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Well-Characterized Monodisperse Latexes as Model Colloids*[†]

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ABSTRACT

Monodisperse polystyrene latexes prepared with persulfate-ion initiator can be ion exchanged to remove the adsorbed emulsifier and solute electrolyte. Rigorous purification of the ion-exchange resins is necessary to avoid contamination with leached polyelectrolytes. These ion-exchanged latexes are stabilized with the residual sulfate end-groups of the polymer molecules, the number of which is determined by conductometric titration. The result is a dispersion of monodisperse spheres with a constant and known surface charge

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due to chemically-bound strong-acid groups. These latexes are ideal models for colloidal studies. Preliminary experiments of stability, adsorption, sedimentation, viscosity, interference colors, and conductance give consistent results, e.g., the particle double-layer interactions determined by viscosity are in accord with the particle spacings estimated from interference colors, the double-layer parameters estimated from conductometric titration and conductance measurements account for the measured decrease in sedimentation rate due to double-layer interactions, and the molecular area of sodium dodecyl sulfate measured by adsorption in latex is in agreement with literature values.

INTRODUCTION

For the past 23 years the Dow Chemical Company has prepared and distributed monodisperse latexes as a scientific service. These latexes have found a wide variety of applications: 1) calibration standards in electron microscopy, optical microscopy, light scattering, ultracentrifugation, aerosol counting, electronic particle counting, and small-angle x-ray diffraction; 2) medical diagnostic tests, e.g., for rheumatoid arthritis, tuberculosis, trichinosis, and human pregnancy; 3) counting of virus particles; 4) determination of the pore size of filters and biological membranes; 5) studies of the reticulo-endothelial system; 6) stimulation of antibody production; 7) purification of antibodies; 8) investigations of the mechanism and kinetics of emulsion polymerization and latex film formation; 9) analysis of flagellate locomotion mechanisms; and 10) model colloids. Despite the obvious utility of their very narrow particle size distributions, these latexes have been used in only a few colloidal studies because little was known about the characteristics of their surface. Therefore, we attempted to characterize these latexes as to the number and acid strength of their surface ionic groups in order to enhance their use in colloidal studies.

As a result, we obtained "clean" (i.e., emulsifier- and electrolyte-free) latexes that were useful not only as model colloids, but also in other applications, e.g., as a substrate for adsorption studies of surfactants and proteins. Moreover, the cleaning techniques developed were useful in preparing special (e.g., radio-iodine-tagged) latexes.

LATEX PREPARATION

The latexes were prepared either by conventional emulsion polymerization (i.e., by forming an emulsion of monomer in water with an

anionic emulsifier and polymerizing with persulfate-ion free-radical initiator) or by seeded emulsion polymerization (by polymerizing additional monomer in a previously-prepared latex, to grow the particles to a larger size without initiating a new crop) [1]. Both types of polymerization give a colloidal dispersion of submicroscopic polymer spheres which bear a negative charge arising from the adsorbed emulsifier.

There is another possible source of negative charge, however, the sulfate end-groups of the polymer molecules. These result from initiation of polymerization by sulfate ion-radicals formed by the decomposition of persulfate ion in the aqueous phase. Sulfate ion-radicals have no tendency to migrate to the particle-water interface, but rather undergo a reaction with the solute monomer to form an oligomeric radical. The oligomeric radical soon grows to such a size that it becomes surface-active and adsorbs at the particle-water interface with the radical oriented toward the monomer-swollen polymer phase. The polymeric radical grows into the particle by the addition of monomer molecules supplied by the continuous diffusion from the aqueous phase. This growth continues until another radical enters and causes termination. This mechanism of initiation gives sulfate emulsifier groups chemically-bound to the particle surface.

LATEX CLEAN-UP

To use these latexes as model colloids, we must know the surface charge density of the particles. In the past, soap titration has been used for this purpose [2, 3], but this method measures only the number of adsorbed emulsifier molecules and completely overlooks the contribution of the charged polymer end-groups. Overbeek et al. [4] used conductometric titration to determine the surface charge density of acidified silver-halide sols, but this technique measures the total number of negative groups and therefore cannot distinguish between sulfate end-groups and adsorbed emulsifier, since often both are strong-acid groups; also, adsorbed emulsifier could desorb during the course of an experiment and thus change the surface charge density.

Therefore, we decided to remove the adsorbed emulsifier as completely as possible and to rely upon the sulfate end-groups to give the particle the required stability. This would give an ideal model colloid, i.e., monodisperse spheres of constant and known surface charge arising from chemically-bound strong-acid surface groups.

It has been reported [2, 3, 5, 6] that the emulsifier is only partly removed from the latex by dialysis. Our own experience corroborated this result [7-9]. Therefore, we used mixed-bed ion exchange to remove the emulsifier from the latex. Only a general outline of the purification

and the use of the ion-exchange resins is given below; the details can be found elsewhere [7-9].

Dowex 50W-X4 sulfonic acid and Dowex 1-X4 quaternary ammonium resins were eluted consecutively with 3 N NaOH, hot water, methanol, cold water, 3 N HCl, hot water, methanol, and cold water at least four times. The purity of the resins was checked by measuring the surface tension, conductance, UV absorption, and amount of acid or base required for neutralization of the wash water. The resins were converted to the H^+ and OH^- forms, respectively, and mixed.

Then, 300-500 ml latex was agitated slowly with an estimated 5-fold excess of resin (based on electrolyte and emulsifier concentrations), filtered, and titrated. This procedure was repeated until a constant charge was obtained. Ion exchange in batch was more efficient than ion exchange in columns. The effectiveness of the ion-exchange latex clean-up has been described in detail elsewhere [7-9].

The latex solids were determined gravimetrically, the average particle sizes by electron microscopy, and the number-average molecular weights by osmometry of tetrahydrofuran solutions of freeze-dried, reprecipitated polymer; some osmometry results were checked by gel permeation chromatography.

CONDUCTOMETRIC TITRATION

After ion exchange, the latex particles are stabilized only by the sulfate end-groups of the polymer chains, all of which are in the H^+ form. Thus their number can be determined by titration with base. These titrations were generally followed conductometrically by recording the voltage drop across a $10\text{-}\Omega$ resistor in series with a dip-type conductance cell and in parallel with a 6-V transformer, while 0.01 N NaOH was added continuously from a constant rate buret. In this way as little as 10^{-6} equiv acid (corresponding to about 10^{-4} moles sulfur/g polymer) could be determined to within 5%.

Figure 1 shows a conductometric titration curve for an ion-exchanged sample of Latex A-2. Both legs of the specific conductance-ml NaOH curve are linear, and extrapolation to intersection gives the equivalence point. The rounded minimum is due mainly to slow attainment of equilibrium near the equivalence point. This curve is typical of what we found in the titration of strong-acid surface groups with a strong base. The descending leg is linear because the strong-acid surface groups have an equal preference for Na^+ and H^+ counterions; however, because of the limited mobility of these counterions in the double layer, its slope is much smaller than for a strong acid in solution. Beyond the equivalence point the specific conductance increases linearly with sodium hydroxide added in excess. An equivalence point of 3.38 ml 0.01 N sodium hydroxide for 1.458 g latex

