The Electrophoretic Mobility of Type II GR-S Latex[1,2]

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Type II GR-S latex is a negatively charged colloidal dispersion of rubber polymer in an aqueous medium and like any such colloid, it can be made to migrate in an electric field toward the anode. By application of the moving boundary technique it is possible to measure the rate of this electrophoretic migration. Since the electrophoretic mobility is related to the charge on the colloidal particles, and since the charge in turn is responsible to a large degree for the stability of the colloid, such measurements can lead to a better understanding of the factors responsible for latex stability and of the way in which these factors are influenced by various modifications of the latex.

In this paper are presented results obtained on the mobility of Type II latex as a function of solids content, pH, temperature, ionic strength and electrolyte type. Also described are some studies made on the effects of creaming and redispersion, and of freezing and thawing of a latex on the mobility. From the mobilities have been calculated also the *zeta* potentials of the latex and the manner in which these potentials vary with temperature, pH and ionic strength.

Experimental

The assembly employed for measuring electrophoretic mobility consisted merely of the electrophoretic cell in series with a source of potential, a variable resistance and a milliammeter. The source of potential was a 90–180 volt B-battery bank whose output was regulated by means of the variable resistance. The milliammeter served to indicate the magnitude and constancy of current flow through the cell. Since latex solutions are turbid, the motion of the boundaries could be followed with a cathetometer positioned in front of the cell, which was kept immersed in a thermostat controlled to better than ±0.1°.

The details of the cell construction are shown in Fig. 1. Two microscope slides, S, each about 1.6 mm. thick, were ground to serve as sliding surfaces for formation of the sharp sheared boundaries. Holes about 8 mm. in diameter were drilled on each side of the slides as shown. A Pyrex U-tube, A, with vertical arms and flatly ground ends was then sealed with deKhotinsky or glycerine–litharge cement to the upper slide in such a manner as to make the tube ends flush with the sliding surface. To the lower slide were sealed in like fashion the lower arms, B, of the cell, due attention being given that the tubes be vertical and that their ground ends be flush with the lower sliding surface. These lower tubes were connected by thick gum rubber tubing to the two vessels, E, containing the electrodes. The electrodes consisted of coils of pure silver wire which were converted into thick silver–silver chloride electrodes by electrodeposition of chlorine upon them. Light copper leads were then hard-soldered to the electrodes for external circuit connection.

The cell was supported in the thermostat in the position shown in the figure by a special brass holder which was slotted horizontally to permit the sliding past each other of the surfaces S. With this arrangement the general procedure for making a run was as follows. Tube A was first inverted and filled completely with the latex dispersion to be studied. Next unit B of the cell was slid over the slide connected to the U-tube, shearing off thus the protruding drops of latex solution and enclosing the latex in the U-tube. In this operation slide B was always so displaced that the tube ends of A and B were closed off. To prevent leakage the ground surfaces of the slides were greased with purified vaseline before each experiment. Finally the electrode vessels E were attached to B, the vessels and tubes filled with enough leading and following solution to cover the electrodes, the center portion of the cell inverted and the entire assembly mounted in the thermostat in the position shown in Fig. 1. The latex portion A of the cell had to be kept in the position shown because the latex solutions were less dense than the electrolyte used for leading and following solutions.

The cell thus assembled was allowed to remain undisturbed in the thermostat until thermal equilibrium had been established. When temperature constancy was attained slide A was pushed manually along slide B until the tubes in A and B were continuous. In this manner two sharp sheared boundaries were obtained between the latex in A and the solutions in the two arms of B. After the boundaries were formed the current was turned on, adjusted to the desired value and kept there thereafter. With a high resistance in the circuit the current could be kept constant without any difficulty and any minor variations in resistance of the solution were not enough to upset the current setting. At various time intervals the positions of the two latex-solution boundaries were measured with the cathetometer.

To keep the potential gradient constant throughout the cell it was necessary to adjust the conductances of the leading and following solutions to those of the latex solution. This adjustment was made by using the same electrolyte for making up the latex as was used for the leading and following solutions and by making the concentrations of the latter such as to be identical with conductances of the latex–electrolyte mixtures. This procedure worked well with electrolytes containing chloride and gave no trouble with gassing at or fouling up of the electrodes. However, when electrolytes which did not contain chloride were used, considerable gassing occurred at the anode and a deposit frequently formed on the electrode. To overcome these difficulties enough sodium chloride was added to such electrolytes to make the concentration of chloride about 0.0002 molar. This small quantity of chloride was sufficient to eliminate the gassing entirely at low currents and to prevent the formation of any deposits on the silver–silver chloride anode.

