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Preparation of Surfactant-free Polystyrene Latices with High Surface Charge and Electrical Double Layer on Their Surfaces

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Polystyrene latices with a wide range of surface charges were prepared in the absolute absence of conventional emulsifiers by controlling the concentration of potassium peroxodisulfate as an initiator and allowing the polymerization to proceed at a relatively high pH to suppress the Kolthoff reaction; $KHCO_3$ or K_2HPO_4 buffer was used to keep the polymerizing system near neutral pH. Conductometric titrations with different bases (NaOH and $Ba(OH)_2$) on latices show that the Stern layer charge increases with an increase in the surface charge of latices (σ_0) and at about the same rate as σ_0 does, leading to a virtually constant diffuse layer charge.

In recent years, monodisperse polystyrene latices have been recommended as a model dispersion for studying a number of fundamental phenomena in the field of colloid science.[1] Main reasons for this recommendation are the high monodispersity of particles and the well-defined composition of surface charge.[2] In considering behaviors of polystyrene latices, it is particularly important whether they have been prepared in the presence or in the absence of emulsifier. If no emulsifiers have been used in the preparation, the surface charge is made up of chemically bound polar groups originating from the initiator used in the polymerization.[3] In the presence of emulsifier, however, besides covalently linked polar groups, adsorbed ionic groups from the emulsifier can contribute to the surface charge. According to Stone-Masui and Wattilon,[4] adsorbed emulsifiers cannot easily be eliminated from the latex surface.

In this study, efforts were first concentrated on preparing monodisperse polystyrene latices with a wide range of surface charge in the absolute absence of conventional emulsifiers and then a study was made on the structure of electrical double layers on their surfaces.

For usual surfactant-free polystyrene latices prepared with potassium peroxodisulfate as an initiator,[3] the surface charge is made up of sulfonato groups originating from the initiator. Therefore, to increase the surface charge, the number of sulfonato groups on the final particle should be made maximal.[5] This can be achieved by choosing relatively high concentrations of potassium peroxodisulfate and allowing the polymerization to proceed at neutral pH in the presence of a buffer agent; the latter condition is to suppress the Kolthoff reaction[6] leading to generation of hydroxyl radicals.

It has been established that, in the neighborhood of a charged particle, there is an ionic atmosphere which is composed of two kinds of layers with different ion distributions, the Stern layer and the Gouy diffuse layer. The present study on the structure of electrical double layers is based on analyses of titration curves of latices. Since the conductivity of a latex suspension is determined by the number and distribution of counter ions in the double layer, conductometric titration curves obtained with various bases can be expected to provide direct information on the structure of electrical double layers. Here, a lot of titrations were carried out by using NaOH and $Ba(OH)_2$ on latices with a wide range of surface charge, and the relation between the surface charge and the double layer structure was discussed on the basis of analyses of titration curves.

Experimental

Materials. The styrene monomer was purified three times by vacuum distillation and the initiator, $K_2S_2O_8$, was recrystallized from water and dried in a desiccator. All the other chemicals were of analytical grade and used without further purification. The water was doubly distilled with an all-pyrex apparatus.

Preparation of Polystyrene Latices. Surfactant-free polystyrene latices were prepared with a modification of the method described by Kotera *et al.*[3] The modification is related to how to agitate the polymerizing system and how to control the pH during the polymerization. In a glass bottle of 250 cm^3, a mixture of 20 cm^3 styrene monomer and 175 cm^3 water or solution of KCl, $KHCO_3$, and K_2HPO_4 in water was purged with argon gas at 70 °C, after which 5 cm^3 of a $K_2S_2O_8$ solution was added. Immediately the bottle had a glass stopper applied, was attached to a wheel designed to rotate at a speed of 50 min^{-1} in a water bath thermostated at 70 °C, and subjected to rotation for 24 h for polymerization. Additional data on the polymerization conditions are given in Table 1.

The average particle size of each sample was determined by measuring the diameter of particles on an electron micrograph equipped with a projection scope.

Titration Experiments. Latex samples were treated with extensively purified Dowex ion-exchange resins according to the method described by Van den Hul and Vanderhoff[7] for converting all charged groups on the latex surface into the H^+ form. After the ion-exchange process, about 40 cm^3 of the latex was titrated under an argon atmosphere with two bases, NaOH and $Ba(OH)_2$ solutions, both potentiometrically and conductometrically, in the same vessel at 25 °C. In these titrations, it was necessary to adjust the solid content at 3—4% w/w, because large experimental errors were produced at lower than 3% w/w and because titration patterns were distorted at higher than 4% w/w due to surface conductivity at the latex-solution interface, as was also found by Wright and James.[8] Potentiometric titrations were performed with a Horiba pH meter (Model F-5) equipped with a glass electrode and conductometric ones with a Philips conductivity meter PW-9501 equipped with a Philips conductivity cell (PR-9515).

