External Double Bonds.[9]—This determination was made by the reaction with perbenzoic acid by a modification of the method of Kolthoff and Lee.[10]

Summary

By means of refractive index measurements, styrene contents have been determined as a function of conversion of products from the sodium-catalyzed copolymerization of butadiene with styrene. Results show styrene to be the more reactive monomer, in contrast to the reaction in emulsion systems.

Refractive indices of sodium-polymerized products are lower than of copolymers from emulsion reactions. This difference is postulated to be due to higher proportions of external double bonds in the former.

BARTLESVILLE, OKLAHOMA RECEIVED JUNE 9, 1948

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[10] Kolthoff and Lee, *J. Polymer Sci.*, **2**, 206 (1947).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

The Electrophoretic Mobility of Type III GR-S Latex

BY S. H. MARON AND W. W. BOWLER[1]

Introduction

Type III GR-S latex is a negatively charged colloidal dispersion of butadiene-styrene copolymer particles in an aqueous medium. The latex is prepared by emulsion polymerization of equal weights of the monomers in the presence of the potassium soap of K-wood rosin as emulsifier. As it appears on the market the latex is stripped of unreacted monomers, and contains neither a shortstopping agent nor an antioxidant.

In a preceding paper from this Laboratory[2] were reported the effects of various factors upon the electrophoretic mobility of Type II GR-S latex. Type II latex differs from Type III in being stabilized by fatty acid soap rather than rosin soap, and in being prepared from a 3:1 proportion by weight of charged butadiene–styrene rather than 1:1. It is of interest, therefore, to determine how these altered conditions influence the mobility, and, in turn, the stability, of Type III latex. Consequently, effects of total solids content, *p*H, ionic strength of added electrolyte, temperature, and soap content on the mobility of Type III latex have been investigated and are reported in this paper. Also given here are the zeta potentials calculated from the data.

Experimental

The moving boundary apparatus and procedure employed were essentially the same as described previously.[2] Disodium phosphate solutions containing a trace of potassium chloride were used as the electrolyte added to the latex, and for the leading and following solutions. For a latex solution 0.05 molar in disodium phosphate, and having a specific conductance of 0.0082 ohm^{-1}, the optimum current through the cell was found to be 1.5 milliamperes. Currents greater than 1.5 milliamperes tended to produce diffuse boundaries and to give uncertain mobility values. For other solutions the current was varied as the square root of the specific conductance on the basis of 1.5 milliamperes for the above 0.05 molar disodium phosphate solution.

Mobilities were calculated from the migration rates of both the advancing (descending) and receding (rising) boundaries, and the averages taken. The mobilities from the two boundaries agreed generally within ±1.5%, and were apart *ca.* ±5.0% only in solutions of low *p*H where the latex solutions were highly unstable.

Three different cells were used in the present work, two constructed from *ca.* 8 mm. and one from 7 mm. Pyrex tubing. All cells gave the same results for a given sample.

Except when otherwise noted, the temperature for all experiments was 30.00 ± 0.05° and the *p*H between 8.7 and 9.3. In experiments where the *p*H was varied, the ionic strength was maintained constant by addition of appropriate quantities of hydrochloric acid or sodium hydroxide to the disodium phosphate buffers. In the runs with added soap, the soap was added to the latex and the solutions adjusted to a disodium phosphate ionic strength of 0.05. No cognizance was taken of the contribution made to the ionic strength by the added soap.

All conductivity measurements were made with a Leeds and Northrup Campbell-Shackelton bridge assembly and Jones Type B conductivity cell. The viscosities of the latex solutions were determined with an Ostwald–Cannon–Fenske pipet, while the densities with Weld Type pycnometers. A Beckman Type G glass electrode assembly was used for all *p*H measurements.

The Type III latex used in this work was a commercial product of originally *ca.* 40% solids. This latex was diluted with distilled water to give a stock solution of 21.7% total solids, 0.0378 normal soap and 0.0037 normal free rosin acid content. All solutions upon which measurements were made were prepared from this stock solution by further dilution with distilled water.