Before initiating systematic measurements, a study was made to ascertain the most favorable currents for mobility determination. For this purpose the mobilities of latex solutions in 0.05 molar disodium phosphate were measured at currents of 5.0 and 1.5 milliamperes. At the latter current strength both ascending and descending boundaries were sharp and the mobilities calculated from their motion checked each other within the experimental uncertainty. When the higher current was used, however, the descending boundary was sharp and gave the same mobility as with a current of 1.5 milliamperes, but the ascending boundary was diffuse and the mobility calculated from its motion did not agree with that for the other boundary. Consequently in all the measurements reported here the current was kept sufficiently low to make both boundaries sharply defined. The optimum current for use with 0.05
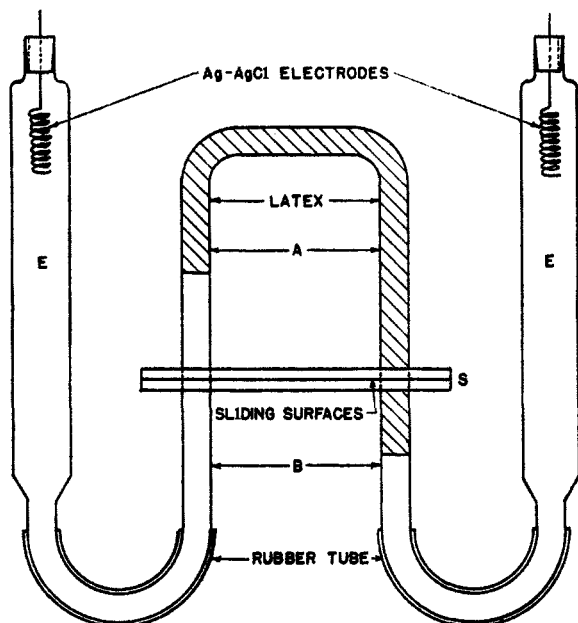
Fig. 1.—Latex electrophoretic mobility cell.

Fig. 2.—Plot of migration distance *vs.* time for Type II Latex no. 3: O, ascending boundary; △, descending boundary.

molar disodium phosphate was taken as 1.5 milliamperes and in all other cases the current was varied as the square root of the specific conductance of the solutions, giving thus approximately equal heating values due to current passage in all determinations.

The consistency of the data within a run was judged in all cases by the uniformity of the motion of the two boundaries. The distances which the boundaries traversed were plotted against time and the plots inspected. Any determinations in which the movements of the boundaries were not uniform or in which the boundaries were diffuse were discarded. Actually not many runs had to be eliminated for the reasons stated and these involved generally quite concentrated solutions of electrolyte or latex. A typical plot of migration distance *vs.* time is shown in Fig. 2. The plot is linear and very nearly identical for both boundaries.

The slopes of plots such as Fig. 2 give directly the actual rate of migration. To obtain from these the mobility the potential gradient under which the migration takes place must be known. This gradient follows readily from the specific conductance of the latex–electrolyte solution, L_s, the cross-sectional area of the tubes, S, and the current i, as $i/L_s S$, and hence the mobility, v, is given by

$$v = (l/t)/(i/L_s S) = l S L_s /it \qquad (1)$$

where l is the distance traversed by the boundaries in time t. In the present work the cross-sectional areas of the migration tubes were determined by calibration with mercury at various heights. In the cells used these areas were uniformly constant within experimental error.