Determination of Coagulation Concentrations. Coagulation concentrations, C_{cfc}, of latex samples for KCl were determined by a static method. In a glass-stoppered tube 1.0 cm^3 latex of *ca.* 0.5% w/w was mixed with one of 4.0 cm^3 KCl solutions of various concentrations and the mixture

Table 1. Preparation and characterization of polystyrene latices with a wide range of surface charge

Sample	Preparation conditions			Characterization		
	$K_2S_2O_8$ concn 10^{-4} M	Electrolyte concn 10^{-2} M	Final pH	Radius nm	Spec. area m^2/g	Surface charge $\mu C/cm^2$
1	2	3	4	5	6	7
N-1	3.71	—	3.2	212	13.5	1.1
N-2	19.07	—	2.6	260	11.0	3.5
N-3	34.21	—	2.3	290	9.9	4.1
		KCl				
K-1	19.2	0.2_7	2.6_5	350	8.5	3.2
K-2	19.2	1.0	2.6_6	528	6.4	3.5
K-3	37.1	0.5	2.6_2	381	7.9	4.3
		$KHCO_3$				
C-1	18.5	1.0	7.6	255	11.2	4.5
C-2	27.7	1.0	7.5	290	9.9	6.9
C-3	37.4	0.5	6.2	280	10.2	7.4
		K_2HPO_4				
P-1	29.3	0.5	7.4	325	8.7	8.1
P-2	36.9	0.5	7.8	300	9.6	8.7

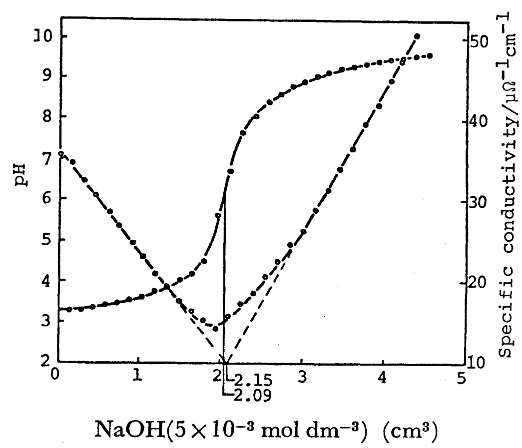

Fig. 1. Conductometric and potentiometric titration curves of latex C-3 after ion exchange.

was kept at 25 °C in a water bath. After an elapse of 20 h for equilibration the transmission coefficient of the supernatant was measured against water using an Atago spectrophotometer (440-S) at wavelength 550 nm. Transmission coefficients were plotted against the KCl concentration. Extrapolation of the linear part of the curve to the horizontal yields a KCl concentration that is taken by us as the coagulation concentration.

Results and Discussion

Preparation and Characterization of Polystyrene Latices. Some examples of results on the preparation and characterization of surfactant-free latices are shown in Table 1. Columns (5) and (6) in this table give average particle sizes determined by electron microscopy. The presence of KCl in the polymerizing system leads to larger particles; compare N-2 with K-1 or K-2. It is seen that in the absence of added electrolyte an increase in the initiator ($K_2S_2O_8$) leads to larger particles. Addition of $KHCO_3$ or K_2HPO_4, however, does not alter the radius significantly; compare N-2 with C-1 or N-3 with P-2. Size distributions are kept very narrow, with $D_w/D_n<1.01$.

The surface charge in column (7) was obtained by titration in an argon atmosphere with bases. As the example in Fig. 1 shows, both the equivalent points determined by the potentiometric and conductometric titrations are in good agreement, and the titration curves show no indication of presence of surface groups other than strong acid groups. These groups are certainly $-OSO_3^-$ groups originating from $K_2S_2O_8$.[2] Such titration curves, however, were observed only for fresh samples; for those latices left long after preparation, there were two break points on the titration curve, which suggests that surface sulfonate groups will be hydrolyzed gradually into hydroxyl or carboxyl groups during storage, with rates dependent on the conditions for storage. In each series the surface charge (σ_0) increases with increasing $K_2S_2O_8$ concentration. This tendency may be predicted from the mechanism of emulsion polymerization. Buffering the system during polymerization leads to higher values of σ_0; compare N-series with C- or P-series. As mentioned before, this is attributed to suppression of the Kolthoff reaction. The highest surface charge attained after ion exchange is 8.7 μC/cm². In the absence of specific adsorption it would lead to diffuse double layer potentials of 190 mV and 80 mV in 10^{-3} or 10^{-1} M† (1-1) electrolytes, respectively. However, due to specific adsorption in the Stern layer, lower values for ζ-potentials will almost certainly be found from electrokinetic study.

