Central Research Laboratory, Mitsubishi Electric Corporation (Japan)

Studies on the stability of styrene-acrylonitrile copolymer latex dispersions

I. Stability and electrophoretic behaviour against simple inorganic electrolyte

H. Ono, F. Sato, E. Jidai and *K. Shibayama*

1. Introduction

A considerable amount of experimental work on the coagulation of colloidal systems has been carried out on the sols of organic substance (1, 2). However, most of this work was centered on the study of polystyrene latex (3 ~7) and a little attention has been paid to the effect of the chemical composition of the dispersed polymer on the stability of polymer latex dispersions.

The present work was carried out in order to study the effect of the chemical composition on the stability of polymer latex dispersions. For this purpose, styrene-acrylonitrile copolymer latex dispersions were prepared by emulsion polymerization using hydrogen peroxide as an initiator. The stability and electrophoretic behaviour of these latex dispersions against simple inorganic electrolyte has been investigated.

2. Experimental

Materials. The deionized water having resistivity of more than 5×10^6 Ω-cm was used throughout all the experiments. Styrene and acrylonitrile were purified by distillation at a temperature of about 35 °C, under reduced pressure in a stream of nitrogen. Hydrogen peroxide (30% wt./vol) was Analar grade and was used without further purification. Sodium lauryl sulphate (SLS) was purified by recrystallization from ethanol.

Preparation of polymer latices. The latex dispersions were prepared by emulsion polymerization at 65 °C using hydrogen peroxide as an initiator. The concentration of SLS used as an emulsifier was 2×10^{-3} mole/1 for all latices. A typical example of the preparation was as follows.

180 g of deionized water was introduced into the reaction vessel set into a water bath. Nitrogen was bubbled through water for 30 minutes under stirring in order to exclude the dissolved oxygen. 0.125 g of SLS, 17.8 g of styrene, and 2.26 g of acrylonitrile were added and the apparatus was brought to the polymerization temperature (60 °C). 0.2 g of hydrogen peroxide was added to the reaction vessel. Polymerization was allowed to proceed for about 4 hr at 60 ± 2 °C in a stream of nitrogen. The latex dispersion was then cooled with a water bath to room temperature and filtered through 100 mesh wire gauge to exclude coagulum.

Dialysis of latices. The latex dispersions obtained contains residual monomer, free emulsifier, and miscellaneous free ions, which were removed by dialysis. Ca. 1% W/V latex dispersion was contained in Visking dialysis tube and dialysed against deionized water. The dialysate was changed every 24 hr.

Electron Microscopy. For electron microscope examination for latex dispersions, a supporting film of collodion coated with a thin layer of carbon mounted on copper gauge was used. Extremely dilute latex dispersions were sprayed from an injection-syringe on to the supporting film. Particle size distributions were determined by measuring the diameters of particles on electron micrographs.

Table 1. The chemical composition of polymers

Latex designation	molar % of component	
	styrene	acrylonitrile
ST	100	0
SA 82	84.6	15.4
SA 64	61.8	38.2
SA 46	44.0	56.0
SA 28	25.0	75.0

Fig. 1. Electron micrographs of polymer latex particles
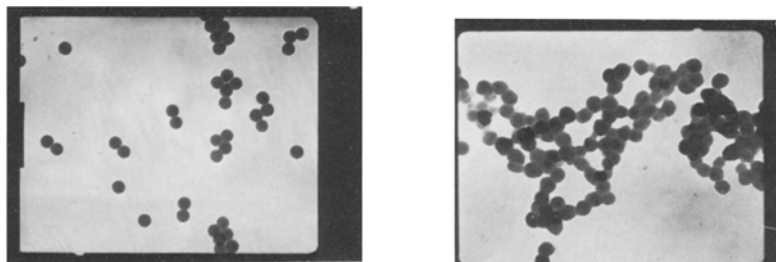
Analysis of the chemical composition. The chemical composition of latex particles was analysed by elemental analysis. The results are summarized in table 1.

Determination of the rates of coagulation. The course of the early stages of coagulation of the latex dispersions was followed turbidimetrically. The change in turbidity with time was recorded continuously commencing 4 ~ 5 sec after the addition of the electrolyte solution.