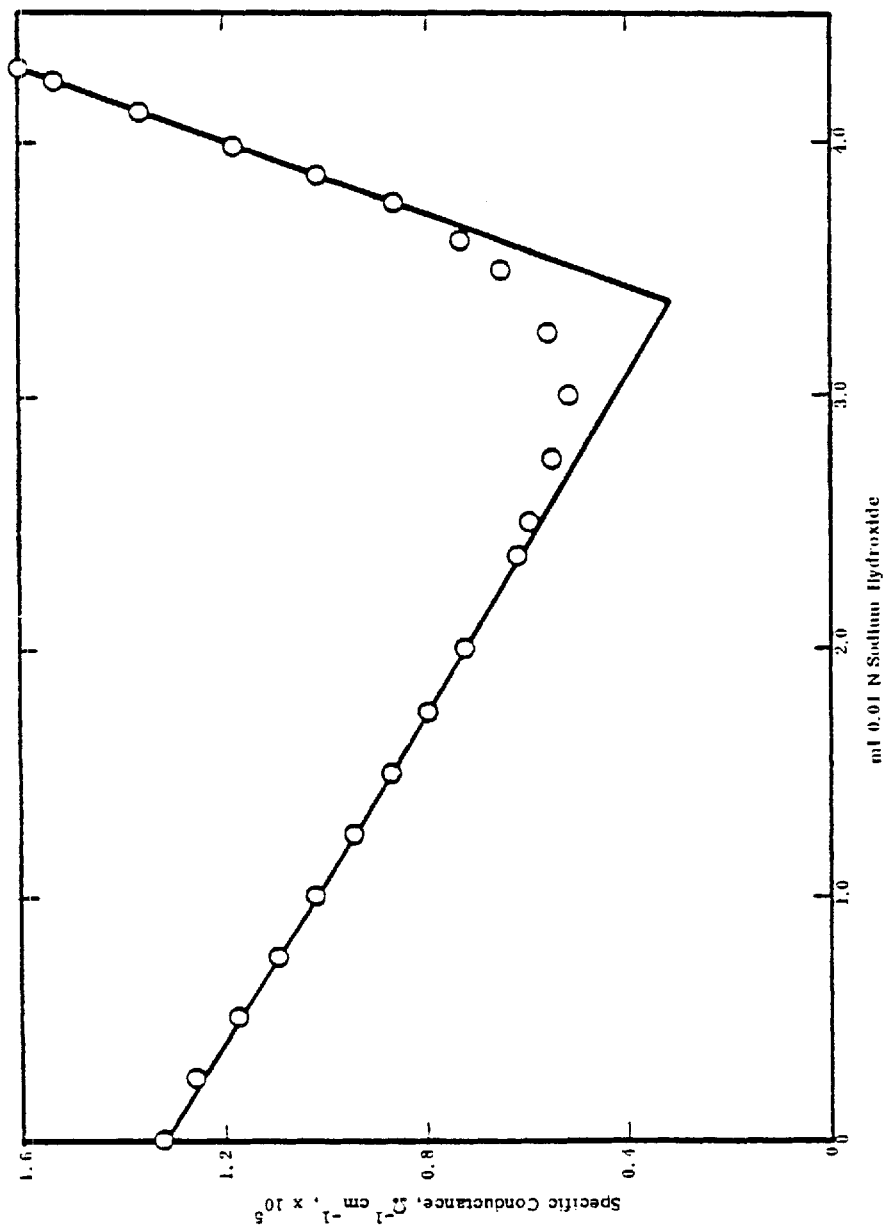


FIG. 1. Conductometric titration of ion-exchanged Latex A-2 with sodium hydroxide.

polymer corresponds to a surface charge of $3.60 \mu\text{C}/\text{cm}^2$ (N.B., we shall define the "surface charge" or "surface charge density" as the total charge measured by titration: this is distinguished from the "effective charge" or diffuse charge, which takes into account any undissociated negative groups and any counterions residing in the Stern layer; thus the effective charge is the product of the surface charge and the "apparent degree of dissociation" α ; we shall see later that the effective charge is much smaller than the surface charge).

Figure 2 shows a conductometric titration curve of the same sample of Latex A-2 with barium hydroxide. Only the ascending leg is linear; the descending leg is curved initially, but eventually becomes linear, so that extrapolation to intersection at 1.84 ml gives the equivalence point. The descending leg is curved because the innermost H^+ ions in the double layer, i.e., those that contribute least to the conductivity of the latex, are replaced first by the Ba^{2+} ions, and only later are the outermost, fastest-moving H^+ ions exchanged. Since the mobilities of the Ba^{2+} and H^+ ions are markedly different, the initial addition of Ba^{2+} ions gives only a slight decrease in the conductivity, but further additions give an increasing decrement in the conductivity until the descending leg becomes linear. An equivalence point of 1.84 ml 0.009 $\underline{\text{N}}$ barium hydroxide for 0.735 g latex polymer corresponds to a surface charge of $3.47 \mu\text{C}/\text{cm}^2$, in good agreement with the value obtained with sodium hydroxide.

These results for the conductometric titration of ion-exchanged Latex A-2 with sodium and barium hydroxides are similar to those obtained earlier [4] for acidified silver iodide sols.

A few potentiometric titrations were also carried out using a glass electrode. The results were identical to those of the conductometric titrations, although the equivalence points were less unequivocal (see Fig. 3). Also, some conductometric titrations of polymer dissolved in dioxane-water mixtures were carried out to determine the total number of sulfate groups; the results were in good agreement with sulfur determinations by x-ray fluorescence.

MECHANISM OF EMULSION POLYMERIZATION

Using this method of latex characterization, we determined the number of sulfate end-groups on the particle surface and inside the particle, the number of hydroxyl end-groups formed by side reactions of the sulfate ion-radical with water, and the pH dependence of the ratio between hydroxyl and sulfate end-groups. These results, which are discussed in detail in Ref. 1, show that the sum of the hydroxyl and sulfate end-groups at each pH is about 2 per polystyrene molecule, as expected for termination by combination without appreciable chain transfer. More than half of the sulfate end-groups are on the particle

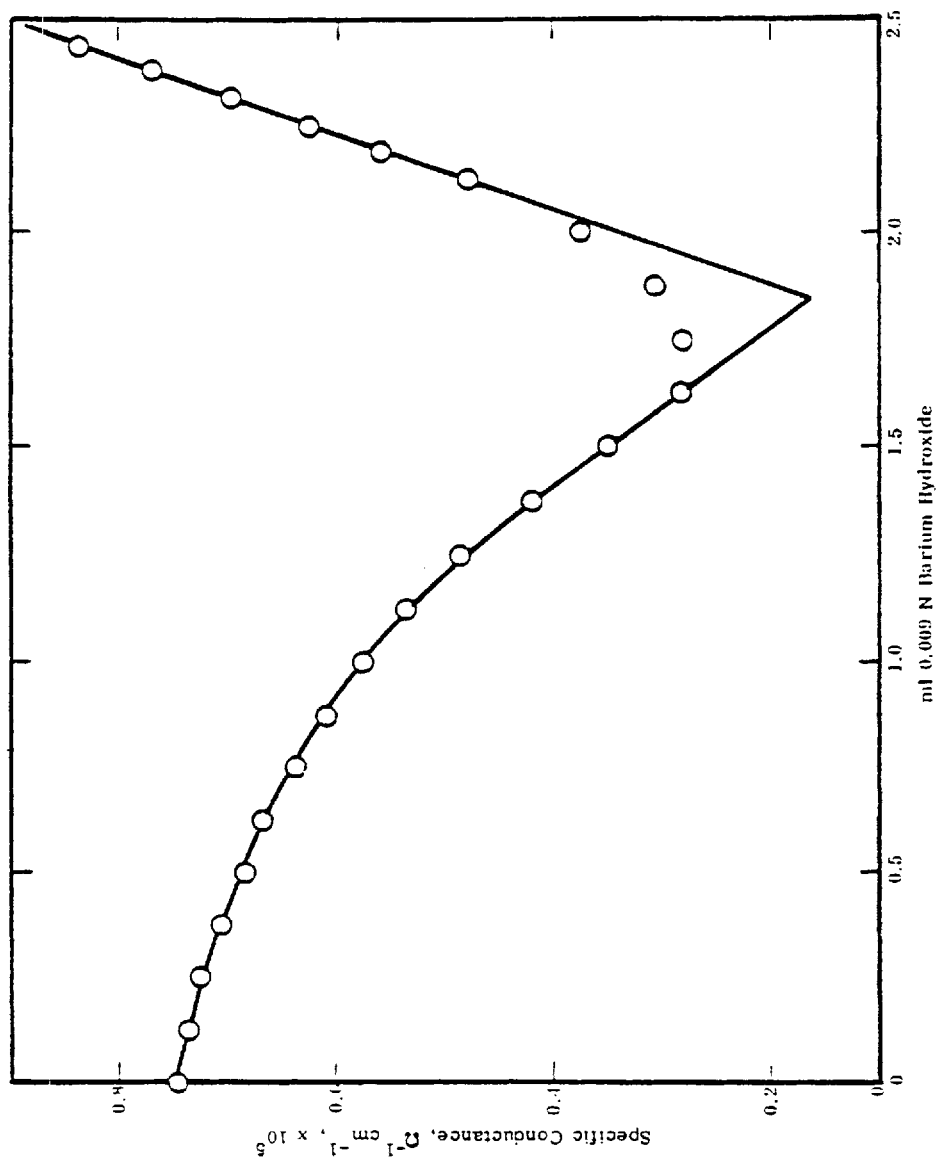


FIG. 2. Conductometric titration of ion-exchanged Latex A-2 with barium hydroxide.