Double Layer Structure and Stability. The present study on the structure of electrical double layers at the polymer-solution interface is based on analysis of titration curves. The titration was carried out only for samples within a few weeks after preparation. Figure 2 shows an example of conductometric titration curves obtained by using two bases. In the case using NaOH, both the descending and ascending legs of the titration curve are linear, and the curve has

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† 1 M=1 mol dm⁻³.

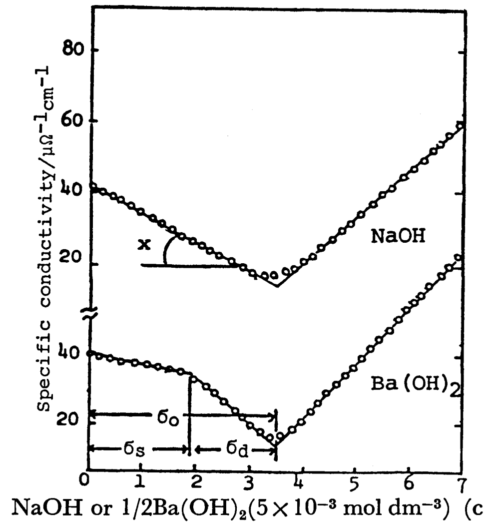

Fig. 2. Conductometric titration curves conducted using NaOH and $Ba(OH)_2$ for latex K-1.
x: Slope of the descending leg of the titration curve, σ_0: surface charge, σ_s: Stern-layer charge, σ_d: diffuse-layer charge.

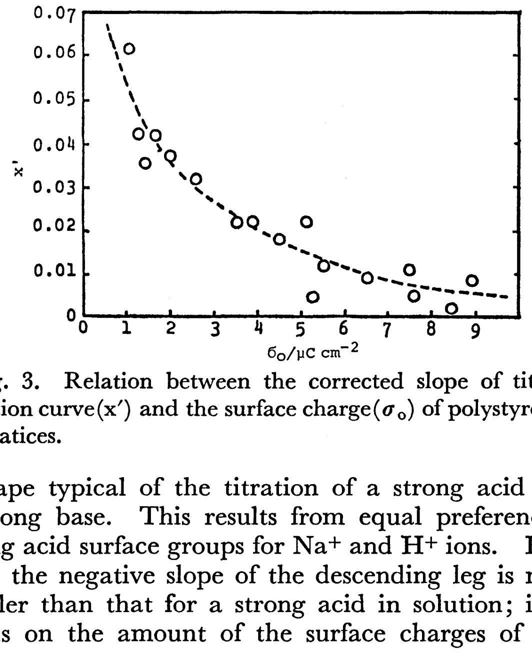

Fig. 3. Relation between the corrected slope of titration curve(x′) and the surface charge(σ_0) of polystyrene latices.

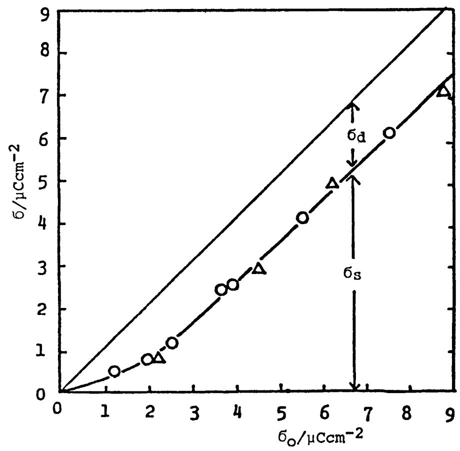

Fig. 4. Charge distribution in the Stern layer(σ_s) and the diffuse layer(σ_d) as a function of the surface charge(σ_0). △: Data reported by W. Norde.

