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CHARGE DISTRIBUTION IN ELECTRIC DOUBLE LAYER ON POLYSTYRENE LATTICES

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Conductometric titration curves using some bases give important knowledge about the structure of the electric double layer on the surface of polystyrene lattices. This analysis showed that the Stern layer charge increases with an increase in the surface charge of latex(δ_o) and at about the same rate as δ_o does, reaching a virtually constant diffuse-layer charge.

Polymer lattices, especially polystyrene lattices(Ps lattices) prepared without using any emulsifier, are used in many scientific fields.$^{1)}$ The main reasons for this are the high monodispersity of the particle and the well-defined composition of the surface charge. This paper will show that the system is also suitable for studying the structure of the electric double layer at the latex-solution interface.

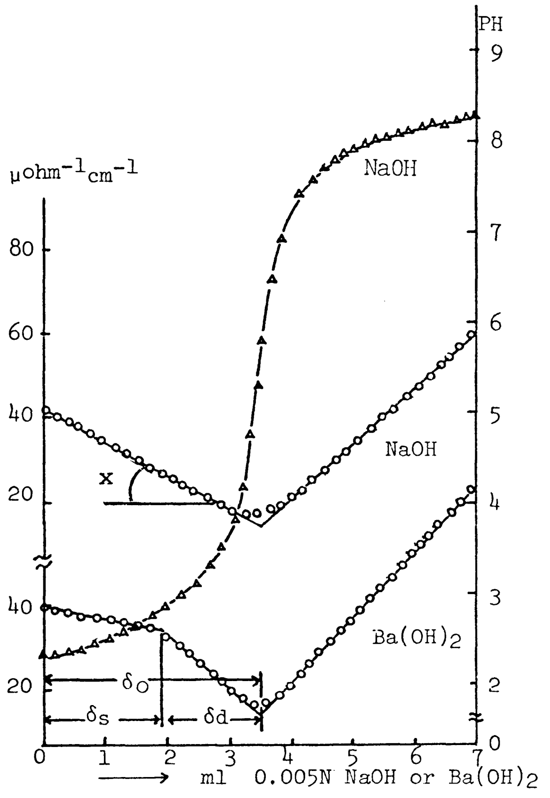
It has been established that, in the neighbourhood of a charged particle, there is an ionic atmosphere which is composed of two kinds of layers which can be distinguished by the charge distribution, i.e., the Stern layer and the Gouy diffuse layer.

The surface charge on Ps lattices comes from the dissociation of surface sulfonato groups($-OSO_3^-$) originating from the decomposition of the potassium persulfate(K.P.S.) used as an initiator. As the conductivity of a latex suspension is determined by the number and distribution of counter ions in the double layer, the conductometric titration curves obtained using some bases can be expected to provide direct information on the structure of the double layer. In this study, numerous conductometric titrations were conducted using NaOH and $Ba(OH)_2$ on the P_s lattices, which have a wide range of surface charges, and the relation between the surface charge(δ_o) and the double-layer structure was considered based on the analysis of the titration curves.

Seventeen kinds of Ps lattices were prepared and characterized according to a procedure described previously.$^{2)}$ The average particle size(the particles ranged in size from 5000 to 8000 A in diameter) was determined by means of an electron microscope, and the high monodispersity was confirmed.

The latex samples had been treated with extensively purified Dowex ion-exchange resins according to the method described by van den Hul and Vanderhoff.$^{3)}$ Thus, all charged surface groups were converted to the H^+ form. After the ion-exchange process, about 30 ml of the latex was titrated under an Ar 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 contents to 3 - 4%, because the experiments caused large errors at less than 3%, while the titration patterns were distorted at higher than 4% by the surface conductivity at the Ps latex-solution interface, as was also found by Wright and James.$^{4)}$ The potentiometric titrations were performed with a Horiba pH meter(Model F-5)equipped with a glass electrode, while the conductometric ones were carried out using a Philips conductivity meter PW-9501 equipped with a Philips conductivity cell(PR-9515). The equivalent points determined by the two techniques using different bases were in good agreement with each other, and the titration curves show no indication of the presence of surface groups other than strong acid groups($-OSO_3^-$) originating from K.P.S..

Figure 1 shows an example of the titration curves. In the case using NaOH, both the descending and ascending branches of the conductometric titration curve are linear, and the shape of curve is typical of what is found in the titration of a strong acid with a strong base. This is the result of an equal preference of the strong acid surface groups for Na^+ and H^+ ions. However, the negative slope of the descending branch is much smaller than that for a strong acid in solution; it depends on the amount of the surface charge of latex, because of the limited mobility of the counter ions in the double layer. Usually, the electric conductivity of a system depends on the product



δo:surface charge.
δs:Stern-layer charge.
δd:diffuse-layer charge.
x :slope of the descending branch of the titration curve.

Fig.1. Conductometric(o) and potentiometric(Δ) titration curves of ion-exchanged latex.

of the number of movable ions and their mobilities. Therefore, the descending slope in the present system is influenced by the following three factors: (a) the latex solid concentration in the sample, (b) the amount of the surface charge, and (c) the degree of binding to the surface of the counter ions, which in turn depends on the structure of the electric double layer. If the (a) and (b) factors can be controlled for the apparent titration slope, which is measured under the same conditions, the residual slope(x) gives the part coming from the (c) factor, which provides useful information on the structure of the electric double layer. Figure 2 shows the plot of the slope obtained by the above process against the surface-charge density(δ_o), which was determined from the equivalent point of the same titration curve. The slope(x), in which the dimension of x is related to the scale of the titration curve, decreases rapidly with an increase in δ_o, and the value of 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.

