Surface Characterization of Soap-Free Carboxylated Polymer Latices

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ABSTRACT: The surface characteristics of carboxylated polymer latices —styrene/acrylic acid copolymer (PS/PAA) and styrene/methacrylic acid copolymer (PS/PMAA)— were investigated. Polystyrene (PS) latex was used as a reference sample. These latices were prepared in a soap-free system, using potassium persulfate as the initiator. Conductometric titration curves of PS and carboxylated latices showed both strong and weak acid groups to exist on the surface of latex particles. The surface charge density (σ) for PS/PAA latex was proportional to the amount of acrylic acid (AA) used in the copolymerization (thus, σ- for PS/PAA$_5$ latex was larger than that for PS/PAA$_2$ latex; the subscripts 5 and 2 represent the mol% of AA monomers used in the copolymerization). However, σ for PS/PMAA$_5$ latex was smaller than that for PS/PAA$_5$ latex, although the mol% of acid monomers used in the copolymerization was the same for both latices. σ for carboxylated latices increased with increasing pH, but the pH dependence of σ for PS latex was not very pronounced. The ζ-pH curves for these latices were considerably different from the σ-pH curves. This is probably because the Stern potential and the position of the shear plane in the electrical double layer differ between the two latices. Methylene Blue adsorption onto PS and PS/PAA latices was measured as a function of pH. The overall tendency of the dye adsorption was more similar to the σ-pH curves than the ζ-pH curves.

KEY WORDS Surface Characterization / Soap-Free / Carboxylated Latex / Conductometric and Potentiometric Titrations / ζ-Potential / Methylene Blue Adsorption /

Polymer latices have many industrial applications in such fields as paint, adhesive, paper and textile. In particular, carboxylated latices prepared by copolymerization with an unsaturated acid monomer play important roles in these fields. Carboxylation of polymer latices is preferred for improving mechanical and freeze-thaw stabilities,[1-3] allowing adhesion and cross-linked reactions,[4,5] and preparing hydrosols.[6] However, since in practice, surfactants are used as emulsifiers in the preparation of carboxylated latices, water-resistance and the luster of the resulting films are lost in many cases.

Many investigations are now being carried out on the biomedical use of polymer latices.

In particular, their application to medical diagnostics,[7] enzyme immobilized latex,[8] and adsorbents for serum proteins[9-11] is being actively examined. Thus, it is very important to clarify their surface characteristics. Further, in many cases, use of soap-free polymer latices is favorable because of the various effects of emulsifiers. However, a special technique is necessary to prepare stable and monodisperse soap-free polymer latices by copolymerization with a hydrophilic monomer. Although Ceska[12,13] and Sakota et al.[14] have investigated soap-free carboxylated latices, the monodispersity of their latex particles should be improved.

In this paper, we report the preparation of

soap-free carboxylated polymer latices, and compare their surface characteristics with those of hydrophobic polystyrene latices.

EXPERIMENTAL

Materials

The styrene, acrylic acid (AA), and methacrylic acid (MAA) used in this work were purified by vacuum distillation under a nitrogen atmosphere. Potassium persulfate (KPS) as the initiator was recrystallized twice from water. Cation- and anion-exchange resins (PK-212 and PA-312, obtained from Mitsubishi Chemical Industries Ltd. and used for purifying latices) were cleaned by the method of van den Hul and Vanderhoff.[15] Methylene Blue (obtained from Wako Pure Chemical Industries Ltd.) was purified twice by recrystallization from water. A carbonate-free sodium hydroxide solution used for titration was prepared from a "Sørensen liquid." All other chemicals were of analytical grade. Distilled-deionized water was used in all experiments.

Methods

Preparation and Purification of Latices. Carboxylated latices —(styrene/acrylic acid) copolymer (PS/PAA) and (styrene/methacrylic acid) copolymer (PS/PMAA)— were prepared by the seed polymerization method with the successive addition of monomers, as described previously.[10] A polystyrene (PS) latex was prepared by the usual heterogeneous polymerization, without soap under a nitrogen atmosphere. The polymerization recipe is given in Table I. The ratio of KPS to total monomer was adjusted to almost the same value in the preparation of each latex.