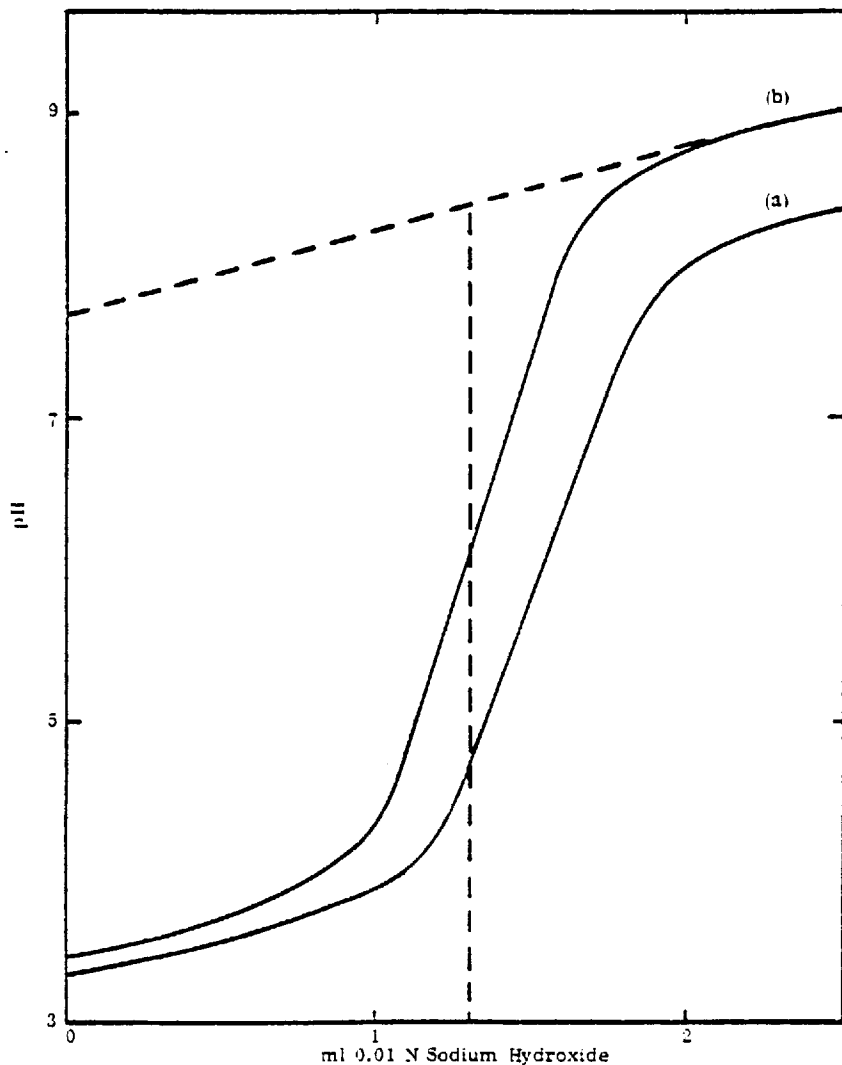


FIG. 3. Potentiometric titration of ion-exchanged polystyrene latexes: (a) Latex A-2; (b) Latex D-4.

surface, which indicates that the initiation of polymerization occurs by addition of styrene to the sulfate ion-radical in the aqueous phase and the formation of surface-active oligomers which are then adsorbed into the micelles, with the sulfate group in the micelle-water interface and the growing chain inside the micellar core.

END-GROUP DETERMINATION

We compared the total number of sulfate end-groups in the particles as determined by conductometric titration in dioxane-water mixtures, by x-ray fluorescence analysis for sulfur, and by the dye partition method of Palit et al. [10], both in benzene and chloroform solution with methylene blue as the dye (in this method, an aqueous dye solution is shaken with a solution of the polymer in an organic solvent, and the optical density of the organic layer is measured to determine the number of dye molecules combined with the sulfate end-groups). The first two methods were in good agreement, but dye partition gave values that were consistently low and dependent on experimental conditions such as the time of agitation, solvent, and polymer concentrations (see Fig. 4). Examples are given in Table 1. Similar results have been obtained by Bitsch [11], who found that the number of end-groups determined for polystyrene by the dye partition method was always much lower than that determined by other methods; however, for the more polar poly(methyl methacrylate), dye partition gave the expected value of two end-groups per polymer molecule.

Because of the (necessarily) poor solubility of the dye in the organic solvent, the dye-endgroup ion-pair must apparently be formed in the water-solvent interface. Because of the apolar nature of polystyrene, few end-groups actually come to this interface and, therefore, the ion-pair formation is not quantitative. As the polymer-polymer interaction increases at higher concentrations, the extent of ion-pair formation decreases. This explanation was confirmed recently by experiments of Huber and Thies [12] on the adsorption of toluene-soluble polymers at the toluene-water interface. They conclude that polystyrene has little affinity for this interface but that poly(methyl methacrylate) adsorbs significantly at concentrations as low as 1.0×10^{-4} g/100 ml. That the sulfate end-groups are not sufficient to bring the polymer to the interface is shown by the fact that a poly(ethylene-co-vinyl acetate) with 11.1 mole % vinyl acetate adsorbs to only a slightly greater extent.

Another point is the presence of carboxyl groups. Ottewill and Shaw [13, 14] found a large proportion of these groups on latex particles prepared with hydrogen peroxide initiator and sodium laurate emulsifier, and cleaned by dialysis. On the other hand, we did not find appreciable concentrations of carboxyl groups in our latexes, whether prepared with

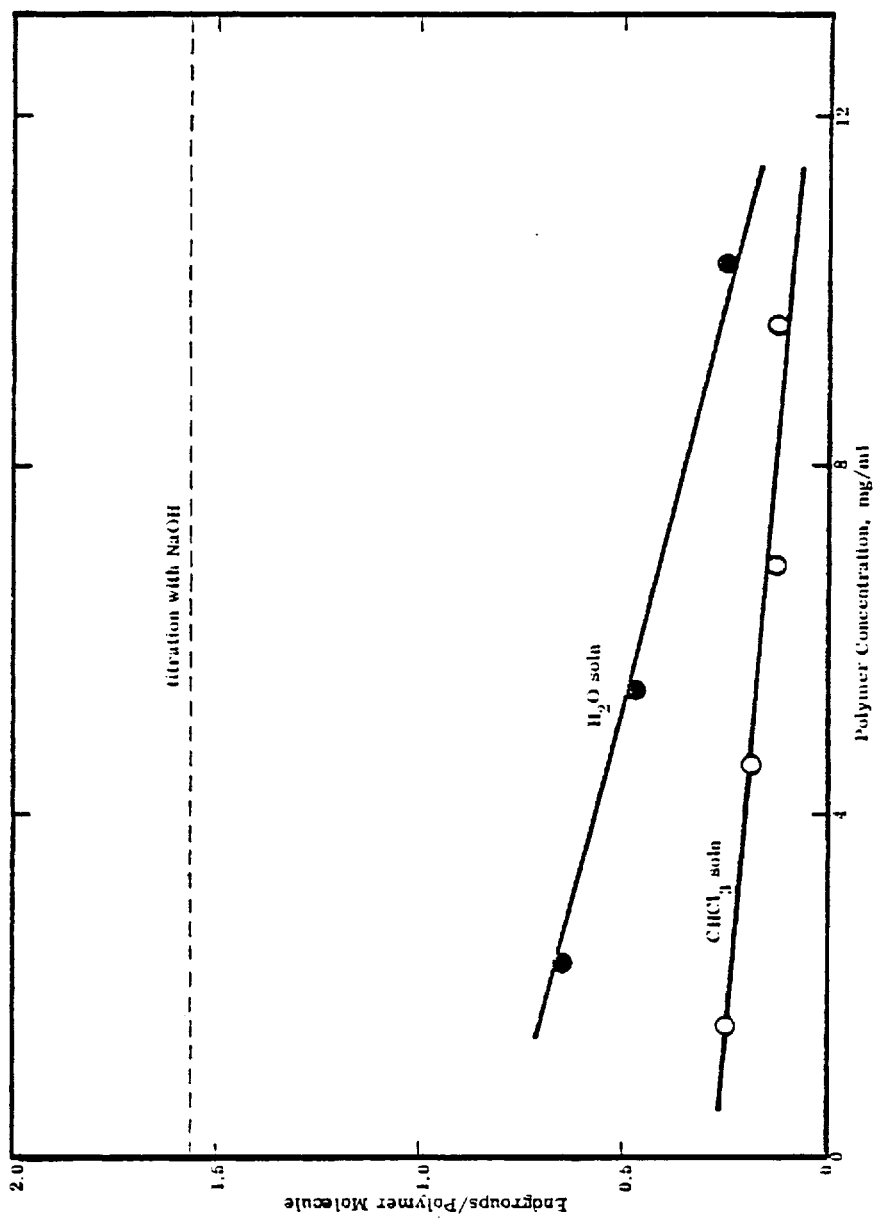


FIG. 4. Comparison of different methods for determination of sulfate end-groups of Latex A-2: (○) dye partition measured in chloroform solution; (●) dye partition measured in aqueous phase, polymer in benzene; (---) conductometric titration after ion exchange.