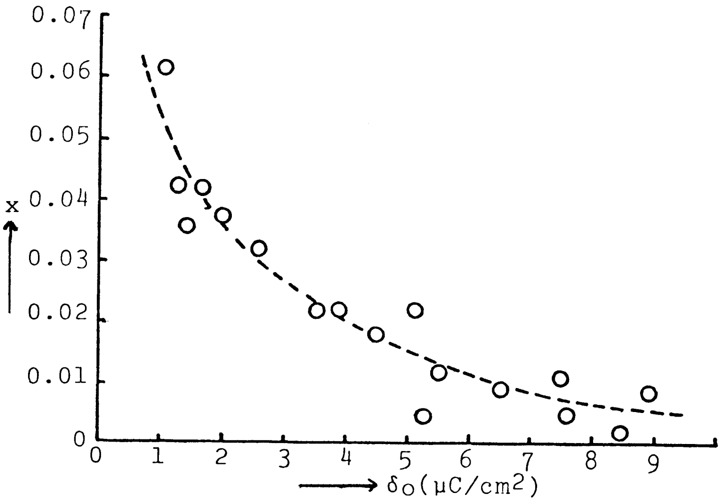
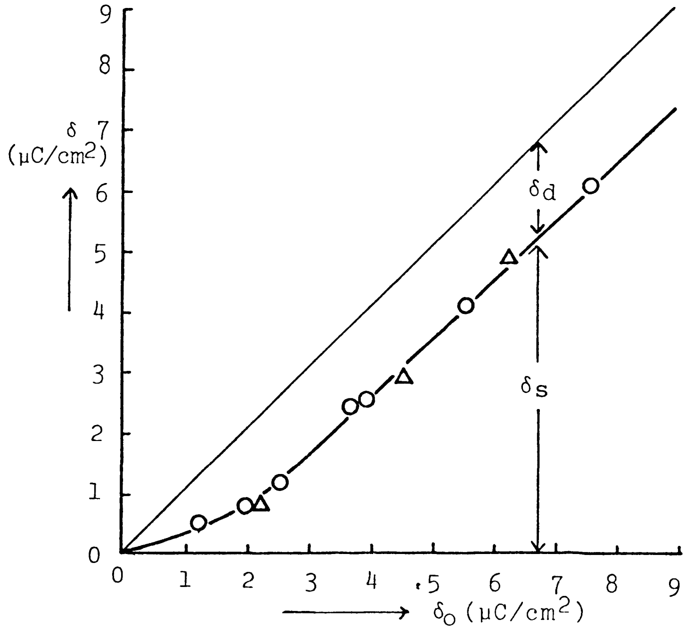


Fig.2. Relation between the corrected slope of the titration curve(x) and the surface charges(δ_o) of Ps lattices.

The lower conductometric titration curve in Fig.1 shows a result obtained using Ba(OH)$_2$, in which an inflection point is found on the descending branch. According to Vanderhoff et al.,$^{5)}$ the occurrence of the inflection point is connected with the fixation of the counter ions in the Stern layer. The counter ions condensed closely on the surface sulfonato groups are exchanged preferentially for Ba^{2+}, and then the dissociated ions in the diffuse double layer are exchanged. The counter ions



Δ:Data reported by W.Norde.

Fig.3. Charge distribution in the Stern layer (δ_s) and the diffuse layer(δ_d) as a function of the surface charge(δ_o).

in the diffuse double layer contribute effectively to the conductivity through their high mobilities.

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 of the descending branch. Figure 3 shows the result obtained from the inflection point, which indicates the charge distribution in the Stern layer(δ_s) and in the diffuse layer(δ_d) as a function of the surface charge(δ_o). It is obvious that, at high δ_o values, δ_s increases at about the same rate as δ_o, leading to a virtually constant value of δ_d. This is identical with the result obtained using NaOH.

A similar result has been reported by W.Norde$^{6)}$ for the Ps lattices prepared by the same method as ours, his result is also plotted in Fig.3. He calculated δ_d from the ζ-potential for the lattices of various surface charges using the Gouy-Chapman equation. In these cases, the ζ-potential was derived following the method of Wiersema$^{7)}$ from the electropholetic mobilities in a 0.01M KNO_3 solution. As can be seen in the figure, his data are located on the same line as ours, which suggests that the region divided by the inflection point of the conductometric titration curve coincides with the slipping plane of the electrophoresis in 0.01M KNO_3.

At any rate, it can be concluded that the conductometric titration curves of P_s lattices give important knowledge regarding the structure of the electric double layer. From these analyses, it is realized that colloid stability depends on the potential at the Stern layer over which the diffuse double-layer charge is distributed, because the coagulation concentration(C_{cfc}) of KCl for the highest-surface-charge latex(δ_o = 8.8 $\mu C/cm^2$) is 4.20 x 10^{-2}M, not much different from C_{cfc} = 4.08 x 10^{-2}M for the usual latex(δ_o = 1.0 $\mu C/cm^2$).

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