The latices obtained were first dialyzed against water, using a well-boiled Visking tube. Subsequently, the latex dispersions were purified by a batch procedure with a mixed bed of cation- and anion-exchange resins. The volume ratios of latex dispersion to ion-exchange resin for PS and carboxylated latices were $4:1$ and $2:1$, respectively.

The particle diameter of each latex was determined by electron microscopy (using a JEM-100V transmission electron microscope, JEOL Ltd.). All micrographs revealed the latices to be highly monodisperse. For example, see the electron micrograph of PS/PAA_2 latex shown in Figure 1. The average diameter, specific surface area, and uniformity ratio (U) for latices are given in Table II. U is defined by[16]

Table I. Preparation of polymer latices (N_2 atmosphere)

Conditions	PS/PAA_2[a]	PS/PAA_5[a]	$PS/PMAA_5$[a]	PS
Styrene (g)	73.96	72.36	71.87	45.34
AA (g)	1.045	2.640	—	—
MAA (g)	—	—	3.130	—
KPS (g)	0.3750	0.3750	0.3750	0.2473
Water (ml)	425	425	425	450
Seed monomer (g)	15	15	7.5	—
Speed of agitation (rpm)	350	350	350	350
Seed polymerization (°C, h)	70, 0.5	70, 0.5	70, 0.5	—
Successive addition of monomer (°C, h)	70, 1.0	70, 1.0	70, 1.0	—
After polymerization (°C, h)	70, 9.0	70, 8.0	70, 7.0	70, 11.0 [b]
Solid content[c] ($g l^{-1}$)	148	148	148	91

[a] Subscripts 2 and 5 represent the mol% of AA or MAA used in the copolymerization.
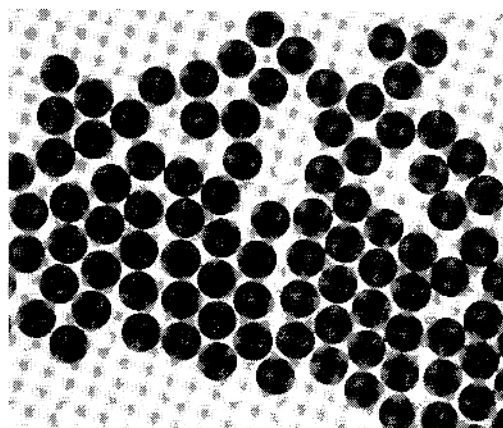
[b] Polymerization time.

[c] Theoretical value.

Figure 1. Electron micrograph of PS/PAA$_2$ latex. ×10,000.

Table II. Particle diameters, specific surface areas, and uniformity ratios of polymer latices

Latex	Particle diameter	Specific surface area	Uniformity ratio
	nm	m^2 g^{-1}	
PS/PAA$_2$	541	10.54	1.0002
PS/PAA$_5$	515	11.04	1.0011
PS/PMAA$_5$	543	10.34	1.0007
PS	526	10.86	1.0003

$$U = D_W/D_N$$

where D_W and D_N are the weight-average and number-average diameters of latex particles, respectively. For $U \leqq 1.01$, latices may be considered monodisperse.

Conductometric and Potentiometric Titrations. All titrations were carried out under a nitrogen atmosphere at 25°C. Conductometric titrations were carried out with a $5 \times 10^{-3} N$ or $1 \times 10^{-2} N$ NaOH aqueous solution as the titrant. For carboxylated latex dispersions, a $5 \times 10^{-4} M$ NaCl aqueous solution was added to facilitate determination of the inflection point of the titration curve.[17] The volume fractions (ϕ) of latices were *ca.* 1.3 and 1.0% for PS and carboxylated latices, respectively. During each titration, the latex dispersion was stirred with a magnetic stirrer. Conductivities were measured using a Toa digital conductivity meter CM-30ET.