In all experiments except those where the effect of temperature was studied, the temperature was kept constant at 30.0 ± 0.1°. Again, except
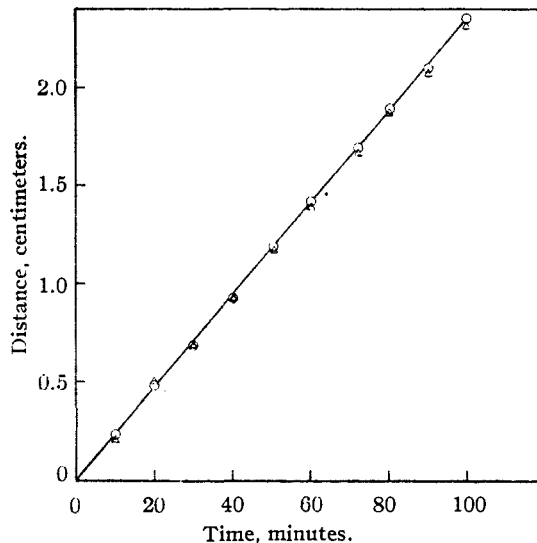
where mobility as a function of pH was investigated, the latter was generally held within the range 8.4–9.0 by addition of disodium phosphate. As will be shown below, in this pH range the mobility is very little affected by pH change. In fact, over this entire range the variation in mobility amounts to only 0.1 micron/second. Finally, since it was found that the total solids content of the latex had practically no effect on the mobility in the concentration interval 9–15 g. per liter, all measurements were confined to lattices falling within this concentration range.

The lattices employed in this study were polymerization products stripped of excess butadiene and styrene, and short-stopped. Latex no. 3 had an initial total solids content of 24.2% and a soap content 0.0362 normal, while Latex no. 7 had a solids content of 28.8% and a soap content 0.0474 normal.

All pH measurements were made with a Model G Beckman glass electrode assembly.

Effect of Various Factors on Latex Mobility.— In initiating this study it was assumed *a priori* that the mobility of a latex may depend upon (a) the total solids content, (b) the pH of the latex–electrolyte solution, (c) the ionic strength of the solution, (d) the temperature and (e) the type of electrolyte used to adjust the latex. In order to check the effects of these possible variables, experiments were designed to vary one variable at a time and to ascertain its effect on mobility.

(a) Effect of Total Solids Content.—Table I shows some results for mobility measurements in 0.05 molar disodium phosphate solutions at 30° on three concentrations of latex ranging from 9.4 to 29.4 g. per liter total solids. These relatively dilute lattices had to be used in the electrophoretic

studies because of density difficulties with either much more concentrated or more dilute dispersions. From Table I it may be seen that between 9 and 15 g. per liter total latex solids the mobility is independent of concentration. However, at 29 g. per liter the mobility is already not constant and, hence, all measurements were limited to the lower concentration interval.

TABLE I

EFFECT OF TOTAL SOLIDS CONTENT ON MOBILITY OF TYPE II LATEX No. 3 AT 30°

Electrolyte: 0.05 Molar Na_2HPO_4

Total solids, grams/liter	Descending boundary	Ascending boundary	Average
	\-—— Mobility (microns·cm./volt-sec.)-——		
9.4	5.58	5.58	5.58
14.7	5.59	5.62	5.61
29.4	5.38	5.49	5.44

(b) Effect of pH.—The effect of pH on latex mobility was studied at 30° at a constant ionic strength of 0.150. The pH's were adjusted to the desired values by addition of appropriate quantities of sodium hydroxide or hydrochloric acid to the disodium phosphate solutions used. The results obtained are summarized in Table II and are shown graphically in Fig. 3.

TABLE II

EFFECT OF pH ON MOBILITY OF TYPE II LATEX No. 3 AT 30° AND μ = 0.150

pH	Mobility microns-cm./volt-sec.
5.10	3.1
5.95	4.1
6.37	4.9
6.85	5.4
7.90	5.6
8.60	5.6
10.5	5.8
11.6	6.0

From this figure it may be seen that the mobility decreases slowly and linearly as the pH is decreased from about 12 to pH 6.85. At the latter pH, however, a sharp and again linear drop in mobility sets in. The measurements along the latter branch of the curve could not be carried below the pH of 5.10 because at the given ionic
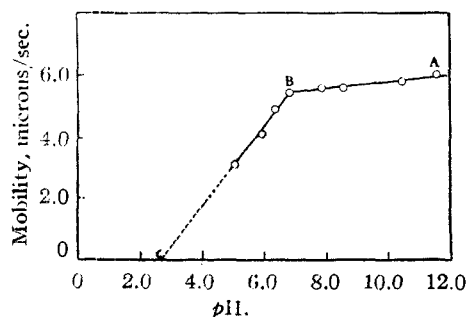

Fig. 3.—Effect of pH on electrophoretic mobility of Type II Latex no. 3 at 30° and μ = 0.150.

strength any further decrease in pH resulted in coagulation of rubber. If it be assumed that the course of mobility variation with pH below 5.10 is continuous with the curve shown, then the extrapolation of this plot to zero mobility yields a pH of 2.7 for the isoelectric point of the latex at μ = 0.150.