Effect of Various Variables on Electrophoretic Mobility

(1) **Total Solids Content.**—It was found possible to get sharp boundaries and concordant mobilities from both advancing and receding boundaries only with latex dispersions of 7–15 g. per liter of total solids. Below 7 g. per liter streaming of the latex produced diffuse boundaries. Above 15 g. per liter the receding boundary became diffuse and yielded a progressively smaller mobility as the concentration increased, while the advancing boundary remained sharp and gave the same mobility as in the more dilute range. In view of this behavior all runs were made at a concentration of 12 g. of latex solids per liter where both boundaries migrated with the same velocity.

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[1] The Firestone Tire and Rubber Company Research Fellow, 1946–1948. Present address: The Firestone Tire and Rubber Company, Akron, Ohio.

[2] S. H. Maron, D. Turnbull and M. E. Elder, THIS JOURNAL, **70**, 582 (1948).

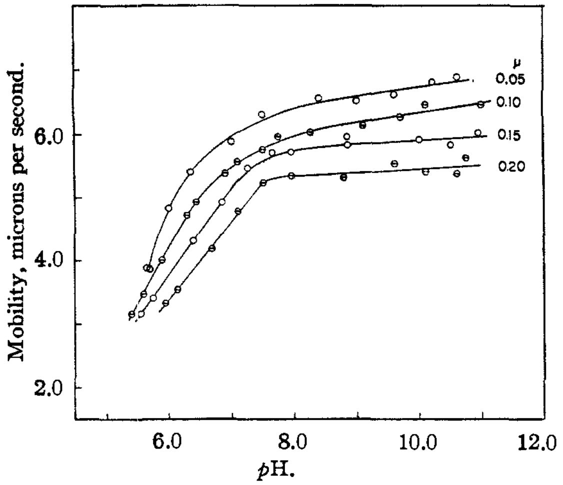

Fig. 1.—Effect of *p*H on mobility of Type III latex at various ionic strengths (30°).

(2) ***p*H.**—The mobility as a function of *p*H was determined at four constant ionic strengths of added disodium phosphate, namely, $\mu = 0.05$, 0.10, 0.15, and 0.20. The results are shown in Fig. 1. In all cases the mobility may be seen to decrease slowly and essentially linearly with decreasing *p*H in the range 11.0 to 8.5 and more rapidly from *p*H 8.5–5.5. Since at constant ionic strength the mobility is directly proportional to the charge on the particles, it is apparent that above a *p*H of 8.5 the charge is only slightly affected by *p*H, while it falls off rather rapidly with decreasing *p*H in the more acid solutions. This slow decrease in the charge with increasing acidity at the higher *p*H's is undoubtedly due to the gradual conversion of rosin soap to rosin acid. After the soap is almost completely converted the charge drops more rapidly, since now the latex particles are dependent for their protection upon a weak acid whose ionization is repressed the more the lower the *p*H. In addition, desorption of acid may occur at low *p*H values. In no case was it found possible to reduce the *p*H below about 5.5 without coagulation occurring before an experiment could be completed. Since the mobility was still 3–4 microns per second at this *p*H, it is evidently not necessary to reduce the charge to zero for coagulation to take place.

(3) **Ionic Strength.**—In Fig. 2 is given a cross-plot of the data in Fig. 1, showing the effect of ionic strength upon mobility at constant *p*H in the range $\mu = 0.05$ to 0.20 for seven different *p*H values from 5.5 to 10.0. It can be seen that at all *p*H values the mobility decreases with increasing ionic strength, but the decrease is more marked at the lower and higher ionic strengths than it is at the intermediate ones.