Potentiometric titrations were carried out with a $2 \times 10^{-2} N$ NaOH solution as the titrant, using a Hitachi-Horiba pH-meter F-7ss. Before titrating with an NaOH solution, the latex dispersion was adjusted to a pH of about 3 and an ionic strength 0.01 by adding $1 \times 10^{-2} N$ HCl and 0.1 M NaCl. The ϕ for PS and carboxylated latices were about 2.3% and 1.1%, respectively. In the same way as in the conductometric titration, the latex dispersions were stirred during the titrations. The surface charge densities (σ) of latices were determined as a function of pH by titrating an equal volume of blank solution (containing only $1 \times 10^{-2} N$ HCl and 0.1 M NaCl) under the same conditions as for the latex dispersions.

Zeta (ζ)-Potentials of Latices. ζ-potentials of the latices were measured by a microelectrophoresis apparatus (Mitamura Riken Co., Ltd.) at 25°C. The electrophoretic mobilities were converted to ζ-potentials according to the treatment of Wiersema *et al.*[18] In measuring the ζ-potential as a function of pH or electrolyte concentration, the pH and ionic strength were adjusted with aqueous HCl, NaOH, and NaCl.

Methylene Blue Adsorption onto Latices. Methylene Blue adsorption onto the latices was measured at 25°C by spectrophotometry. After a Methylene Blue solution was mixed with a latex dispersion, the sample solution was centrifuged in a high-speed centrifuge (Kubota KH-180). The amount adsorbed was determined from the difference between the initial and equilibrium concentrations. The wavelength of light used was 670 nm. Preliminary experiments showed that adsorption equilibrium should be reached in 2 h. Hence, all data were taken 2 h after the test solutions were made. The pH and ionic strength of test solutions were adjusted with aqueous HCl, NaOH, and NaCl.

RESULTS AND DISCUSSION

Conductometric Titration of Latices

The conductometric titration curves for carboxylated polymer latices are shown in Figure 2. These curves are similar to each other. Two distinct inflection points (*i.e.*, two endpoints of titration) are observed for each latex. The first endpoint (a) corresponds to the equivalence point of strong acid $(-OSO_3^-)$ derived from decomposed initiator fragments, and the second endpoint (b) to that of weak acid $(-COO^-)$ derived from acid monomers. There is little difference in the titration volume of the strong acid among these three latices, because the ratio of KPS to total monomer was adjusted to almost the same value for each latex.

Figure 3 shows the conductometric titration curve of PS latex. Two endpoints of titration are observed as in carboxylated latices. In the case of PS latex, weak acid groups $(-COO^-)$ appear to originate from the oxidation of hydroxyl groups $(-OH)$,[19,20] probably formed by the Kolthoff reaction[21] of sulfate groups $(-OSO_3^-)$. The oxidation of $-OH$ can be performed even under a nitrogen atmosphere.[21,22]

Surface charge densities (σ) of latices were determined by the following equation:
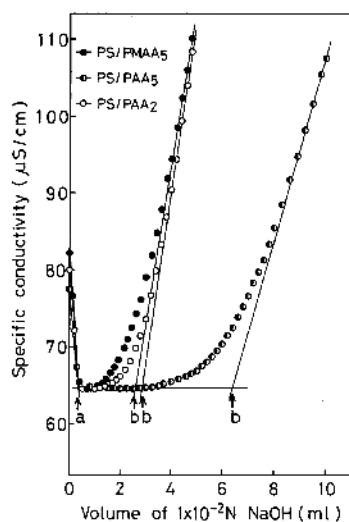
$$\sigma = cfF/S \qquad (1)$$

where c is the titrant (NaOH solution) quantity consumed up to the endpoint of titration (mol), f the factor of titrant, F the Faraday constant $(C\,mol^{-1})$, and S the total surface area of latex particles (cm^2). The σ-values obtained are given in Table III. It can be seen from Table III that the σ-value of weak acid (σ_w) for PS/PAA$_5$ latex is 2.61 and 2.47 times greater than those for PS/PAA$_2$ and PS/PMAA$_5$ latices, respectively. The difference in σ_w of PS/
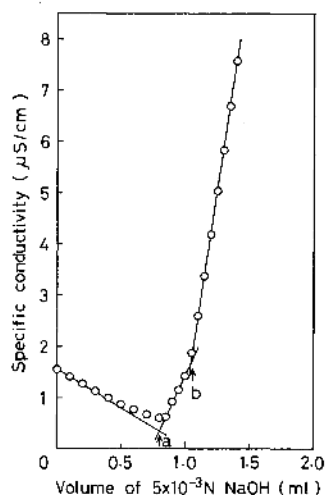

Figure 3. Conductometric titration curve of PS latex (25°C).