TABLE 1. Comparison of End-Group Determinations

Method	Number of sulfate groups/molecule	
	Latex A-2	Latex D-4
Latex surface titration	0.98	0.93
Polymer solution titration	1.57	2.07
X-ray fluorescence	1.5	2.0
Dye partition	0.08-0.30	0.06-0.12

sulfonate or carboxylate emulsifier, as evidenced by both conductometric and potentiometric titration curves, IR spectra of the polymer, and electrophoretic mobility of the particles (however, the IR spectra gave evidence for hydroxyl groups).

SURFACE CHARGE DENSITY

Table 2 shows that 45-100% of the sulfur incorporated into the polymer is present on the particle surface. In terms of the surface charge, these amounts cannot be neglected as a factor in latex stability, both during and after polymerization. (This accounts for the fact that polymerizations with hydrogen peroxide initiator and low emulsifier concentrations frequently coagulate at low conversions.) For Latexes B-1, B-2, and D-4, the charge density due to sulfate end-groups is, respectively, at least 4, 8, and 1.6 times the charge due to adsorbed emulsifier. For the other latexes, it amounts to 20-100% of the emulsifier adsorbed. Thus this permanent charge is an important factor that has been overlooked in earlier studies of latexes at low emulsifier coverage [15, 16].

COLLOIDAL PROPERTIES OF THE ION-EXCHANGED LATEXES

The latexes were ion-exchanged at low solids concentrations, usually 5% or less, depending upon the particle diameter. After 15-30 min of contact with the ion-exchange resin, the viscosity of the latexes increased at least twofold, the conductance decreased greatly, and, in some samples, interference colors appeared. These changes are

TABLE 2. Residual Charge of Polystyrene Latexes After Ion Exchange

Latex ^a	Particle diameter (Å)	Surface charge, ($\mu\text{C}/\text{cm}^2$)	M_n^b	Surface area/charge (Å)	Number of sulfate groups/molecule	
					Surface	Total
A-1	250	0.5	-	3100	-	-
A-2	880	3.3	43,000 ^c	500	0.99	1.57
A-3	2340	2.0	173,000 ^c	800	0.87	1.59
B-1	1580	4.2	80,600 ^c	390	1.26	1.21
B-2	2480	5.7	75,000	280	1.02	1.23
C-1	2540	5.4	75,800	300	0.95	0.94
D-1	1090	1.6	106,000	1000	0.95	-
D-2	1870	1.8	106,000	910	0.90	-
D-3	2850	4.9	101,000	330	1.03	1.63
D-4	4470	8.1	85,200	200	0.93	2.07

^aA series: Aerosol MA bis-1,3-dimethylbutyl sodium sulfosuccinate, American Cyanamid Co. B series: SIPON WD sodium lauryl sulfate, Alcolac Chemical Corp. C series: Aerosol OT di-2-ethylhexyl sodium sulfosuccinate, American Cyanamid Co. D series: Potassium oleate.

^bNumber-average molecular weight determined by osmometry.

^c M_n values of 45,300, 170,700 and 85,600, respectively, determined by gel permeation chromatography.

indicative of the reduction of the electrolyte concentration to a low level and the resulting expansion of the electric double layer.

This makes these latexes even more suitable as model colloids: not only do we have a stable dispersion of monodisperse spheres with a known and fixed charge, but this charge and the ionic strength can be varied systematically by the addition of emulsifier or salt. Also, the low-electrolyte latexes themselves have interesting properties. In the following sections, examples are given of their use in studies of: 1) stability, 2) adsorption, 3) sedimentation, 4) viscosity, 5) interference colors, and 6) conductance.

Stability

The emulsifier- and electrolyte-free latexes form excellent models to test the theory of colloidal stability [17], e.g., the effect of particle size and surface charge. A number of such studies have been reported by Ottewill and Shaw [13, 18] and by Watillon and Joseph-Petit [19] using systems similar to ours. Some quantitative data concerning the effect of the cleaning procedure and resin purity on latex stability were presented by McCann et al. [20].

We noted that most of the latexes listed in Table 2 were stable after ion exchange. For example, Latex A-2 (880 Å, $3.3 \mu\text{C}/\text{cm}^2$ surface charge) showed no coagulation during ultracentrifugation at 14,300 rpm, either in the electrolyte-free latex or in the presence of 100 mM KNO_3 or 2.5 mM $\text{Ba}(\text{NO}_3)_2$. Latex A-1 (250 Å, $0.5 \mu\text{C}/\text{cm}^2$), however, flocculated at least partially during ion exchange and completely upon titration with NaOH, presumably because of its combination of small particle diameter and low surface charge. Also, Latexes D-1 (1090 Å, $1.6 \mu\text{C}/\text{cm}^2$) and D-2 (1870 Å, $1.8 \mu\text{C}/\text{cm}^2$) flocculated slowly upon standing after titration (excess of 10^{-4} N NaOH), presumably because of their low surface charge. The other latexes were stable enough to be used as model colloids.

The critical coagulation concentrations (c.c.c.) determined turbidimetrically for Latex A-2 with NaCl, CaCl_2 , AlCl_3 (pH3), and AlCl_3 (pH 7) were 180, 18.5, 0.37, and 0.15 mM, respectively (the values for NaCl and CaCl_2 were independent of pH). These results do not follow the inverse sixth-power Schulze-Hardy rule derived by Verwey and Overbeek [17, 21] for the dependence of c.c.c. on valence. Instead, the log c.c.c.-log valence plot has a slope of about 3.3. This could indicate a low ζ -potential for this system since, in the limiting case of low potentials where the Debye-Hückel approximation applies, the derived dependence is second-power [21]. However, more extensive data are required before it can be concluded that this case deviates from the "normal" sixth-power Schulze-Hardy rule.

It should be noted that Ottewill and Shaw [18] measured c.c.c. values

of 14.1-28.2 mM $\text{Ba}(\text{NO}_3)_2$ for latexes with diameters of 300-2115 Å and ζ -potentials of 1-12 mV; our value of 18.5 mM for CaCl_2 falls in this range.

The data of AlCl_3 at pH 3 and pH 7 show that the effect of metal-hydroxo complexes is also operative here. Matijević et al. [22] suggested that these complexes, which are formed at $\text{pH} \approx 3$, are adsorbed specifically onto the colloid particles, thus effectively lowering the c.c.c.

Adsorption

The saturation adsorption of sodium dodecyl sulfate (SDS) on clean Latex A-2 was first determined by the soap titration technique of Maron et al. [23]. Conductometric titration gave a total adsorption of $2.2 \pm 0.1 \times 10^{-4}$ moles/g polymer at a critical micelle concentration (c.m.c.) of about 6×10^{-3} M. Direct adsorption measurements using a Cenco-DuNouy ring tensiometer gave $2.3 \pm 0.5 \times 10^{-4}$ moles/g, but these measurements were rather inaccurate. Also, a surface tension (γ)-log c plot was obtained, from which a c.m.c. of $6-8 \times 10^{-3}$ M and, by differentiation, an adsorption at the air-water interface of 0.33×10^{-9} moles/cm² was derived. This adsorption is equivalent to a molecular area of 48 Å for the adsorbed SDS molecule. In both experiments the SDS used was Sipon 12 (kindly supplied by Sinova, France) which was specified as >99.5% pure; the γ -log c plot showed a slight minimum.

More accurate data were obtained using a very pure sample of SDS (obtained from Eastman Organic Chemicals) and a Cahn microbalance with a surface tension attachment and a pendant Pt slide; this gave measurements to within <0.01 dyne. Adsorption measurements were carried out at $25 \pm 0.001^\circ\text{C}$. First, the interfacial tension of the octane-water interface was determined as a function of SDS concentration. Increments of SDS were added, and γ was recorded continuously and read when a constant equilibrium value was obtained. The resulting γ -log c curve (Fig. 5) shows no minimum, and the c.m.c. is determined to be 7.9×10^{-3} M, in good agreement with literature values [24, 25]. By differentiation according to the Gibbs adsorption equation

$$\Gamma = (-1/2RT) (\partial \gamma / \partial \ln c)$$

where Γ is the adsorption at the water-octane interface in moles/cm², the adsorption isotherm of $\Gamma = f(c)$ is obtained (Fig. 6). The isotherm does not show a saturation plateau, but the adsorption at the c.m.c. is 0.365×10^{-9} moles/cm², which is equivalent to a molecular area of 46 Å, in good agreement with the values reported by Cockbain [24]