(4) **Temperature.**—The mobility of Type III latex was measured between 15 and 40° at ionic strengths of disodium phosphate from $\mu = 0.05$ to 0.20. The *p*H in all the experiments was kept essentially constant and equal to 8.8–9.2. The results, presented in Fig. 3, show a linear dependence of mobility on temperature of the same kind as found before with Type II latex.[2] The mobility, *v*, in microns per second, can be represented as a function of both μ and *t*, the temperature in °C, by the empirical equation

$$v = 2.32 - 365\mu^4 + \left(0.102 + \frac{0.0092}{\sqrt{\mu}}\right)t \qquad (1)$$

In Fig. 3 the points are the experimentally determined mobilities, while the lines are those calculated from equation 1. The agreement throughout is within experimental error.

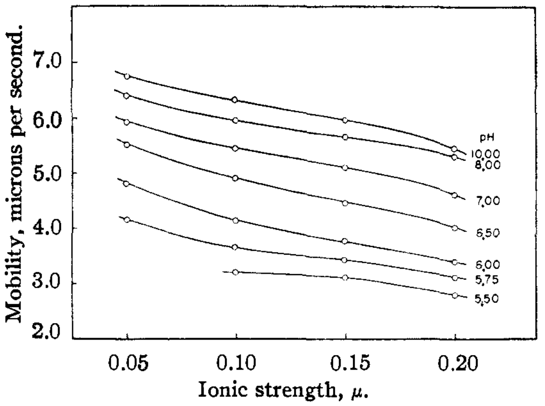

Fig. 2.—Effect of ionic strength on mobility of Type III latex at constant *p*H (30°).

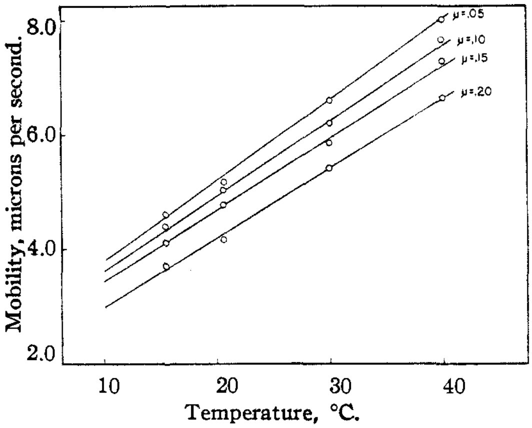

Fig. 3.—Variation of Type III latex mobility with temperature (*p*H 8.8–9.2): points, experimental; lines, equation (3).

(5) **Addition of Soap.**—A series of experiments were performed to ascertain the effect of additional soap upon the mobility of Type III latex. For this purpose solutions of sodium and potassium soaps of K-wood rosin were added to the latex, then disodium phosphate to give an ionic strength of 0.05 of this electrolyte, and the mobilities measured. The results obtained are shown in Fig. 4, where a plot of mobility *vs.* molarity of *added* soap is given. The total soap content of the latex was that indicated along the abscissa plus 0.0021 molar present initially.

TABLE I

CALCULATED ZETA POTENTIALS AT VARIOUS IONIC STRENGTHS AND TEMPERATURES

(η in millipoises; Z in volts)

		15.5°		20.65°		30.0°		40.0°	
μ	$6/f(\kappa r)$	η	Z	η	Z	η	Z	η	Z
0.05	4.53	11.8	−0.0838	10.36	−0.0872	8.28	−0.0912	6.81	−0.0956
.10	4.37	11.9	− .0772	10.46	− .0805	8.39	− .0838	6.89	− .0873
.15	4.30	12.0	− .0727	10.55	− .0759	8.48	− .0794	6.95	− .0827
.20	4.26	12.1	− .0647	10.66	− .0684	8.58	− .0728	7.02	− .0766

For both soaps the mobility decreases linearly with increasing soap concentration from the value corresponding to no added soap. The concentration of soap at which soap micellization occurs, and at which the rubber particles are covered with a monolayer of soap, has been found experimentally[3] to occur at 0.0136 mole of total soap per liter, or 0.0115 mole per liter of added soap (line AB in Fig. 4). These values refer to no added electrolyte. In presence of disodium phosphate the point of micellization and surface coverage with soap should, if anything, come at a lower total soap concentration. It is of interest to note that no discontinuity in the mobility–soap concentration curves is observed on passing the soap micellization point. This fact would seem to indicate that, when micellization occurs in solution, no fundamental change takes place in the character of the soap adsorbed on the rubber particles, and that the observed mobilities are not dependent upon changes in the aggregation of the soap in solution.