Table III. Surface charge densities of the polymer latices

Latex	Surface charge density		
	$\mu C\,cm^{-2}$		
	$\sigma_s^{\,a}$	$\sigma_w^{\,a}$	$\sigma = \sigma_s + \sigma_w$
	Strong acid $(-OSO_3^-)$	Weak acid $(-COO^-)$	
PS/PAA$_2$	−5.11	−33.3	−38.4
PS/PAA$_5$	−5.49	−87.0	−92.5
PS/PMAA$_5$	−6.08	−35.2	−41.3
PS	−4.52	−1.41	−5.93

^{a} σ_s and σ_w from the strong and weak acid, respectively.

Figure 2. Conductometric titration curves of carboxylated latices (25°C).

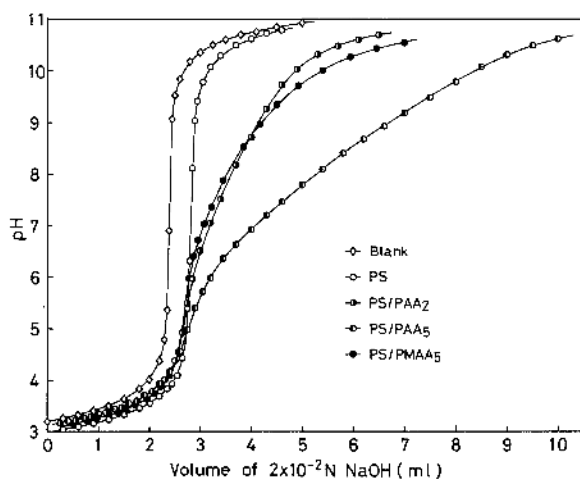**Figure 4.** Potentiometric titration curves of PS and carboxylated latices (25°C, ionic strength ≅ 0.01).

PAA$_2$ and PS/PAA$_5$ latices is proportional to the difference in mol% of acrylic acid used in the copolymerizations of these two latices. However, despite the same mol% of acid monomer being used in their copolymerizations, σ_w of PS/PMAA$_5$ latex is much smaller than that of PS/PAA$_5$ latex. This may indicate that the total amount of acid monomer incorporated into the latex particles does not differ, but there is a difference in the amount of acid monomers existing on the latex surfaces. That is, more acrylic acid can exist on the surface of latex particles than methacrylic acid, depending on the distribution coefficient[23] between water and the styrene monomer.

Potentiometric Titrations of Latices

Figure 4 shows the potentiometric titration curves for PS and carboxylated latices. The curve of PS latex is similar to that of the blank solution, whereas the curves of carboxylated latices are fairly different from that of PS latex; the titration volume for carboxylated latices is considerably greater than that for PS latex, particularly in the alkaline pH region.

Assuming the difference in titration volume of NaOH solution between the latex dispersion and blank solution in a potentiometric titration to be proportional to the number of
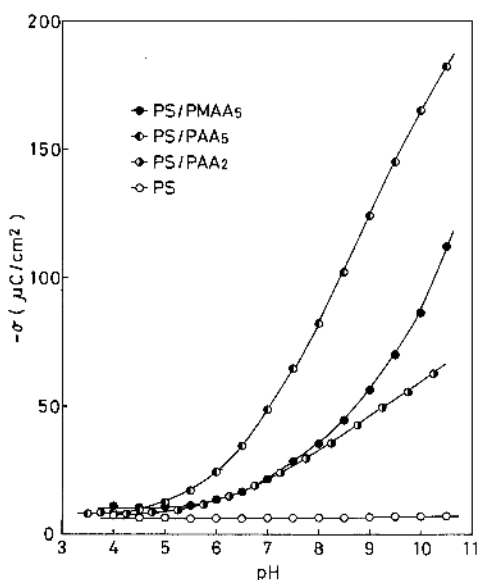