At pH's above about ten the emulsifier in Type II latex is present entirely as the sodium soap of the fatty acids used in polymerization. When the pH is lowered progressively below 10 conversion of the soap into a mixture of soap and fatty acid takes place until eventually all the soap is transformed into fatty acid. The slow decrease in mobility along curve AB in Fig. 3 is in all probability to be ascribed to the gradual change of soap into fatty acid, with consequent gradual decrease in the charge on the polymer particles. As the pH of 6.9 is reached this transformation of soap into acid is quite advanced and, hence, thereafter mostly fatty acid is present to give the latex stability. It is known that fatty acids are not so strongly adsorbed by the rubber as soap. Further, since fatty acids are weak acids their ionization is small. Consequently, appreciable conversion of soap into fatty acid leads to a decided decrease in charge of the latex particles and hence also to a decided decrease in their mobility. With still further decrease in pH all soap is removed and the ionization of the fatty acids is strongly repressed. Hence, the charge and mobility drop rapidly and the latex system becomes sufficiently destabilized to precipitate rubber. From what has been experienced with coagulation difficulties below a pH of 5.1 it would appear that it is not necessary to reduce the charge or mobility to zero in order to precipitate rubber. Rather, it is only necessary to reduce the charge and hence mobility to a low critical value, which in this case lies at a pH of about 5 at μ = 0.150.

(c) Effect of Temperature.—The effect of temperature on Type II latex mobility was studied in disodium phosphate solutions of μ = 0.144 and pH 7.9–9.0 over the temperature range 1–35°. The results obtained are summarized in Table III. They can be represented by the linear equation

$$v = 2.40 + 0.107t \qquad (2)$$

as may be seen from the comparison of the observed and calculated mobilities given in the last two columns of the table. This rate of change of mobility with temperature corresponds to an in-

TABLE III

EFFECT OF TEMPERATURE ON ELECTROPHORETIC MOBILITY OF TYPE II LATEX No. 3 AT μ = 0.144

Temp., °C.	Number of determinations	Mobility (microns-cm./volt-sec.) Observed	Calculated equation (2)
1.0	2	2.54 ± 0.03	2.51
20.0	2	4.48 ± .07	4.54
30.0	4	5.62 ± .06	5.61
35.0	1	6.13	6.15

crease of *ca.* 2% per degree at 25° which is of the same order of magnitude as the rate of change of mobility with temperature of ordinary ions.

(d) Effect of Ionic Strength and Electrolyte Type.—To obtain the effect of ionic strength on latex mobility measurements were made at 30° in disodium phosphate solutions ranging from 0.0077 to 0.240 molar, *i. e.*, μ = 0.023–0.720. The mobilities of Latex no. 3 thus obtained as a function of μ are shown in curve 2 of Fig. 4. From this curve it is seen that between μ = 0.023 and μ = 0.058 the mobility increases with ionic strength to go through a maximum at the latter value of μ. Beginning at μ = 0.058 and up to about μ = 0.43 the mobility decreases practically linearly with ionic strength. Thereafter the mobility becomes essentially independent of μ until an ionic strength of *ca.* 0.65 is reached. Beyond
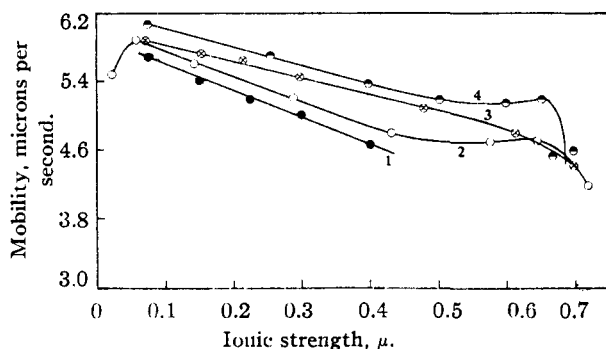

Fig. 4.—Effect of ionic strength on mobility of Latex no. 3 at 30° (*p*H range 8.2–9.0): O, Na_2HPO_4; ⊗, Na_2HPO_4–Na_2SO_4 (1:3 moles); ●, Na_2HPO_4–NaCl (1:4.5 moles); ◐, Na_2HPO_4–KCl (1:4.5 moles).

the latter value of ionic strength measurements of mobility become very difficult due to particle aggregation and consequent rubber segregation from the latex. However, the result obtained at μ = 0.72 shows, as might be expected, that at salt concentrations very near to those causing rubber separation a very sharp drop in mobility takes place. This particular result was obtained on a latex dispersion in disodium phosphate which did not segregate in the electrophoretic cell but separated on standing for several hours after completion of the run.