Mobility measurement. The electrophoretic mobilities of polymer latex dispersions were determined using a moving boundary apparatus based on the design of *Kerker*, *Bowman*, and *Matijević* (8).

Determination of latex stability. As shown in our previous work (9) the change of turbidity with time is given by

$$\tau_t = A N_o V_o^2 (1 + K N_o t) \qquad [1]$$

in the *Rayleigh* region where τ_t = turbidity at time t, A = optical constant (10), N_o and V_o = number of particles and volume per particle present in the initial stage, respectively, and K = rate constant for coagulation process. While the experimental stability ratio, W is defined by

$$W_{exp} = K_o/K \qquad [2]$$

where K_o = rate constant for rapid coagulation.

Calculation of the Stern potential, ψ_δ, and the Hamaker constant, A

The *Stern* potential, ψ_δ, was calculated using equation derived by *Reerink* and *Overbeek* (11). The *Hamaker* constant, A, was calculated using the following equation [12]

$$\text{c.c.c.} = \frac{8 \times 10^{-22} \cdot \gamma^4}{A^2 \cdot \nu^6} \text{ (in millimole/1)} \qquad [3]$$

where c.c.c. = critical coagulation concentration,

ν = electrolyte valence, and

$$\gamma = \frac{\exp (\nu_e \psi_\delta/2kT) - 1}{\exp (\nu_e \psi_\delta/2kT) + 1}$$

Here, e = electronic charge, k = *Boltzmann* constant, and T = absolute temperature.

3. Results

Electron Microscopy. A few examples of the electron micrographs obtained with the latex dispersions are given in fig. 1. The electron micrographs for latices ST, SA 82, SA 64, and SA 46, show that the shape of these latex particles is almost a perfect sphere. But the particles for latex SA 28 were found to be somewhat collapsed and they are not true spheres any more. The modal diameters obtained from the particle size distribution curve are listed in table 2.
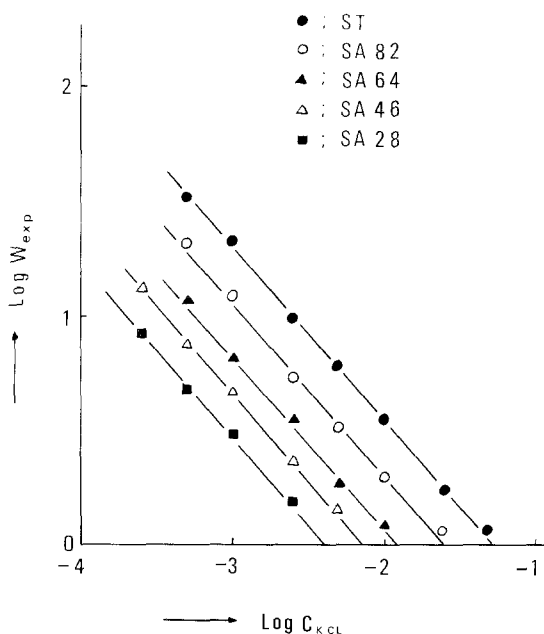