Figure 5. Surface charge densities for PS and carboxylated latices as a function of pH (25°C, ionic strength ≅ 0.01).

charged groups on the surface of latex particles, we can determine the surface charge density (σ) of the latex as a function of pH using eq 1. The results are shown in Figure 5. Up to a pH of about 5, σ for carboxylated latices is almost equal to that of the PS latex since carboxyl groups hardly dissociate in this

pH region. However, at pH higher than about 5, σ for the carboxylated latices increases with increasing dissociation of carboxyl groups (*i.e.*, with increasing pH). Further, at the same pH in the alkaline region, σ increases in the order, $PS/PAA_2 \lesssim PS/PMAA_5 < PS/PAA_5$. But little pH dependence of σ is observed for PS latex. This may be because carboxyl groups on the PS latex surface are far fewer than those on the carboxylated latices (see Table III). The results of conductometric titrations (*i.e.*, σ-values for carboxylated latices in Table III) suggest the equivalence point of these latex dispersions to be found at a pH of about 8.4 at which σ for each carboxylated latex in Figure 5 is close to the value ($\sigma = \sigma_s + \sigma_w$) in Table III. Therefore, the σ for carboxylated latices appear to approach their plateau values above pH 8.4, since all carboxyl groups on the particle surface are titrated at this pH. However, as can be seen from Figure 5, the σ for these latices still increase with increasing pH. Thus, not only the carboxyl groups on the latex surface but also those in the interior near the particle surface are titrated in this pH region since the surface polyacrylic (or polymethacrylic) acid layer of these latices swells with increasing pH. This is supported by the results on PS/PAA_2 and $PS/PMAA_5$ latices in Figure 5. That is, σ-values for $PS/PMAA_5$ latex are greater than those for PS/PAA_2 latex above pH *ca.* 8.4, because methacrylic acid is more likely to exist in the interior of latex particles than acrylic acid.

ζ-Potentials of Latices

Figure 6 shows ζ-potentials of PS and carboxylated latices as a function of pH. It can be seen that these latices have negative charges associated with the acid monomer and/or initiator fragment. The ζ for each latex increases from acidic to neutral pH probably as a result of the dissociation of carboxyl groups on the latex surface. However, in contrast to the σ-pH curves (Figure 5), ζ for PS latex is larger than that for carboxylated latices throughout the

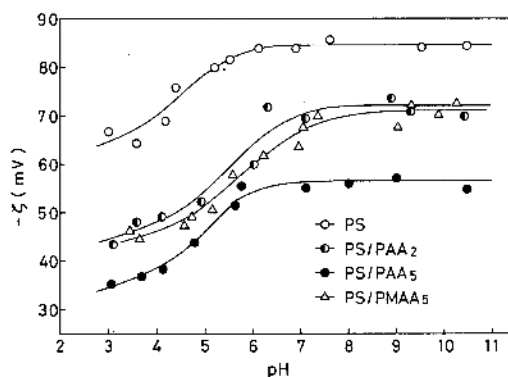**Figure 6.** ζ-Potentials of PS and carboxylated latices as a function of pH (25°C, ionic strength 0.01).
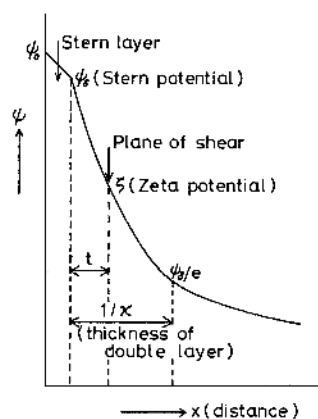

Figure 7. Potential distribution for the Gouy–Chapman–Stern model of the electrical double layer as a function of the distance from the solid-liquid interface.

entire range of measured pH. The following reason may explain the difference in tendency between σ-pH and ζ-pH curves: σ represents the charge of all ionized groups on the latex surface while ζ is the potential on the shear plane of the electrical double layer. To clarify this, we attempted to estimate the position of the plane of shear on the basis of the Gouy–Chapman–Stern model for double layers.