Similar data for Latex no. 7 are shown in curve 2 of Fig. 5. These data indicate in essence a similar dependence of mobility on ionic strength except that the maximum appears at a higher value of μ.

In order to ascertain whether ionic strength alone or electrolyte specificity as well are factors determining mobility variation a series of experiments were carried out on latex dispersions in Na_2HPO_4–NaCl, Na_2HPO_4–Na_2SO_4 and Na_2HPO_4–KCl mixtures. These electrolytes were used in presence of Na_2HPO_4 because the desired *p*H control could not be obtained with NaCl, Na_2SO_4 and KCl alone. In using these salts the
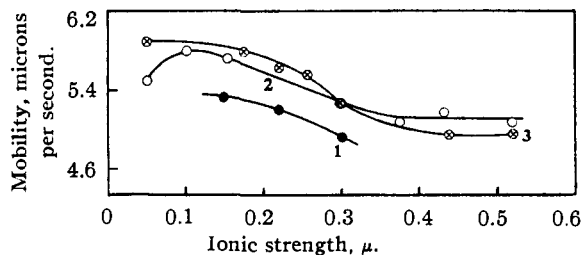

Fig. 5.—Effect of ionic strength on mobility of Latex no. 7 at 30° (*p*H range 7.9–8.7): O, Na_2HPO_4; ⊗, Na_2HPO_4–Na_2SO_4 (1:3 moles); ●, Na_2HPO_4–NaCl (1:4.5 moles).

molar ratio of Na_2HPO_4 to the second salt was kept constant in each series but the over-all concentration of the solution was varied to obtain different ionic strengths. The results obtained are depicted in curves 1, 3 and 4 of Fig. 4 and curves 1 and 3 of Fig. 5. In both figures the measurements on the Na_2HPO_4–NaCl solutions could not be carried to higher ionic strengths than those shown due to rubber segregation from the latex–salt mixtures.

From the positions of the various curves in the two figures it is quite evident that ionic strength alone is not the factor responsible for mobility variation, but that the nature of the electrolyte as well is significant. At any given ionic strength NaCl is most effective in lowering mobility, followed in turn by Na_2HPO_4, Na_2SO_4 and KCl. This order is the same as that observed in this laboratory for the effectiveness of the various electrolytes as precipitating agents for rubber from Type II latex. However, the specificity of electrolyte action is not as pronounced as Figs. 4 and 5 would tend to suggest. If the data in Fig. 4 for Latex no. 3 be replotted to show mobility as a function of total cation concentration in equivalents per liter we obtain Fig. 6. Plotted in this
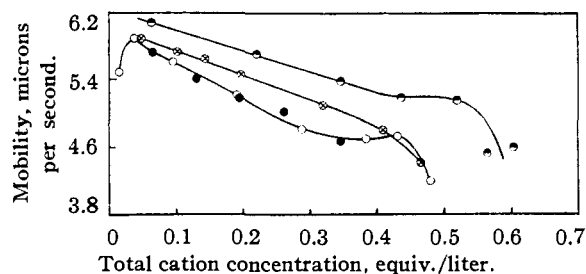

Fig. 6.—Mobility of Latex no. 3 as a function of total cation concentration at 30° (*p*H range 8.9–9.0): O, Na_2HPO_4; ⊗, Na_2HPO_4–Na_2SO_4 (1:3 moles); ●, Na_2HPO_4–NaCl (1:4.5 moles); ◐, Na_2HPO_4–KCl (1:4.5 moles).

manner the data for Na_2HPO_4 and Na_2HPO_4–NaCl can be made to fall along the same curve but the data for Na_2HPO_4–Na_2SO_4 and Na_2HPO_4–KCl mixtures still remain displaced. Essentially the same picture is given by a replot of the data for Latex no. 7 except that here the Na_2HPO_4–

Na₂SO₄ data lie closer to those for Na₂HPO₄ and Na₂HPO₄–NaCl. These observations suggest, at least in the case of the electrolytes containing sodium only, that to a large degree the lowering in mobility is a function of the total cation concentration present but that this action of the sodium ions is modified by the nature of the particular co-ion with which it is associated.