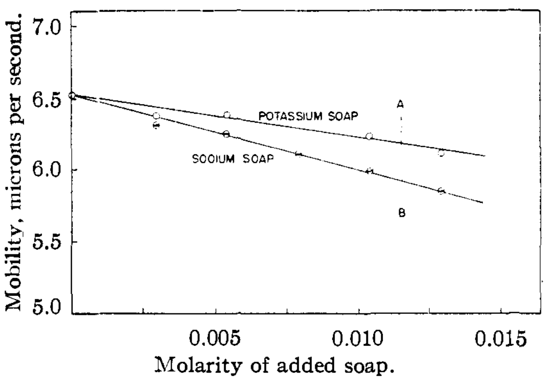

Fig. 4.—Effect of soap addition on mobility of Type III latex at 30°.

The mobility of latex might be expected to increase with addition of soap, inasmuch as added soap which is adsorbed on a particle would operate to increase its net negative charge. However, the observed decrease in mobility may be due to a simultaneous increase in the viscosity and ionic strength of the latex dispersions resulting from the soap addition. Both of these factors would lead to a drop in mobility, and apparently the drop more than compensates for any mobility increase to be anticipated from increase in charge of the rubber particles.

From Fig. 4 it is evident that the presence of sodium ions affects the latex mobility more than that of potassium ions. This observation is in agreement with two well-known facts. First, the viscosity of potassium rosin soap solutions is lower than that of the corresponding sodium soaps at the same concentration and temperature. Hence, on addition to latex potassium soaps may be expected to affect the viscosity less than sodium soaps, and thereby also to change the mobility to a lesser degree. Second, sodium ions destabilize a latex considerably more than a corresponding concentration of potassium ions, and consequently a lower mobility is to be anticipated in presence of sodium than of potassium ions at the same concentration.

The Zeta Potential of Type III Latex.—The zeta potentials may be taken as being related to the mobility by the Henry[4] equation, where Z is

$$Z = \frac{(300)^2 \pi \eta v}{D} \frac{6}{f(\kappa r)} \qquad (2)$$

the zeta potential in volts, η the viscosity of the latex in poises, v the mobility in centimeters per second, D the dielectric constant, and $f(\kappa r)$ is a function of the Debye κ, the reciprocal of the thickness of the ionic atmosphere, and r the radius of the particles. The value of the factor $6/f(\kappa r)$ varies from 6 when $\kappa r \ll 1$ to 4 when $\kappa r \gg 1$. The average radius of the particles in the latex sample used in this work was taken as 2.5×10^{-6} cm. This value is in line with the number average radii determined with the electron microscope for several Type III latices in this Laboratory.

In Table I are given the experimentally deter-

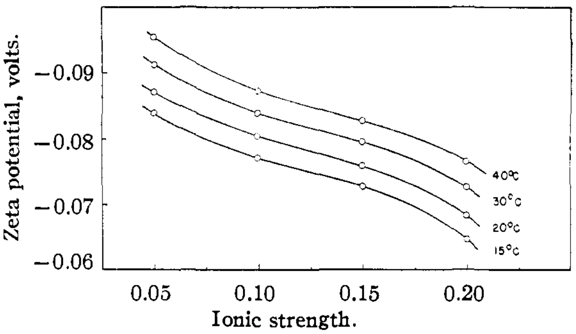

Fig. 5.—Effect of ionic strength on zeta potential of Type III latex (*p*H 8.8–9.2).

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[3] Method to be published at a future date.