Figure 7 shows the potential (ψ) distribution in this double layer model as a function of the distance from the solid-liquid interface, where ψ_0 is the surface potential. The position (t) of the shear plane was estimated by the treatment of Eversole-Boardman,[24] who expressed the

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dependence of ζ-potential on the electrolyte concentration as

$$\ln \tanh (ze\zeta/4kT) = \ln \tanh (ze\psi_\delta/4kT) - \kappa t \tag{2}$$

where z is the valence of ions, e, the charge of an electron, k, the Boltzman constant, T, the absolute temperature, ψ_δ, the Stern potential, and κ, the Debye–Hückel parameter. For the 1-1 electrolyte, eq 2 can be written for water solutions at 25°C as follows:

$$\ln \tanh (9.727 \times 10^{-3}\,\zeta) \\ = \ln \tanh (9.727 \times 10^{-3}\,\psi_\delta) - 0.3285\,\sqrt{c}\ t \tag{3}$$

where ζ, c (electrolyte concentration), and t are in mV, mol l^{-1}, and Å, respectively. Thus, t can be estimated from the slope of the straight line suggested by eq 3.

First, the ζ-potentials of PS and carboxylated (PS/PAA) latices were measured as a function of the electrolyte (NaCl) concentration. For PS/PAA$_5$ latex, the ζ-potentials were also measured at an alkaline pH (pH of about 10.3 obtained by adding aqueous NaOH). In other cases, the pH was fixed to about 6 regardless of the electrolyte concentration, since the measurement solution of the latex dispersion contained only NaCl as the electrolyte. In Figure 8, the ζ-potentials of these latices exhibit maxima at *ca.* a 3×10^{-3} mol l^{-1} NaCl concentration. The increase in the ζ-potential up to this NaCl concentration may be due to the adsorption of

Cl$^-$ from a bulk solution onto the particle surface.[25] The rapid decrease in the ζ-potential above this NaCl concentration most likely results from compression of the electrical double layer with increasing electrolyte concentration.

The data of Figure 8 were used to make the Eversole-Boardman's plot in Figure 9. The values of t and ψ_δ calculated by the least-squares method from the slopes and intercepts of the indicated straight lines are given in Table IV. The values of t for PS/PAA latices are larger than that for PS latex. Furthermore, t increases with increasing mol% of acrylic acid used in the copolymerization or pH.

These results indicate that, in the case of carboxylated latices, hydrous polyacrylic (or polymethacrylic) acid layers exist on the sur-
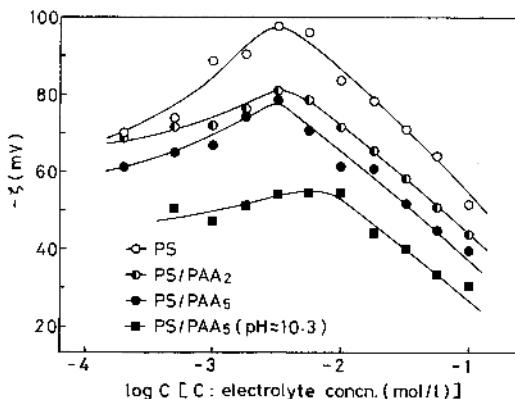

Figure 8. ζ-Potentials of PS and carboxylated latices as a function of electrolyte concentration (25°C).
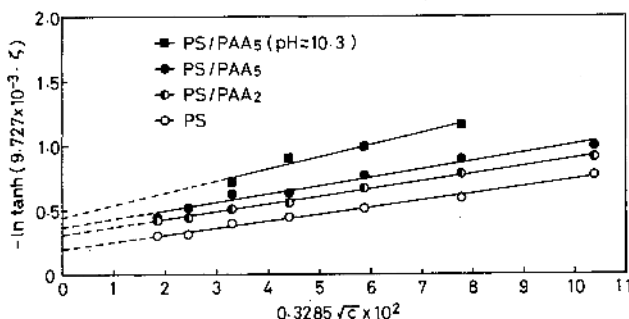