Fig. 2. Log W_{exp} against log C_{KCl} curves for styrene-acrylonitrile copolymer latex dispersions
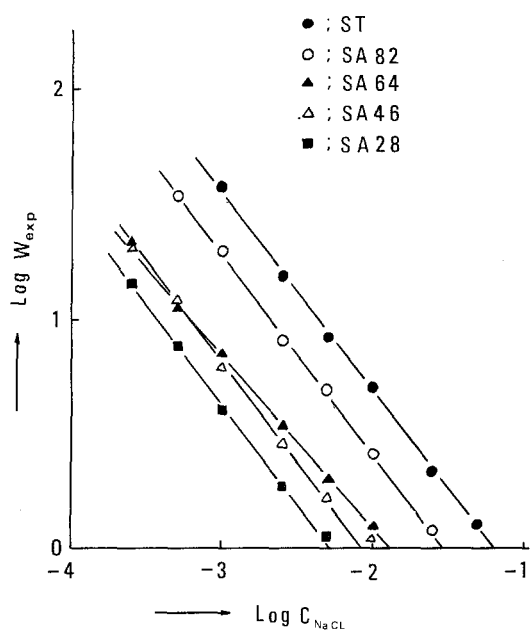
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Fig. 3. Log W_{exp} against log C_{NaCl} curves for styrene-acrylonitrile copolymer latex dispersions
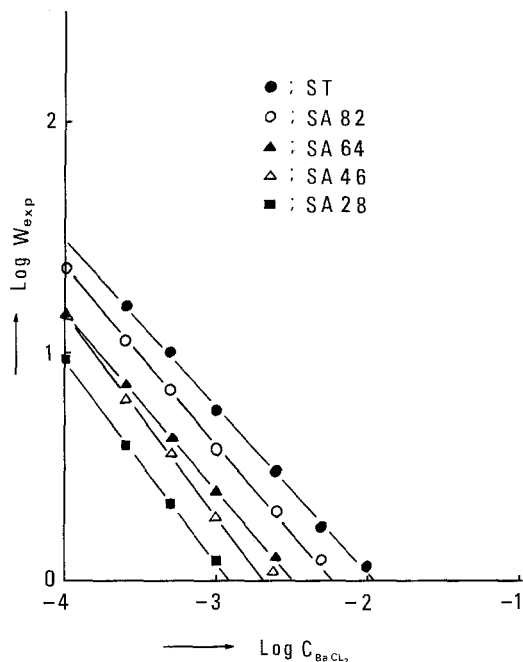

Fig. 4. Log W_{exp} against log C_{BaCl_2} curves for styrene-acrylonitrile copolymer latex dispersions

Table 2. Diameters of polymer latex particles

Latex designation	Modal diameter (A)	Standard deviation (A)
ST	790	± 121
SA 82	740	± 80.5
SA 64	680	± 77.6
SA 46	740	± 54.8
SA 28	800	± 68.5

Conductivity of latex dispersions. The values of specific conductivity of the dialysed polymer latex dispersions are in the range of 7.8×10^{-6} to $8.1 \times 10^{-6} \; \Omega^{-1} \; cm^{-1}$ and are found to be almost identical.

Stability of latex dispersions. The stability curves obtained against potassium chloride, sodium chloride, and barium chloride are

shown in fig. 2, 3, and 4, in the form of log W_{exp} against log C_e curves respectively, where C_e is the concentration of electrolyte added to the latex dispersion. The curves were approximately linear over the range investigated and can be represented by an equation of the following form

$$\log W_{exp} = -K_1 \log C_e + K_2 \qquad [4]$$

The values of the slope of the stability curve and the c.c.c. of the latex dispersions are given in table 3. The values of the c.c.c. were determined by extrapolating the log W_{exp} values down to log $W_{exp} = 0$, and reading up log C_e at the point of intersection.

Zeta potential of latex dispersions in the presence of simple inorganic electrolyte. The mobility

Table 3. The slope of the stability curves and the c.c.c. of the latex dispersions against inorganic electrolytes

Latex designation	$-d \log W_{exp}/d \log C_e$			c.c.c. (mole/1)		
	Na Cl	K Cl	Ba Cl$_2$	Na Cl	K Cl	Ba Cl$_2$
ST	0.86	0.77	0.73	6.3×10^{-2}	5.3×10^{-2}	1.1×10^{-2}
SA 82	0.88	0.76	0.78	2.9×10^{-2}	2.5×10^{-2}	5.8×10^{-3}
SA 64	0.77	0.76	0.78	1.3×10^{-2}	1.2×10^{-2}	3.2×10^{-3}
SA 46	0.88	0.77	0.89	8.3×10^{-3}	7.1×10^{-3}	2.0×10^{-3}
SA 28	0.89	0.78	0.89	5.0×10^{-3}	4.0×10^{-3}	1.2×10^{-3}

results obtained were converted into zeta potential using the *Overbeek* (13) formula for unsymmetrical electrolytes. The results obtained against potassium chloride, sodium chloride, and barium chloride are given in fig. 5, 6, and 7, in the form of zeta-potential against log C_e curves, respectively.