The less effective action of potassium chloride in lowering mobility is in all probability due to exchange of sodium ions in the adsorbed soap layer for potassium. Potassium soaps are much more difficult to salt out from a latex than sodium soaps and this fact may be taken to indicate that electrolytes are less effective in desorbing potassium than sodium soaps. Consequently, the charge on latex particles in presence of potassium ions is preserved more effectively and the mobility does not fall as rapidly with ionic strength as in presence of sodium ions alone.

It is to be expected that all the curves in Fig. 4 and those in Fig. 5 should extrapolate to common values of mobility at zero ionic strength. The course of curves 1, 3 and 4 in Fig. 4 and of curves 1 and 3 in Fig. 5 is such as to suggest that the common extrapolation limit cannot be obtained by prolongation of these curves to $\mu = 0$. Instead, curves 2 in these figures suggest that the extrapolation limit may be obtained by passage of the v–μ curves through a maximum followed by a drop in mobility as $\mu = 0$ is approached. In other words, in all probability the effect of ionic strength is first to increase the mobility at low values of ionic strength up to a maximum value for each electrolyte, followed thereafter by a decrease along the lines shown in the figures.

The initial rise in mobility at low ionic strengths may be due primarily to adsorption of anions. It is felt that the ionic strengths at which this increase takes place are still too low to lead to any significant desolvation of the soap. At the same time the effect of the ionic atmosphere and possible cation adsorption, which would operate to decrease the mobility, come into play, and hence the mobility goes through a maximum and then decreases. The levelling off in this decrease, setting in at μ values of 0.3–0.4, may be due to the counterbalancing action of desolvation, which would tend to increase charge density and hence mobility. The final sharp drops in mobility are definitely due to desorption of soap with attendant discharge of the latex particles. Surface tension studies have shown that near the coagulation point this desorption of soap takes place quite sharply and, hence, the drop in mobility should also be quite sharp near the rubber precipitation point as is actually the case.

Mobility of Creamed and Redispersed Latex. —On addition of a large quantity of sodium chloride to a latex, the rubber precipitated out is highly aggregated and cannot be redispersed. However, by controlled addition of salt it is possible to "cream" a latex, remove part of the serum and then to redisperse the "cream" in water or an electrolyte solution. In such a redispersion the soap which was desorbed in the creaming is not entirely readsorbed, as is evidenced by the comparatively low surface tension of the redispersed latex. It is also quite probable that the mean particle size of the redispersed latex is larger than that present in the original colloid. It is of some interest, therefore, to ascertain how the mobility of the latex is modified by the changes accompanying creaming and redispersion.

A sample of latex was creamed with sodium chloride and after filtering off serum the rubber was redispersed in a disodium phosphate solution of $\mu = 0.145$. The total solids content of the redispersion was about that of the original latex, although some of the rubber did not redisperse. The mobility was then measured again at 30°. It was thus found that the mobility of the redispersed latex was 6.10 microns/second as against 5.62 for the untreated latex; i. e., the mobility of the redispersed latex was about 8.5% higher than the untreated latex at the same ionic strength, temperature and pH.

Mobility of Frozen Latex.—Previous work in this Laboratory[4] has indicated that latex may be destabilized and even coagulated by freezing. If the latex is frozen and then rewarmed before any appreciable coagulation occurs, a large number of particles of microscopic size can be detected in the dispersion and the surface tension is found to have dropped to 30–40 dynes/cm. These observations indicate that in the freezing and rewarming operation the particle size is increased and that part of the soap is desorbed.

To ascertain what effect these changes have on mobility latex solutions were frozen, rewarmed and then made up in disodium phosphate solutions of $\mu = 0.145$ as described. A number of mobility determinations were then carried out at 30° on different frozen samples of the same latex. The results thus obtained in ten separate determinations gave for the mobility $v = 6.24 \pm 2.7\%$ as against 5.62 microns/second for the unfrozen samples. This 11% increase in mobility here and the 8.5% increase in the mobility of creamed and redispersed latex are off-hand surprising. However, they may be accounted for by the increase in the particle size attending the above manipulations. Although both creaming and redispersion and freezing and rewarming result in loss of soap by the rubber, nevertheless the higher mobility of the resulting particles indicates that these carry upon them more soap and, hence, a higher charge. By increasing the size of the particles at total constant concentration the number of these is considerably decreased, and apparently whatever soap is available is sufficient to yield a higher surface soap concentration per particle than in the original latex. To test this supposition it would be of in-

(4) Results to be published at a future date.

terest to investigate the mobility of latex dispersions with added soap.

