

Figure 1. Colloid titration curve of PEI with KPVS at ionic strength of 0.

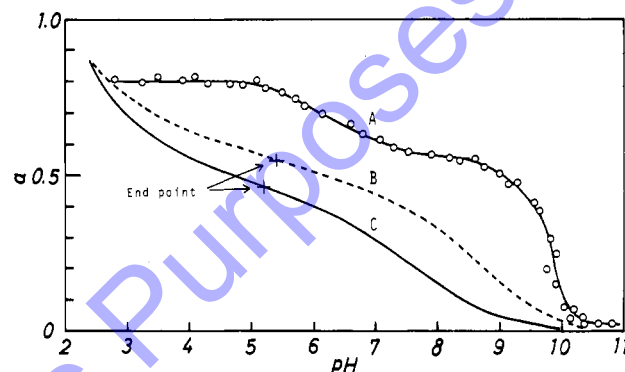


Figure 2. The curves of α vs. pH. Curve A (ionic strength 0) was obtained from Figure 1. Curve B (ionic strength 0.1) and curve C (ionic strength 0) were calculated from the results of potentiometric titrations by the following equation: $\alpha = \alpha_n + (C_{OH^-} - C_{H^+})/C_P$, where α_n represents the degree of neutralization, C_{H^+} and C_{OH^-} are the molarity of protons and hydroxyl ions, and C_P is the molar concentration of the total amino groups in PEI.

Colloid Titration Behavior of Poly(ethyleneimine)

Poly(ethyleneimine) (PEI) is a branched polymer and thus contains primary, secondary, and tertiary amino groups. From the study on the polymerization mechanism, Dick and Ham¹ showed that the ratio of primary, secondary, and tertiary amino groups was 1:2:1. This was confirmed by Lukovkin et al.² from the result of NMR study. The dissociation behavior³⁻⁵ of the amino groups in PEI was evaluated by potentiometric titration and was known to be different from other polyacids and polybases.

In the present study, the mechanism of the formation of polyion complex between PEI and a linear polyanion was investigated by means of the colloid titration which was originated by Terayama.⁶ Potassium poly(vinyl alcohol) sulfate (KPVS) was used as the linear polyanion. The result of the colloid titration was compared with that of the potentiometric titration, and the stoichiometry of the salt-linkage formation between three amino groups in PEI and $-\text{OSO}_2\text{O}^-$ groups in KPVS was discussed.

Experimental. PEI was obtained from Tokyo Kasei Kogyo Co., Ltd. The polymer was fractionated and purified in the same manner as described in the literature.⁷ The weight-average molecular weight of the fraction used here was 1.1×10^5 , as estimated by the viscometric measurement.⁵ The result of elemental analysis was: H, 11.9; C, 55.7, N, 32.4. These values agree with those (H, 11.6; C, 55.8; N, 32.6) calculated by the assumption that the PEI contains 25% of primary and tertiary amino groups and 50% of the secondary amino group. The physical properties of KPVS were already characterized in the previous study.⁸ The degree of esterification for KPVS was 0.924, as estimated from the sulfur content (19.3%).

The colloid titration was carried out at 25 ± 0.1 °C in a nitrogen atmosphere using a Hirama Automatic Re-

cording Titrator. The PEI (0.211 mg) was dissolved in 50 mL of distilled water, and then the pH of the solution was adjusted with 0.1–1 M HCl and NaOH. The sample was titrated with 0.00252 N KPVS solution adjusted to the pH of the sample. The end point of the titration was indicated by the turbidimetric and conductometric measurements.

The potentiometric titration was also carried out to investigate the dissociation behavior of the amino groups in PEI. The sample solution (containing 8.98 mg of PEI in 50 mL of solvent) was titrated at 25 ± 0.1 °C in an atmosphere of nitrogen with 0.107 N HCl using a Toadenpa Automatic Titration Apparatus (Model HMS-10A pH stat equipped with Model XYR-2A recorder). The ionic strength of the titration system was adjusted with NaCl.

Results and Discussion. The colloid titration curve was obtained by plotting the reciprocal of equivalent weight (E_w) of PEI against pH. The result is shown in Figure 1. The curve has three plateaus at the regions of pH < 5, 7.5–8.5, and > 10.5. The electrophoretic study of KPVS in the previous paper⁸ showed that the dissociation of $-\text{OSO}_2\text{O}^-$ groups in KPVS is independent of pH in the region of 3–11. Therefore, it is considered that the change of $1/E_w$ on pH can be related to the dissociational change of three amino groups in PEI.

In order to investigate the mechanism of complex formation between PEI and KPVS, the relation between pH and the degree of dissociation (α), which was calculated by $\alpha = (1/E_w)/(1/E_w^0)$, was obtained from Figure 1. The E_w^0 value (43.2) represents the value of E_w at $\alpha = 1$ and is calculated from the nitrogen content of PEI. The curve of α vs. pH is shown in Figure 2, together with those

obtained by the potentiometric titrations at ionic strengths of 0 and 0.1. From the α vs. pH curves obtained by the potentiometric titrations, it is found that the amino groups which were neutralized with HCl are 45–55% of the total amino groups in PEI. Thiele and Gronau⁴ reported that the potentiometric titration curve of PEI with HCl reaches to the end point at about $\alpha = 0.67$, although the ionic strength of the titration system is very high. This behavior was interpreted by a possible strong interaction of charged neighbors on uncharged groups along the branched polymer chain,⁵ i.e., “the nearest neighboring interaction” which was originally proposed by Katchalsky and co-workers.⁹ In contrast to the α vs. pH curve obtained by the potentiometric titration, that obtained by the colloid titration shows three plateaus. Furthermore, the value of α at all pHs is larger than that obtained by the potentiometric titration. From these results, it is considered that “the nearest neighboring interaction” does not play an important role in the complex formation between PEI and KPVS.

The result of colloid titration was also investigated to obtain information about the stoichiometry for the salt-linkage formation of each amino group in PEI with $-\text{OSO}_2\text{O}^-$ groups in KPVS. The plateau regions mentioned above seem to be the pH regions where each amino group in PEI is dissociated completely: pH <5, primary; pH 7.5–8.5, secondary; and pH >10.5, tertiary. The difference in the α value between the plateau regions of pH <5 and of pH 7.5–8.5 is about 0.25, and the difference between the plateau regions of pH 7.5–8.5 and of pH >10.5 is about 0.5. Therefore, it is found the PEI contains 25% of the primary amino group and 50% of the secondary amino group. The contents of the primary and secondary amino groups agree with those estimated from the studies of polymerization mechanism¹ and NMR.² This indicates the stoichiometric salt-linkage formations of the primary and secondary amino groups with $-\text{OSO}_2\text{O}^-$ groups in KPVS. However, the content of the tertiary amino group is about 3%, as estimated by the curve of α vs. pH at the plateau region of pH >10.5. This could be understood by the explanation that the tertiary amino group is situated in the branching point of the PEI chain and does not form stoichiometrically the salt-linkage with the $-\text{OSO}_2\text{O}^-$ group in KPVS because of the steric hindrance of the polymer chain.

The study of the colloid titration reported above is not only interesting as an analysis of the mechanism of the complex formation between branched polyion and linear polyion, but it is also interesting as an assay of amino group contents in PEI.

References and Notes

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