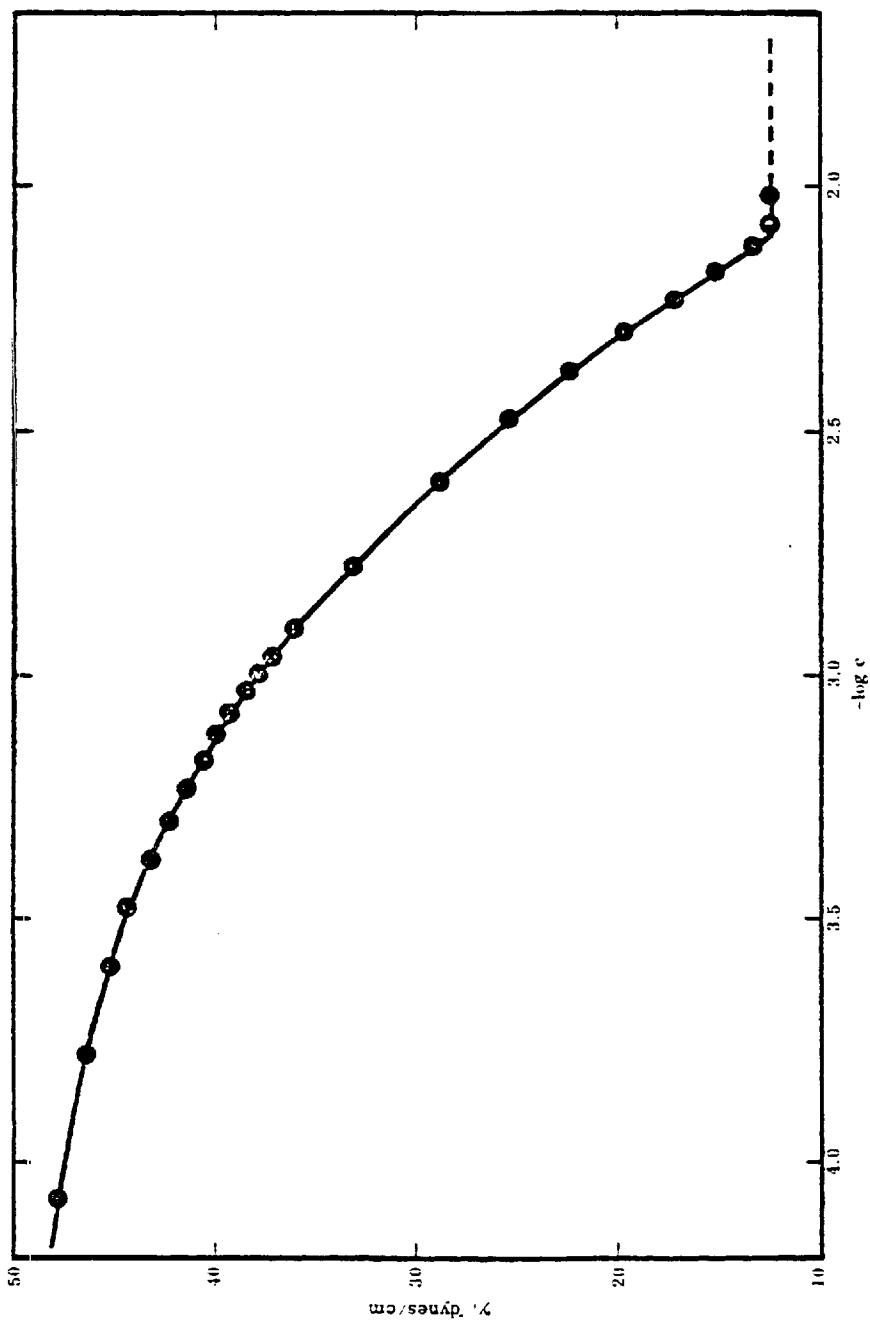


FIG. 5. Variation of interfacial tension γ at the octane-water interface with SDS concentration c .

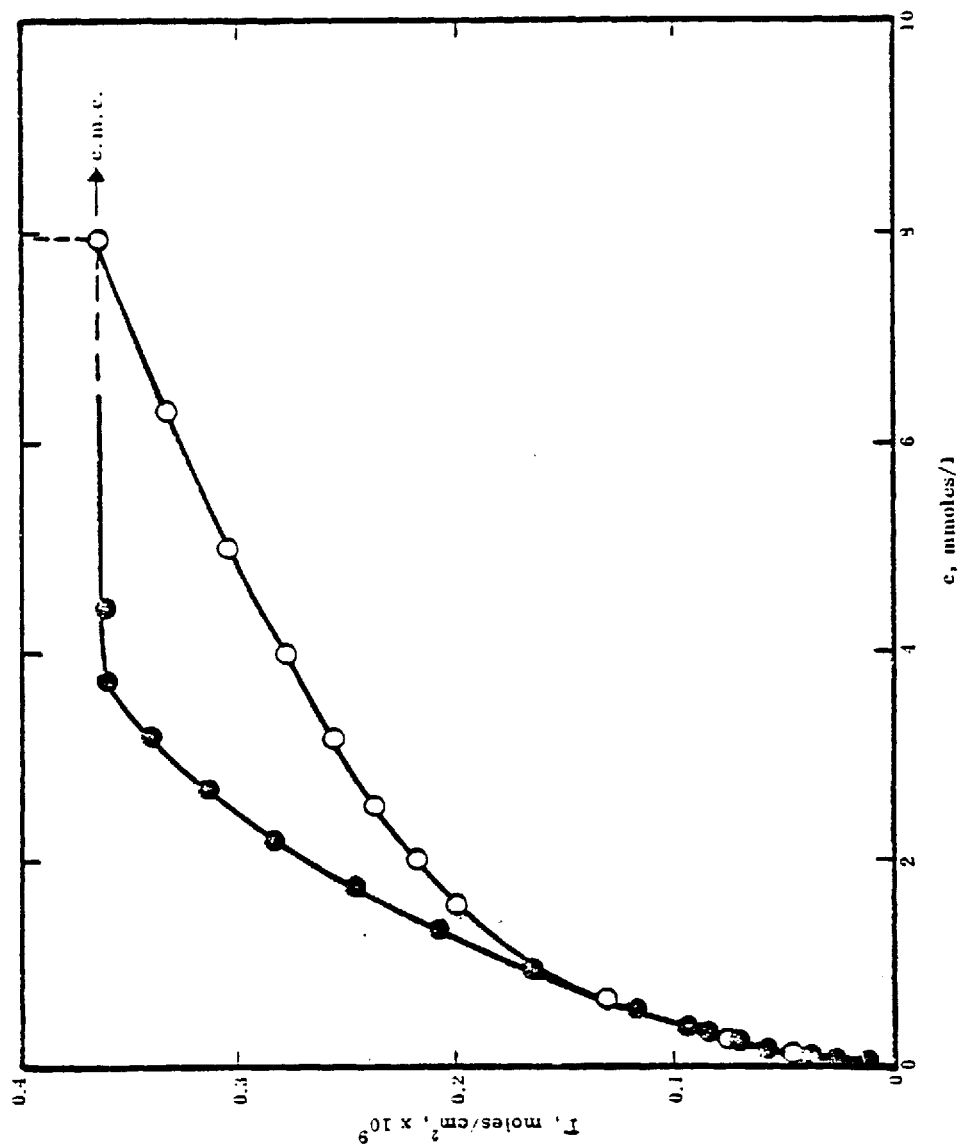


FIG. 6. Adsorption of SDS at (○) the octane-water interface and (●) the polymer-water interface of ion-exchanged Latex A-2.

and Sawyer and Rehfeld [26]. Note that we use the $2kT$ factor in the Gibbs equation for anionic SDS in the absence of salt (also see Ref. 27).

The isotherm can also be written as

$$1/n = (1/N) + (c^{-1}/NK)$$

where n is the number of molecules adsorbed per cm^2 , $N = n$ at saturation (i.e., at the c.m.c.), and $K = (B_1/B_2)e^{W/RT}$, in which $B_1/B_2 = 0.86$ liter/mole and W the adsorption energy. For the adsorption of long-chain ions, the experimental W is split up into a chemical term W_0 and an electrical term $e\psi_0$; W_0 is 810 cal/ CH_2 group at the oil-water interface. Figure 7 shows the variation of $1/n$ with $1/c$; the intercept $1/N$ (the molecular area of SDS) is 46.7 Å as expected, and from the slope of the linear part of the curve ($n < 1 \times 10^{14}$) the value of W is 350 cal/ CH_2 group, which corresponds to a surface potential of 230 mV in the Langmuir region.

Then the variation of surface tension with SDS concentration was determined for clean Latex A-2 (0.576 g of polymer). The adsorption isotherm calculated from γ is also shown in Fig. 6. In the low concentration region the two isotherms are identical, but at intermediate concentrations the adsorption at the polymer surface is greater and a definite plateau is observed at 0.26×10^{-3} mole/g polymer. This corresponds to a surface area of 72 m^2/g , or a particle diameter of 790 Å if the molecular area is 46 Å as found above. Although this diameter is significantly smaller than the electron microscope value of 880 Å, it is in excellent agreement with the ultracentrifuge diameter to be reported below and literature values of 760 [28] and 800 Å [29] determined by light scattering and 780 Å [30] determined by small-angle x-ray scattering for this same latex. The adsorption isotherms have not yet been completely evaluated, but it will be interesting to compare the adsorption at the octane-water interface with that at the polymer-water interface and the effect of the resident charges (sulfate end-groups) on this adsorption.