Figure 9. Plots of $-\ln \tanh (ze\zeta/4kT)$ as a function of electrolyte concentration (Eversole–Boardman's plot) at 25°C.
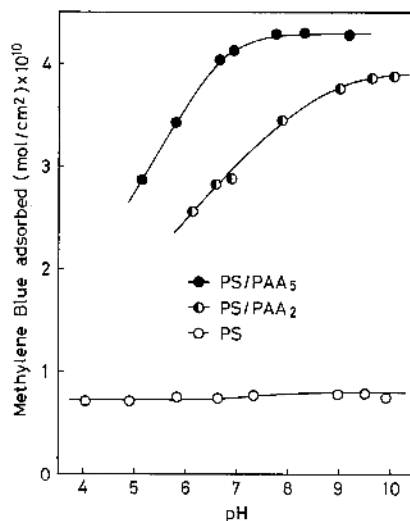
Table IV. Values of t and ψ_δ for PS
and carboxylated latices

Latex	t	ψ_δ
	Å	mV
PS	5.4	−119
PS/PAA$_2$	5.9	−96.2
PS/PAA$_5$	6.4	−87.8
PS/PAA$_5$ (pH ≅ 10.3)	9.3	−78.0

Figure 10. Methylene Blue adsorption onto PS and PS/PAA latices as a function of pH (25°C, ionic strength 0.01).

faces and shift the plane of shear away from the particle surfaces. Therefore, the greater the t value is, the smaller the potential at the plane of shear (*i.e.*, ζ-potential) becomes (see Figure 7). This may be one reason why the ζ-potentials of carboxylated latices are smaller than that of the PS latex. The Stern potentials (ψ_δ) for PS/PAA latices are smaller than that for PS latex (see Table IV). This probably leads to low ζ-potentials of carboxylated latices, even though the surface potentials (ψ_0) of the latices are high. Thus, it may be concluded that the lower ζ-potentials of carboxylated latices are due to larger t and smaller ψ_δ.

Methylene Blue Adsorption onto Latices

Prompted by the above findings, Methylene Blue (basic dye) adsorption onto polymer latices was investigated. Figure 10 shows the pH dependence of Methylene Blue adsorption onto PS and PS/PAA latices. The overall tendency of the adsorption is similar to the σ-pH curves (Figure 5) but not to the ζ-pH curves (Figure 6). This may be explained by the fact that these latices and Methylene Blue molecules have opposite charges and consequently, the dye molecules are adsorbed electrostatically on the surface charge groups regardless of the value of the ζ-potential. Therefore, the pH dependence of Methylene Blue adsorption onto PS latex can hardly be observed, as is the case for the σ-pH curves, and the amount of Methylene Blue adsorbed onto PS/PAA latices increases with increasing pH (*i.e.*, with increasing dissociation of car-

boxyl groups). Furthermore, it can be seen that the amount adsorbed onto PS/PAA$_5$ latex is larger than that onto PS/PAA$_2$ latex at the same pH value.

The ratio (r) of the number of Methylene Blue molecules adsorbed (n_1) to the number of surface charged groups (n_2) was calculated as a function of pH, where n_1 and n_2 were obtained from the amount of dye adsorbed and the surface charge density of the latices, respectively. r for the PS latex was found to be about 1.09, independent of pH. However, r for PS/PAA latices decreased gradually with an increase in pH (*i.e.*, r for PS/PAA$_2$ decreased from 1.74 to 0.61, and r for PS/PAA$_5$ decreased from 2.05 to 0.31). The ratio r is a measure of electrostatic interaction between dye and latex. For $r=1$, each dye molecule is adsorbed on a single site of surface charge groups of latex particles. Thus, Methylene Blue adsorption onto PS latex is considered to occur mainly electrostatically. In the acidic region (where the dissociation of carboxyl groups is not very large), r for PS/PAA latices was larger than 1. This may be attributed to hydrogen bonding of the nitrogen atoms of the

dye molecules with the carboxyl groups of the latex as well as to the effect of electrostatic attraction. In the alkaline pH region, r was smaller than 1, indicating the number of dye molecules adsorbed to be smaller than that of the surface charge groups. Since the Methylene Blue molecule has a definite area for adsorption, dye molecules cannot adsorb any more even if the adsorption sites increase.

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