a shape typical of the titration of a strong acid with a strong base. This results from equal preference of strong acid surface groups for Na^+ and H^+ ions. However, the negative slope of the descending leg is much smaller than that for a strong acid in solution; it depends on the amount of the surface charges of latex due to the limited mobility of counter ions in the double layer. Usually, the electrical conductivity of a system depends on the product of the number of mobile ions and their mobility. Therefore, the descending slope in the present system is influenced by the following three factors: (a) total surface area, (b) the amount of surface charges, and (c) the degree of binding of counter ions to the surface, which depends on the structure of the electrical double layer. If factors (a) and (b) can be controlled, the residual slope (x′) gives the contribution from factor (c), which provides useful information on the structure of electrical double layer. Figure 3 shows a plot of slopes obtained by the above process against surface-charge density (σ_0) as determined from equivalent points for the same titration curves. The slope (x′), in which the dimension of x is related to the scale for the titration curve, decreases rapidly with an increases in σ_0, and the value for the highest surface-charge latex is about one-sixth that of the lowest one. This indicates that the higher the surface charge, the more tightly are the counter ions held on the surface.

The lower conductometric titration curve in Fig. 2 shows a result obtained using $Ba(OH)_2$, in which an inflection point is found on the descending leg. According to Van den Hul and Vanderhoff,[2] the occurrence of the inflection point is connected with fixation of counter ions in the Stern layer. Counter ions condensed closely to surface sulfonato groups are exchanged preferentially for Ba^{2+}, and then dissociated ions in the diffuse double layer are exchanged. Counter ions in the diffuse double layer contribute effectively to the conductivity through their high mobility.

Using this concept, we can determine the number of counter ions located in the Stern layer and in the diffuse layer from the position of the inflection point on the descending leg. Figure 4 shows a result derived on the basis of inflection points, which gives charge distributions in the Stern layer (σ_s) and in the diffuse double layer (σ_d) as a function of surface charge (σ_0). It is obvious that, at high σ_0 values, σ_s increases at about the same rate as σ_0, leading to a virtually constant value of σ_d.

A similar result has been reported by W. Norde[9] for polystyrene latices prepared by the same method as ours, his result being included in Fig. 4. He calculated σ_d from ζ-potentials for latices of various surface charges using the Gouy-Chapman equation. In this case, ζ-potential was derived following the method of Wiersema[10] from electrophoretic mobilities in a 0.01 M KNO_3 solution. As can be seen from Fig. 4, his data are located on the same line as ours, which suggests that the region given by the inflection point of the conductometric titration curve corresponds to the slipping plane of the electrophoresis in 0.01 M KNO_3.

According to the Derjaguin-Landau-Verway-Overbeek (DLVO) theory,[11] coagulation concentration, C_{cfc}, serves as a means for quantifying the sta-

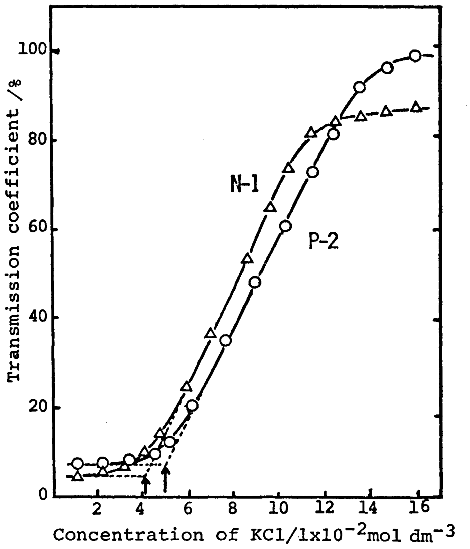

Fig. 5. Transmission coefficient *vs.* concentration of KCl plots for latex N-1(△) and latex P-2(○).
The arrow indicates the derived coagulation concentration.

TABLE 2. COAGULATION CONCENTRATION OF KCl FOR THE LATICES WITH A DIFFERENT SURFACE CHARGE

Sample	Surface charge $\mu C/cm^2$	Coagulation concn 10^{-2} M
N-1	1.1	4.02
K-1	3.2	4.35
C-2	6.9	4.71
P-2	8.7	4.97

bility of an electrostatically stabilized dispersion. Figure 5 shows an example plot of transmission coefficient *vs.* concentration of KCl. Values of C_{cfc} for latices with different surface charges are given in Table 2. It is seen that C_{cfc} increases with increasing surface charge, as expected from the DVLO theory, but C_{cfc} for the highest surface-charge latex (P-2) is not much different from C_{cfc} for the lowest-charge latex (N-1).

At any rate, it can be concluded that conductometric titration curves of polystyrene latices furnish important knowledge regarding the structure of electric double layers. From these analyses and coagulation experiments, it is realized that colloidal stability depends on the potential at the Stern layer over which the diffuse double-layer charge is distributed, because C_{cfc} is not much dependent on the surface charge of latex samples.

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