Other data were obtained by adsorption of nitrogen at -196°C according to the classical BET method [31]. Clean latexes were coagulated by freezing and thawing; the polymer was dried and out-gassed under vacuum for 48 hr at room temperature to prevent coalescence. The adsorption isotherm for Latex A-2 polymer (Fig. 8) shows a small hysteresis loop indicating some microporosity; the Point B saturation adsorption is 17.6 ml/g; the same value is found from the linearized BET isotherm in the relative pressure range 0.05-0.3. Using 16.2 Å for the molecular area of nitrogen, the specific surface area of the polymer is $77.5 = 2 \text{ m}^2/\text{g}$ (av of three

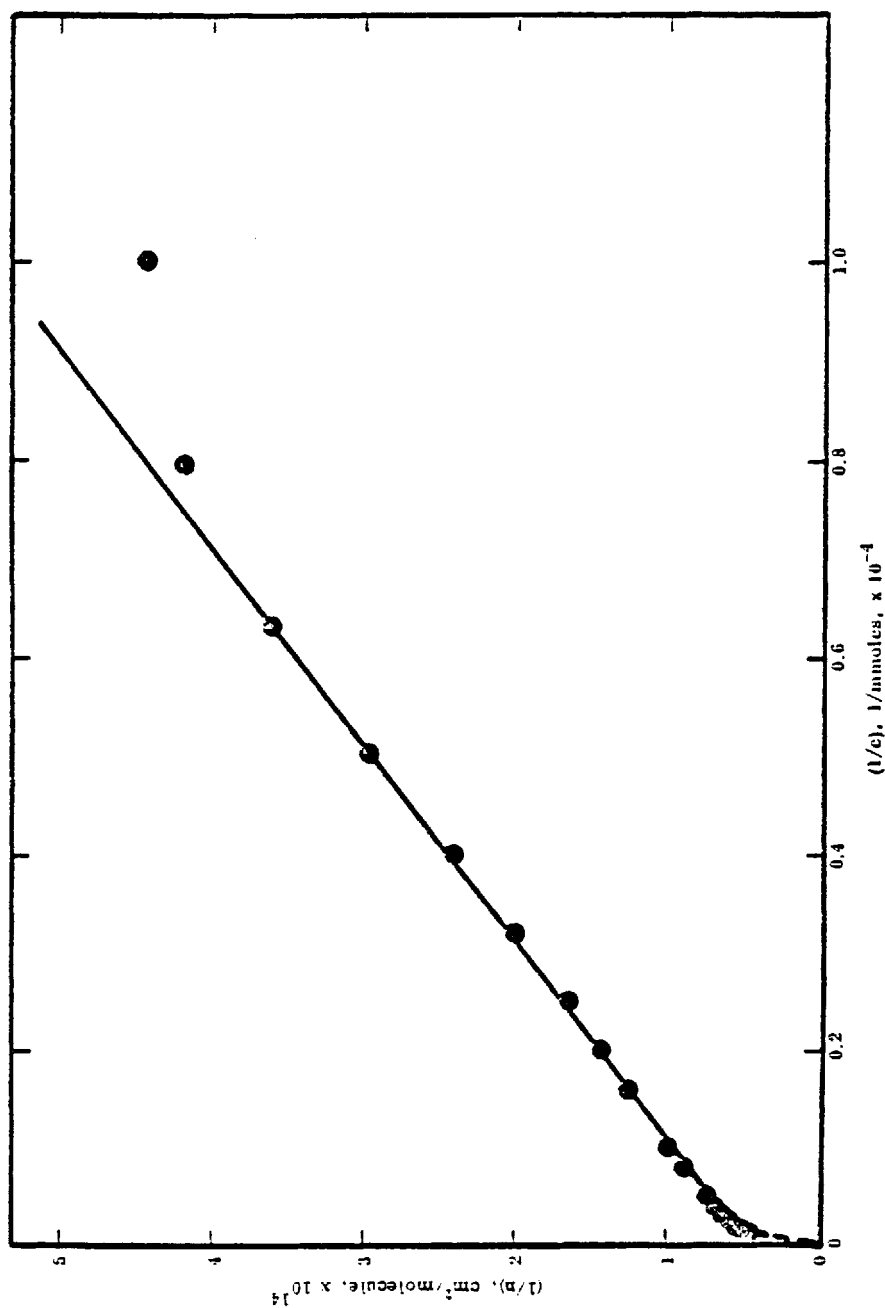


FIG. 7. Variation of $1/n$ with $1/c$ for the adsorption of SDS at the octane-water interface.

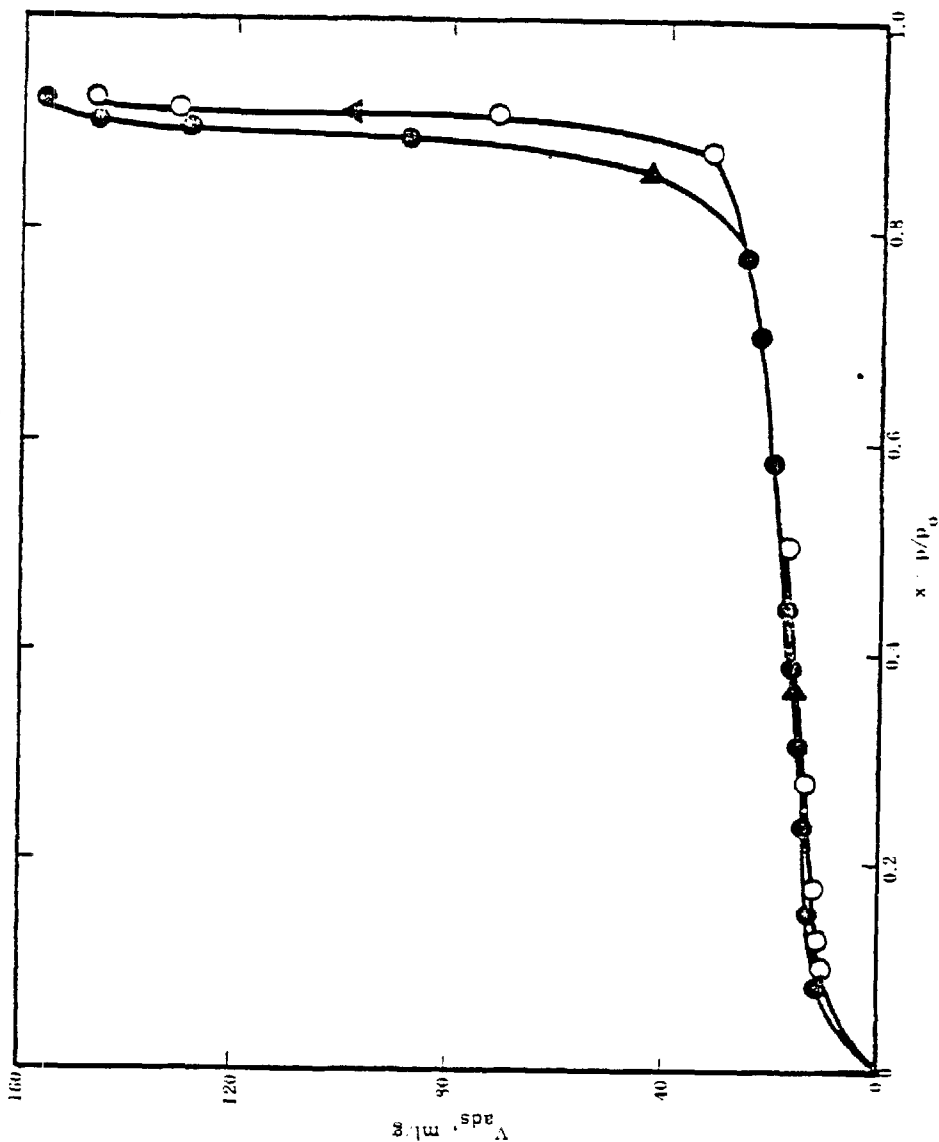


FIG. 8. Adsorption and desorption isotherms of nitrogen at -196°C on Latex A-2 polymer: (○) adsorption; (●) desorption. The arrowheads indicate the direction of the experiment sequence.

determinations) which corresponds to an average particle diameter of 740 Å. This value also is in the same range as those determined by SDS adsorption, light scattering, and ultracentrifugation, and is significantly smaller than the electron microscope value. Moreover, the surface areas of larger particle size latexes determined by nitrogen adsorption also deviated from the geometrical areas calculated from electron microscope measurements (Table 3).