Mobility of Soap.—Since latex owes its mobility primarily to the charge imparted to it by the adsorbed soap it is of considerable interest to see how the mobility of soap itself compares with that of the latex particles. To obtain the mobility of soap a single measurement was made upon a 0.01 molar solution of RS soap chips in 0.004 molar sodium chloride at 30° with phenolphthalein as an indicator. The moving boundaries were not as sharp here as with latex; however, the experiment could be carried out to yield for the mobility of the soap 6.31 microns per second. Although the experimental conditions were quite different in the measurements of the latex and soap mobilities, nevertheless it is of importance that the mobilities of the soap and the latex are of the same order of magnitude. In fact, it would not be too surprising to find that they are more or less identical under comparable experimental conditions since it has been shown that the mobilities of proteins and various materials coated with proteins are the same.

The *Zeta* Potentials of Latex.—Type II GR-S latex particles are known to be spherical in shape and of the order of 800–1000 Å. in diameter. For such particles the *zeta* potential, Z, is related to the mobility by the expression[5] at 30° for v in

$$Z = 4\pi\eta v/D = -1.18 \times 10^{-2} v \qquad (3)$$

microns per second and where η is the viscosity coefficient of the medium and D is the dielectric constant. The minus sign is included since in fact v is negative. In view of the direct proportionality between Z and v all the conclusions drawn with respect to variation of mobility at 30° with respect to solids, pH, ionic strength and type of electrolyte apply equally well to the effect of these on *zeta* potentials.

The effect of temperature on *zeta* potentials of Latex no. 3 at $\mu = 0.144$ and average pH of about 8.5, can be obtained from the combination of the mobility data summarized by equation (2) and the effect of temperature on viscosity and dielectric constant. For lattices as dilute as those used here

(5) H. A. Abramson, L. S. Moyer and M. H. Gorin, "Electrophoresis of Proteins," Reinhold Publishing Corporation, New York, N. Y., 1942, p. 109.
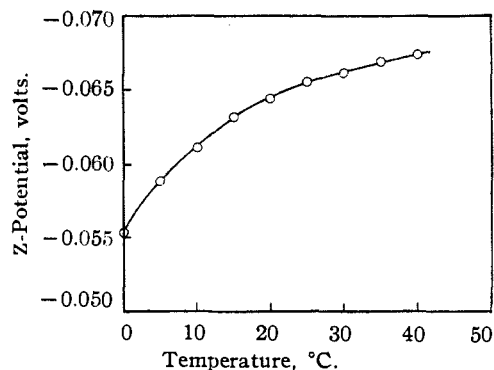

Fig. 7.—Effect of temperature on Z-potentials of Latex no. 3 at $\mu = 0.144$ and pH 7.9–9.0.

the viscosity is essentially the same as that of pure water. The dielectric constants of water as a function of temperature have been given by Wyman.[6] The *zeta* potentials thus calculated at various temperatures from 0 to 40° are shown in Fig. 7. From this plot it may be seen that the *zeta* potentials of the latex increase continually over the entire temperature range. The increase is quite rapid between 0 and 20°, and then becomes much more gradual thereafter. This increase in *zeta* potentials with temperature is again in accord with the observations in this laboratory, to be published later, that Type II latex shows increased stability in presence of added electrolytes at higher temperatures than at lower ones.

Summary

A very simple procedure is described for measuring the electrophoretic mobility of latex by the moving boundary method. This method has been applied to the determination of the mobilities of Type II GR-S latex as a function of total solids, pH, ionic strength, electrolyte type at 30° and of temperature between 0 and 35°.

The effects of creaming and redispersion and of freezing and thawing of lattices on mobility have also been determined.

The above data were used to estimate the isoelectric point of latex and to calculate the *zeta* potentials as a function of the various variables.

(6) J. Wyman, *Phys. Rev.*, **35**, 623 (1930).