4. Discussion

The stability curves for all latex dispersions using potassium chloride as the coagulating agent are given in fig. 2. The order of the c.c.c. values was found to be ST > SA 82 > SA 64 > SA 46 > SA 28, and value of log W_{exp} was in the order, ST > SA 82 > SA 64 > SA 46 > SA 28, over all range investigated. The stability curves using sodium chloride, and barium chloride as the coagulating agent are given in fig. 3 and 4, respectively. The order of the c.c.c. values against sodium chloride and barium chloride is both ST > SA 82 > SA 64 > SA 46 > SA 28, similar to that against potassium chloride. The values of c.c.c. for each latex dispersion against potassium chloride and sodium chloride are all quite alike to each other. Meanwhile the values of c.c.c. against barium chloride for each latex dispersion are all not in accordance with those predicted by the inverse sixth law. This difference seems to be caused by the extremely low surface potentials at c.c.c. for these latex dispersions in the present case.

The values of the *Stern* potential calculated using *Reerink–Overbeek* equation [11] for all latex dispersions against sodium chloride,
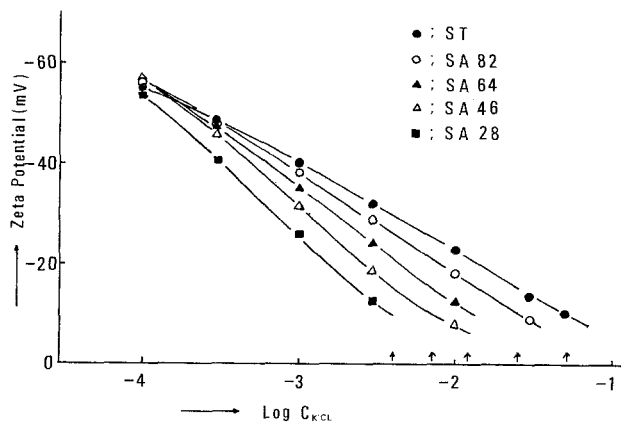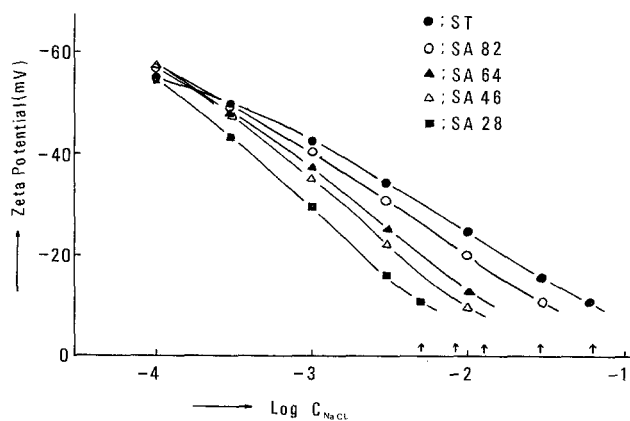

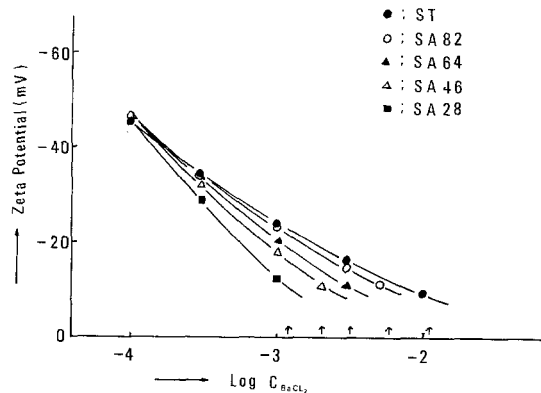Fig. 6. Curves of zeta potential against log C_{NaCl}

Fig. 7. Curves of zeta potential against log C_{BaCl_2}

potassium chloride, and barium chloride are summarized in table 4. The difference in *Stern* potential for these five latex dispersions was found to be very small in every coagulating agent, so that, there seems to be no definite correlation between chemical composition of polymers and the values of the *Stern* potential for these latex dispersions. Thus the value of *Stern* potential for styrene-acrylonitrile latex particles was found to be almost independent on the chemical composition of polymers.

