for the type of particle that we have been led to describe. It therefore must be recognized that differences between predicted ζ-potentials and those calculated from mobility measurements may be partially ascribed to failure of the WLO assumptions.

CONCLUDING REMARKS

The increasing ζ-potential that is observed with emulsifier-free homopolymer latexes as the electrolyte concentration is increased, is attributed to changes or modification in the surface layer of the particles. The electrokinetic behaviour of these latexes is different from that of copolymer and conventional latexes and limits their use as model colloids. The electrokinetic behaviour of latexes depends on how the nature of the surface region is modified by the presence of polymeric or oligomeric species carrying functional groups.

REFERENCES

1. Kotera, A., Furusawa, K. and Takeda, Y., Kolloid Z.u.Z. Polymere 229, 677 (1970).
2. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Brit. Polym. J. 5, 347 (1973).
3. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., Colloid Polymer Sci. 252, 464 (1974).
4. Labib, M.E., This thesis, Chapter II.
5. Overbeek, J.Th.G. in 'Colloid Science' (H.R. Kruyt, ed.), Vol. I, Elsevier, Amsterdam and New York (1952).
6. Shaw, D.J., 'Electrophoresis', Academic Press, London and New York, p. 60 (1969).
7. Labib, M.E., This thesis, Chapter VII.
8. Labib, M.E., This thesis, Chapter IV.
9. Everett, D.H. and Gültepe, M.E. in 'NATO Advance Study Institute-Polymer Colloid Reprints', The Norwegian Institute of Technology, Trondheim (1975).
10. Wiersema, P.H., Loeb, A.L. and Overbeek, J.Th.G., J. Colloid Interface Sci. 22, 78 (1966).
11. Labib, M.E. and Robertson, A.A., J. Colloid Interface Sci. 67, 543 (1978).
12. Ottewill, R.H. and Shaw, J.N., J. Electroanal. Chem. 37, 133 (1972).
13. Stigter, D. and Mysels, K.J., J. Phys. Chem. 59, 45 (1955).
14. Meijer, A.E., van Megen, W.J. and Lyklema, J., J. Colloid Interface Sci. 66, 49 (1978).
15. Haydon, D.A., Proc. Roy. Soc. A258, 319 (1960).
16. Goosens, J.W.S. and Zembrod, A., Colloid Polymer Sci. 257, 437 (1979).

CLAIMS TO ORIGINAL RESEARCH

The work reported in this thesis contributes to the physical, analytical, and polymer chemistry of synthetic latexes. Many of the conclusions of this work can be extended to include other dispersions. Several accomplishments and findings are noted:

(1) The agreement between the sizes of emulsifier-free homopolymer latexes prepared in this work and the results of Goodwin establishes the predictability of particle sizes in the emulsifier-free polymerization of styrene.

(2) Novel preparations of copolymer latexes with predictable sizes and surface charges have been introduced by performing the polymerizations in the presence of 30% methanol. These latexes are prepared with high solid contents and the type and number of surface charges are readily controlled by varying the type and the amount of comonomer(s) used.

(3) A diafiltration technique has been used for the first time in the cleaning, equilibration, concentration, and fractionation of polymer latexes.

(4) Diafiltration has proven to achieve better cleaning of latexes with saving of time and effort. The technique is able to remove soluble non-ionic material and adsorbed species from the latex.

(5) The conductometric titration technique for the determination of stoichiometric amounts of surface groups has been revised to give reliable and consistent results. Practical extrapolation methods have been developed on the basis of a realistic analysis of the system.

(6) Back titrations with acids have been used to achieve consistent determination of stoichiometric amounts of surface groups in latexes.

(7) A practical method has been introduced in plotting the conductivity data of the forward and back titrations in order to give reliable estimates of surface charge.

(8) Criteria for complete and successful conductometric titrations of latexes have been established.

(9) The titrations of model systems with intentionally added impurities have proven that strong acid impurities, either free or adsorbed, are titrated with surface strong acid.

(10) The titration of free weak acid has been shown to appear as a separate slope in the conductometric titration curve before the titration of bound weak acid.

(11) It has been demonstrated that adsorbed weak acid appears with bound weak acid in the titration curve as one slope.

(12) Ion exchange has been shown to have limitations in cleaning synthetic latexes containing polyelectrolytes or oligomers prepared in situ.

(13) It has been demonstrated that diafiltration cleaning followed by ion exchange is a proper method of cleaning latexes.

(14) Criteria of cleanness of latexes are established on the basis of the titration curves.

(15) Oscillometry has proven to be a reliable technique for latex titrations and gives results in agreement with the conductometric technique. Oscillometry has the advantage of greater sensitivity and the elimination of the problems of immersed electrodes.

(16) It has been demonstrated that emulsifier-free homopolymer latexes cannot be used as model colloids. The surface charge of these latexes has shown to desorb by dilution and diafiltration stripping.

(17) It has been suggested that some of the surface charges on emulsifier-free latexes are due to adsorbed oligomeric species and that the latter is in equilibrium with the same species in bulk.

(18) The oligomers in the bulk have been detected by GPC, IR, dye-interaction and dye-partition techniques, and electrokinetic titrations.

(19) The effect of electrolytes on desorption of surface oligomers from the particles of emulsifier-free latexes has been consistent with the idea that changes or modification in the adsorption characteristics and in the surface layer occur as the electrolyte is added.

(20) The increase of ζ-potential of emulsifier-free homopolymer latexes with increasing electrolyte concentration has been found to be consistent with the concept that the structure of the surface and double layers changes as the electrolyte concentration is increased.

(21) The procedure of plotting mobility values against κa on graphs showing the predicted mobility values at constant ζ-potential after employing WLO corrections for the retardation and relaxation effects is convenient in the interpretation of electrophoresis results.

(22) Copolymer latexes have been found to show no charge desorption upon dilution or diafiltration stripping; this proves that the surface charges of these latexes are well integrated into the polymer particles.

(23) The effect of the nature and the structure of the surface layer of latexes on their electrokinetic properties has been demonstrated and shown to affect the suitability of using latexes as model colloids.

SUGGESTIONS FOR FUTURE RESEARCH

The copolymer latexes which have been introduced in this work can be prepared with a wide range of surface charge density and with different types of surface groups. The sizes of these monodisperse latexes can be varied in a predictable way by controlling the polymerization conditions. These copolymer latexes can be cleaned and characterized by the cleaning and characterization techniques established in this work.

The copolymer latexes described above can be used as model colloids to study the following topics:

(a) Electrokinetic properties such as the relationship between the surface potential (ψ_o) and the titration surface charge density (σ_o).

(b) Surface conductance of model suspensions.

(c) Particle interaction in latexes.

(d) Adsorption of polymers from solutions.

(e) Determination of adsorbed polymer layer thickness by mass transport electrophoresis or other techniques.

(f) Rheological properties of dispersions.

(g) Properties of ordered latexes.