TABLE 3. Electron Microscope and Nitrogen Adsorption Areas Before and After Heat Treatment

Latex	Surface area (m^2/g) ^a			
	Before heat treatment		After heat treatment	
	S_{EM}	S_{BET}	S_{EM}	S_{BET}
A-2	64.7	77.5	41.6	55.0
B-1	36.0	50.5	25.8	28.6
A-5	7.2	12.7	-	-
A-6	5.5	10.0	5.6	6.9
C-1	22.4	37.2	25.5	31.9
D-4	12.7	18.3	-	-

^a S_{EM} : Electron microscope surface area. S_{BET} : Nitrogen adsorption surface area.

Apparently these latex particles are not just smooth, impermeable spheres, but instead have uneven surfaces or are somewhat porous (although Latex A-2 polymer did not show any evidence of porosity by mercury porosimetry). To investigate this point, four latexes were heated for several hours at 120°C, well above the glass transition temperature (~100°C), on the assumption that at this temperature the uneven surfaces would smoothen or the pores would close up because of the force exerted by the polymer-water interfacial tension and the greater mobility of the polymer chains. Indeed, after this treatment the surface areas of the latex polymers were considerably smaller; however, electron microscopy showed that the particles of Latexes A-2 and B-1 had agglomerated to form uniform-size larger

spheres comprised of four and three primary particles, respectively; Latexes A-6 and C-1 showed no evidence of such agglomeration. The agreement between the nitrogen adsorption and electron microscope surface areas was better after the heat treatment than before except for Latex A-2, which displayed the same $13\text{-m}^2/\text{g}$ difference. Thus we conclude that with this exception the latex particles were porous or had uneven surfaces, which could influence the structure of the electrical double layer and the adsorption of small molecules.

Sedimentation

Ultracentrifuge (UCF) experiments were carried out to determine the latex particle size and the effect of adsorbed soap and of the electrical double layer on the sedimentation rate. The experiments were carried out at $3\text{-}4^\circ\text{C}$ (to minimize convection) and 2,200-14,000 rpm. A polymer concentration of 0.08% was chosen after it had been shown that in this range the sedimentation rate is virtually independent of concentration. The sedimentation was followed by a photoelectric scanner detector. The reproducibility was very good, e.g., Latex A-2 in 0.1% Aerosol MA solution gave diameters of 854, 856, and 854 Å in three consecutive experiments.

UCF measurements of particle size have the advantage that no preparation other than dilution is required; thus the particles are not affected by the measuring technique. One drawback, however, especially for polystyrene particles, is the sensitivity to density variations. The particle radius r is calculated from the sedimentation constant S_t according to

$$r^2 = (9/2) (\eta_0 S_t) / (\rho - \rho_0)$$

where η_0 is the viscosity of the medium and $(\rho - \rho_0)$ the difference between the densities of the polymer and the medium. With $\rho_0 = 1.00$ and $\rho = 1.05$, an uncertainty in the polymer density of 0.001 (i.e., 0.1%) results in an uncertainty of 1% in the value of r . We chose the average literature value of 1.054 for the density of emulsion polystyrene. Table 4 shows that the UCF diameters calculated using this value are on the average about 6% smaller than the electron microscope (EM) diameters. This could be explained by a polymer density of 1.048, but this value seems unreasonably low. This discrepancy recalls similar differences reported by various investigators [28-30, 32-34] between light scattering and small-angle x-ray scattering diameters of Dow monodisperse latexes and the EM values supplied by Dow [35]. The average difference for 11 latexes is about 5%, with a tendency toward the deviation decreasing with increasing particle size. These latexes fall in the same

TABLE 4. Electron Microscope and Ultracentrifugation^a Particle Diameters

Latex	Average particle diameter (Å)		Difference (%)
	Electron microscope	Ultracentrifugation	
A-2	880	822	-6.4
LS-1044-E	1,090	1,020	-6.0
LS-052-A	1,260	1,100	-12.4
B-1	1,580	1,460	-7.9
A-4	1,760	1,690	-4.0
A-3	2,340	2,180	-6.8
LS-1010-E	3,570	3,330	-6.5
D-4	4,470	4,260	-4.7
LS-1029-E	5,000	4,770	-4.5
LS-063-A	5,570	5,140	-7.7
LS-1012-E	7,140	6,860	-3.8
A-5	7,940	7,870	-0.9
LS-449-E	7,960	7,190	-9.6
A-6	10,440	10,610	+1.6
LS-1028-E	10,990	10,010	-9.0
		av	-6.0

^aMedium 0.1% Aerosol MA solution.

size range as those of Table 4, but only two were still available: LS-063-A with an average of 5360 Å (three methods) or 3.8% smaller, and A-2 with an average of 790 Å or 10.7% smaller. The latter value is confirmed by our adsorption values of 790 and 740 Å and the UCF value of 780 Å calculated from McCormick's data [36] for $\rho = 1.054$. One suggestion to explain this discrepancy is that the nonconducting particles are charged in the electron beam, giving rise to refraction which gives a slightly larger projected image. Other explanations such as "cold flow" of the particles on the substrate have been ruled out by the study of Bradford and Vanderhoff [35].

Next we studied Latex A-2 more extensively to determine the effect

of the double layer on the sedimentation rate. In Table 5, the electrolyte value is the overall average of the $787 = 8 \text{ \AA}$ value for 10^{-4} to 10^{-1} N KNO_3 , the $800 = 10 \text{ \AA}$ value for 2.5×10^{-3} to $10^{-5} \text{ N Ba(NO}_3)_2$, and the $783 = 11 \text{ \AA}$ values for 10^{-6} to $5 \times 10^{-5} \text{ N Al(NO}_3)_3$. Coagulation occurred for all three electrolytes at a concentration twice that of the foregoing upper limit concentrations. The variation of particle diameter with electrolyte concentration was not significant although the values obtained at the lower limit concentration were the smallest.

TABLE 5. The Particle Diameter of Latex A-2 as Determined by Ultracentrifugation

Latex treatment, medium	Particle diameter (\AA)
Ion-exchanged, in water	756
in electrolyte	790
in 0.1% Aerosol MA	822
Original latex, in 0.1% Aerosol MA	854
(Electron microscope)	(880)

To interpret these data, let us assume that the 790- \AA value for the ion-exchanged latex in electrolyte represents the actual diameter of the polystyrene particles, since the thickness of the double layer is minimized in this medium and no emulsifier is present. This value thus replaces the 822- \AA value in Table 4 for 0.1% Aerosol MA. Presumably these particles are covered with a 16- \AA -thick layer of emulsifier. If this represents a monolayer, the 854- \AA -diameter of the original latex diluted in emulsifier solution is just 32 \AA larger, suggesting that the particles of this sample are covered with a bimolecular layer of emulsifier.

On the other hand, the value of 756 \AA for the ion-exchanged latex diluted in water should show the effect of the expanded double layer on the sedimentation rate. Taking the value of $\alpha = 0.21$ (to be defined later) determined by conductance measurements for this latex, let us assume that 79% of the counterions are in the Stern layer and 21% in the diffuse double layer. Using the potentials calculated from the tables of Loeb et al. [37], this gives, at an electrolyte concentration of $2.6 \times 10^{-6} \text{ M}$, -190 mV for the Stern potential and 0.23 for κa , where κ is the reciprocal thickness of the double layer and a is the particle radius. Substituting these values in Booth's equation [38] for the change in sedimentation rate due to the double layer, we obtained a sedimentation diameter of 760 \AA , in excellent agreement with the measured value of 756 \AA .

Viscosity

The viscosity of the small particle size latexes increased greatly during ion exchange because of the removal of electrolyte, e.g., the ion exchange of Latex A-2 was limited to solids concentrations of 5% or less because at higher concentrations the latex became gelled. The addition of electrolyte, however, decreased the viscosity, so that emulsifier-free latexes of higher solids contents can be prepared by evaporation. The viscosity of the original and the ion-exchanged Latex A-2 was measured at small values of the volume fraction of polymer ϕ . The viscosity behavior of the original latex was Newtonian at values of ϕ below 0.15. The ion-exchanged latex, however, displayed non-Newtonian behavior at values of ϕ as small as 0.0047 (0.5% solids). The addition of small concentrations of electrolyte, e.g., 10^{-3} N KNO_3 , was sufficient to restore the Newtonian flow.