On the other hand, the values of the *Hamaker* constant calculated using eqn. [3] are given in table 5. The *Hamaker* constant increases uniformly with the increase of the content of acrylonitrile in the copolymer. Thus the difference in the c.c.c. values for these latex dispersions is scarcely dependent on the electrical repulsion but dependent on the *van der Waals* attraction. In this way, the values of c.c.c. increase with the decrease of *Hamaker* constant.

Fig. 5. Curves of zeta potential against log C_{KCl}

Table 4. Values of *Stern* potential ψ_δ, and zeta potential ζ, of the latex dispersions

Latex designation	ψ_δ (mV)			ζ (mV)		
	Na Cl	K Cl	Ba Cl$_2$	Na Cl	K Cl	Ba Cl$_2$
ST	—10.2	— 9.8	— 9.7	—10.2	—10.0	— 8.8
SA 82	—11.1	—10.2	—10.4	—10.8	—10.2	—10.4
SA 64	—10.7	—10.7	—10.8	—10.7	—10.7	—10.5
SA 46	—11.1	—10.2	—10.9	—10.8	—10.0	—11.0
SA 28	—10.7	— 9.8	—10.6	—10.5	— 9.7	—10.5

In order to clarify the correlation between the chemical composition of polymers and the surface potential of the latex particles for the present system, the electrophoretic behaviour of these latex dispersions has been investigated. The results are given in fig. 5, 6, and 7, in the form of zeta potential against log C_e curves. As shown in these figures, the values of zeta potential for these latex dispersions in the region of low electrolyte concentration are almost quite alike. However, the slope of zeta potential — log C_e curves is in the order: SA 28 > SA 46 > SA 64 > SA 82 > ST for every coagulating agent. Therefore the order of zeta potential at high electrolyte concentration is ST > SA 82 > SA 64 > SA 46 > SA 28 as shown in fig. 5 ~7. The values of zeta

Table 5. Values of *Hamaker* constant, A, of the latex dispersions

Latex designation	A (10^{-14} erg)		
	Na Cl	K Cl	Ba Cl$_2$
ST	3.6	3.5	3.7
SA 82	5.8	5.4	5.8
SA 64	8.4	8.5	8.5
SA 46	10.9	10.4	11.1
SA 28	13.0	12.8	13.2

potential at c.c.c. given in fig. 5 ~7 are summarized in table 4. These values of zeta potential are quite identical to those of *Stern* potential. These values also indicate that the experimental zeta potentials at c.c.c. for styrene — acrylonitrile latex particles are quite alike and they are almost independent on the chemical composition of polymers. Thus the electrophoretic behaviour of these latex dispersions shows that the difference present in the c.c.c. values is not caused by the difference of electrical repulsion between particles in the

present case. The dependence of *Hamaker* constant on the content of acrylonitrile seems to be due to the strong interaction between polar groups of acrylonitrile. It is, however, scarcely possible to determine the *Hamaker* constant for homopolymer of acrylonitrile experimentally because it is almost impossible to prepare stable polyacrylonitrile latex dispersion by emulsion polymerization owing to the strong coagulating tendency of acrylonitrile in the polymerization process.

In any case, the *Hamaker* constant for these copolymer latex dispersions depends on the fraction of acrylonitrile, i.e., the attractive energy between particles increases with the increase of the content of acrylonitrile.