[4] H. A. Abramson, L. S. Moyer and M. H. Gorin, "Electrophoresis of Proteins," Reinhold Publishing Corp., New York, N. Y., 1942, p. 121.

mined latex-electrolyte mixture viscosities, the values of the factor $6/f(\kappa r)$ as given by Abramson, Moyer and Gorin,[4] and the Z's calculated by means of equation (2). The requisite values v were obtained from equation (1), and of D from the data of Wyman.[5] In Fig. 5, Z is plotted as a function of ionic strength at four temperatures from 15 to 40°. The zeta potentials may be seen to decrease with ionic strength throughout the range studied in much the same manner as do the mobilities (Fig. 2). At each temperature the zeta potential apparently attains its highest values at ionic strengths below 0.05. Consequently, as may be expected, the latex is most stable at low salt concentrations. Since no reproducible results could be obtained below $\mu = 0.05$, it is not certain whether the zeta potential-concentration curves exhibit a maximum at low ionic strengths in this system, or whether they extrapolate directly to the $\mu = 0$ axis.

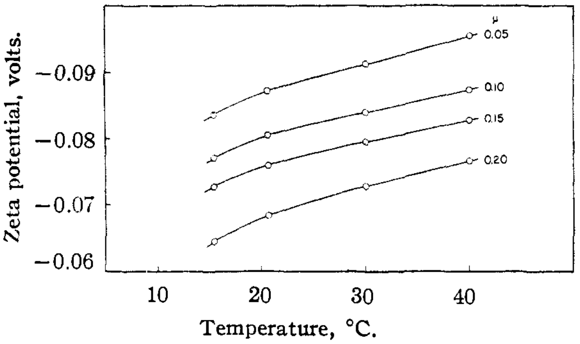

Fig. 6.—The effect of temperature on the zeta potential of Type III latex (pH 8.8–9.2).

In Fig. 6, in turn, are plotted the zeta potentials as a function of temperature at various constant ionic strengths. For all ionic strengths the zeta potentials show a continual increase with temperature rise. Such behavior of the zeta potentials is in agreement with the observation that a higher concentration of electrolyte is necessary to destabilize a latex at temperatures above 25° than at room temperature or below.

Comparison with Type II Latex

Under the same conditions of temperature and ionic strength the mobilities and zeta potentials of Type III latex are about 5–15% higher than those of Type II latex. Again, although the shape of the mobility-pH curves at $\mu = 0.15$ is similar for the two types of latices, the points of sharp change in slope are somewhat different for the two, being at pH 7.3 for Type III latex and at pH 6.9 for Type II latex. Outside of these two factors the behavior of the two types of latices is essentially the same as far as the effects of ionic strength, temperature, and viscosity are concerned.

Since Type III latices are considered to be more stable than Type II latices, this close similarity in the electrophoretic mobility of the two classes of latices is rather surprizing. However, it should be remembered that the mobility measurements were made on latices containing only 12 g. of solids per liter, whereas the latices are generally handled at concentrations of 250–400 g. per liter. This difference in solids contents may account on the one hand for the essential identity of electrokinetic behavior observed here, and on the other for the higher stability of Type III latex noticed when more concentrated dispersions are investigated.

Acknowledgment.—The authors wish to express their appreciation to The Firestone Tire and Rubber Company for its financial support of this research, and to Drs. F. W. Stavely and O. D. Cole of this organization for their continued interest in this work.

Summary

1. The electrophoretic mobility of Type III GR-S latex has been studied by the moving boundary technique as a function of total solids content, pH, ionic strength of added electrolyte, temperature and soap content.

2. From the available data were calculated the zeta potentials of the latex, and the effects of ionic strength and temperature upon these.

3. The electrokinetic behavior of Type III latex has been found to be very similar to that of Type II latex investigated previously.

CLEVELAND, OHIO RECEIVED MAY 10, 1948

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[5] J. Wyman, *Phys. Rev.*, **35**, 623 (1930).