A detailed analysis of the viscosity of the electrolyte- and emulsifier-free latexes at low electrolyte concentration is possible only if the electrokinetic parameters of the latex are known. These have not yet been determined, but the results can be discussed in terms of the effective volume fraction of polymer ϕ_f . Table 6 shows

TABLE 6. Reduced Specific Viscosity for Emulsifier- and Electrolyte-Free Latex A-2

ϕ (%)	Reduced specific viscosity
3.07	143
1.90	91
0.95	76
0.47	65
0.09	29

the variation of the reduced specific viscosity $(\eta - \eta_0)/\eta_0 \phi$ with ϕ . These values are much greater than the limiting value of 2.5 for the reduced specific viscosity.

It is of interest to determine whether this large electroviscous effect observed in ion-exchanged Latex A-2 is a primary effect, i.e., due to distortion of the electric field around the particle by the flow, or a secondary effect; i.e., due to double layer interaction (more detailed studies of electroviscous effects in latexes have been made by

Stone-Masui and Watillon [39] and Wang [40]). Booth's treatment of the primary electroviscous effect [41], when applied to our results, accounts for only 1-5% of the observed increase in viscosity, depending upon the value selected for the ζ -potential. Therefore, the secondary effect is predominant, as is also expected from the non-Newtonian viscosity behavior (see Ref. 42).

Our data were analyzed by the method of Saunders [43], who re-wrote Mooney's equation [44] in the form

$$\phi / \log \eta_r = (2.303/k_0 f) - (2.303z/k_0 f) \phi$$

in which η_r is the relative viscosity, z is the so-called self-crowding factor, f is the ratio ϕ_f/ϕ , and k_0 has the value 2.5. The values of $\phi / \log \eta_r$ varied linearly with ϕ , so that f , and hence ϕ_f , could be determined from the intercept. The effective volume fraction corresponds to an effective particle radius that is indicative of the double layer interaction. The calculated values for this effective particle radius are 458 Å for the original Latex A-2, 474 Å for the ion-exchanged latex in 10^{-2} N KNO_3 , and 1250 Å for the ion-exchanged latex in water. The first two values are in good agreement with the sum of the electron microscope radius and the thickness of the double layer, 470 Å. The effective particle radius of 1250 Å for the ion-exchanged latex in water is the same as that indicated by the interference colors of the latex (see following section). Thus the viscosity measurements show that the double layer expanded greatly when the electrolyte was removed by ion exchange but decreased in thickness to the original value when electrolyte was added back to the ion-exchanged latex.

Interference Colors

Dried films of certain monodisperse polystyrene latexes display brilliant iridescent colors. These colors have been attributed to the diffraction of visible light by latex particle crystallites [45-47]. Polystyrene latexes form opaque, white, friable, discontinuous films when dried at room temperature. Electron micrographs of surface replicas of these films show the monodisperse spheres packed in uniform hexagonal arrays without appreciable coalescence [48]. If the distance between the particle centers is within a certain range, the crystallite diffracts visible light and the interference colors are observed. These color combinations are specific for the latex particle diameter (Table 7).

These interference colors are occasionally seen in the latex, on the wall of the sample bottle, or floating on the surface. In these cases the

TABLE 7. Interference Colors of Dried Polystyrene Latex Films

Approximate particle diameter range (\AA)	Color combinations ^a
Less than 1700	No colors
1700-2200	Yellow violet
2200-2700	Pink green
2700-2900	Turquoise gold
2900-3100	Red olive green ^b
About 3500 and greater	Rainbow colors ^c

^aWhich color is observed depends upon the angle of observation.

^bThe olive green is seen only infrequently.

^cThe rainbow colors are usually weak in intensity.

colors presumably arise from the diffraction of light by "tactoids," i.e., aggregates of latex particles packed in orderly arrays. In some cases the color combinations observed in the latex are the same as those observed in dried films of the same latex; in others, however, the color combinations are different. This is explained by the fact that the distance between the particle centers may be greater in the tactoid than in the dried film. In the latex the mutual approach of neighboring particles is hindered by the double-layer repulsion, so that particles aggregated in orderly arrays may not be in actual contact with one another; however, during drying the water-air interfacial tension forces the particles into close-packed arrays despite the double layer repulsion [49]. This difference in the distance between the particle centers could be great enough to give a different color combination since some of the size ranges shown in Table 7 are narrow.

The ion exchange not only desorbs the emulsifier from the particle surface but also removes the electrolyte from the aqueous phase. This decrease in electrolyte concentration increases the thickness of the double layer so that neighboring particles interact with one another at greater distances. For example, the original Latex A-2 (880 \AA diameter) displayed no interference colors, either in the latex or in the dried film. After partial ion exchange, however, the yellow-violet combination was observed, indicating that the distance between the particle centers was at least 1700 \AA . After complete ion exchange the pink-green combination was observed in the latex, indicating that this distance had increased to at least 2200 \AA . This sample also contained

microscopic-size (10-300 μ) blue and green tactoids, not only on the wall of the container and surface of the latex, but throughout the body of the sample [9]. These tactoids disappeared when the sample was shaken or heated to 35-40°, only to reappear again upon standing at room temperature. Such tactoids observed here in samples containing only 1-2% polymer are similar to those observed earlier by Luck and Wesslau [46] in samples of much higher solids contents. Another sample of Latex A-2 after exhaustive ion exchange showed different color combinations upon dilution, the yellow-violet combination observed at 3.24% polymer changing to violet-green at 2.00% and pink-green at 1.00 and 0.50%, indicating that the distance between particle centers increased upon dilution.

In another example the original Latex A-4 (1760 Å diameter) displayed the yellow-violet combination both in the dried film and in the latex. After extensive dialysis the pink-green combination was observed in the latex, indicating that the distance between particle centers was 400-900 Å greater than the particle diameter. After only one ion-exchange cycle the rainbow colors were observed, indicating that this 400-900 Å distance had increased to at least 1200 Å.

Hiltner and Krieger [50] described a quantitative method to determine particle spacings in these systems by means of diffraction. They confirm that the particle spacings in electrolyte-free latexes increase upon dilution from values close to the particle diameter to several times that value. The order, which is either face-centered cubic or hexagonal close-packed, is maintained throughout the latex (in our case, down to 0.5% solids).

This order can be explained at least qualitatively by the fact that the electrical double layer surrounding the particles prevents close contact. The ion-exchange treatment reduces the electrolyte level such that the double layer is expanded greatly. Estimates of the double layer thickness $1/\kappa$ from conductance and pH measurements show that the interparticle distance is of the order of $2/\kappa - 4/\kappa$. The potential-energy curve is probably fairly steep, thus preventing large fluctuations in particle spacings. In other words, if repulsion keeps the particles a distance $4/\kappa$ apart, the result is a suspension of spheres with an effective radius of $r + 2/\kappa$, i.e., electrolyte-free Latex A-2 containing 2% solids will be as crowded as the original latex containing 46% solids.

The arrays of perfect order comprising the tactoids may result from a shallow potential energy minimum (although estimates of the Van der Waals energy seem to contradict this). Our observation that the tactoids are easily disrupted and reformed is consistent with the shallowness of the so-called secondary minimum found by theoretical calculations. Further study of these tactoids should elucidate these long-range interaction effects.

Conductance

In most colloidal properties, e.g., stability, viscosity, or sedimentation, it is the potential of the outer Helmholtz layer ψ_s (or the diffuse double-layer potential) that is more important than the surface potential ψ_0 . The values of ψ_0 are calculated from the surface charge, i.e., the total charge measured by conductometric titration. The values of ψ_s are calculated from the "effective charge" or diffuse charge, which takes into account undissociated negative groups and counterions in the Stern layer and which is represented by the surface charge multiplied by the "apparent degree of dissociation" α . If the values of α can be determined, then the values of ψ_s can be calculated and compared with such direct experimental measures of the ζ -potential as the electrophoretic mobility.

To obtain accurate measurements of α , the specific conductance of the ion-exchanged latexes was measured at different concentrations in a Washburn-type cell at $25 \pm 0.01^\circ\text{C}$. It was assumed that the electrolyte concentration of the ion-exchanged latexes was zero and that the conductance was due mainly to the counterions, the contribution of the charged particles to the conductance being 10% or less. Therefore, α is defined as the ratio of the measured conductance to the conductance expected from the known number of H^+ ions (from the conductometric titration). The measured conductances were corrected for the conductance of pure water and the expected conductances for the presence of the charged particles. Table 8 shows the values of α determined in this manner for six latexes. These values range from

TABLE 8. "Apparent Degree of Dissociation" α of the Surface Groups

Latex	Surface charge ($\mu\text{C}/\text{cm}^2$)	α
A-3	2.0	0.39
D-1	1.5	0.35
A-2	3.3	0.21
B-1	4.2	0.10
B-2	5.7	0.054
D-4	8.1	0.05

0.05 to 0.39 and generally decrease with increasing surface charge, indicating that the greater the surface charge, the more tightly are the counterions held in the double layer.

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