On the other hand, since the values of *Stern* potential for these latex dispersions are almost identical, the potential energy of repulsion between particles for these latex dispersions
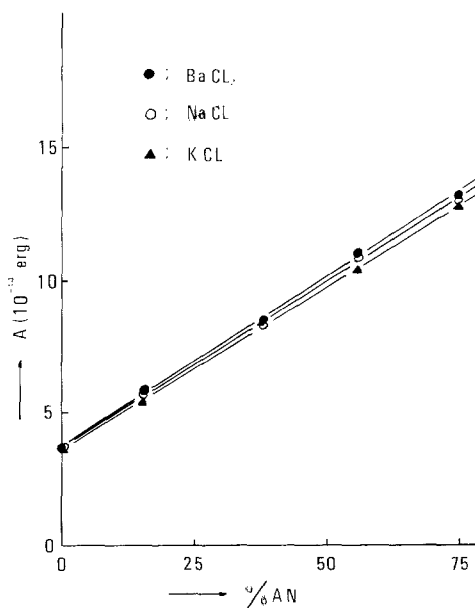
Fig. 8. Dependence of A on the fraction of acrylonitrile in the copolymer

must be almost identical. Therefore the difference present in the stability against simple electrolyte for styrene-acrylonitrile copolymer latex dispersions is due to the difference in the potential energy of attraction between particles, which is caused by the difference of chemical composition of latex particles.

The dependence of *Hamaker* constant on the fraction of acrylonitrile is shown in fig. 8. The *Hamaker* constant for the copolymer latex dispersions increases with the increase of the fraction of acrylonitrile in the copolymer, and the rate of increase in *Hamaker* constant is almost proportional to the fraction of acrylonitrile. Thus, the *Hamaker* constant for these latex dispersions investigated here is determined by the content of acrylonitrile. The dependence of the attractive energy between particles on the chemical composition of copolymers found in the present case is considered as follows.

The cohesive energy density of acrylonitrile homopolymer is widely known to be larger than styrene homopolymer, i.e., the attractive energy between molecules for acrylonitrile is larger than that for styrene. Therefore, the attractive energy between particles is expected to increase with the increase of the fraction of acrylonitrile in the polymer particles. Thus the results concerning latex stability against simple inorganic electrolyte obtained for acrylonitrile-styrene copolymer latex dispersions seem to be reasonable in the light of attractive energy consideration.

Summary

Styrene-acrylonitrile copolymer latex dispersions were prepared using hydrogen peroxide as an initiator by emulsion polymerization. Particle size distributions were determined by measuring the diameter of particles on electron micrographs. The chemical composition of the latex particles was determined by elemental analysis. The stability and electrophoretic behaviour of these latex dispersions against simple inorganic electrolyte has been investigated. The value of the critical coagulation concentration was found to increase with the decrease of the fraction of acrylonitrile in the polymer particles. The value of *Stern* potential calculated was found to be independent on the chemical composition of polymers. The difference present in the latex stability seems to be mainly due to the difference in the attractive energy between particles, i.e., the *Hamaker* constant increases almost linearly with the increase of the content of acrylonitrile in the copolymer.

Zusammenfassung

Styrol-Acrylnitril-Mischpolymer-Latices wurden unter Verwendung von Wasserstoffperoxyd als Initiator von Emulsionspolymerisation hergestellt. Verteilungen der Partikelgrößen wurden durch Messen des Teilchen-Durchmessers auf Elektronenmikrographien bestimmt. Die chemische Zusammensetzung der Latex-Teilchen wurde durch Elementar-Analyse festgestellt. Stabilität und elektrophoretische Beweglichkeit dieser Latex-Dispersionen gegen einfache inorganische Elektrolytlösungen wurden untersucht. Der Wert der kritischen Koagulationskonzentration nahm mit abnehmendem Anteil von Acrylnitril in den Polymer-Partikeln zu. Der Wert des *Stern* Potentials war unabhängig von der chemischen Zusammensetzung der Polymere. Der Unterschied in der Stabilität scheint vorwiegend auf den Unterschied der Anziehungsenergie zwischen Partikeln zurückgeführt werden zu können, d.h. die *Hamaker* Konstante nimmt beinahe geradewegs mit der Zunahme des Gehaltes von Acrylnitril im Mischpolymer zu.

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Authors' address:

Mr. *H. Ono*, Mr. *F. Sato*, Mr. *E. Jidai*, and Dr. *K. Shibayama*
Central Research Laboratory,
Mitsubishi Electric Corporation
80 Nakano, Minamishimizu, Amagasaki, Hyogo Prefecture (Japan 661)