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Ion Association of Protonated Poly(vinylamine) and Poly(ethylenimine) with Poly(vinyl sulfate) and Dodecylbenzenesulfonate as Special Reference for Colloidal Titration

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Ion association constants of two types of poly(vinylamine) and poly(ethylenimine) were determined from pH measurements of the polyamine/counter ion mixtures at an aqueous solution of the polymers (5×10^{-4} equiv mol dm^{-3}). The results are discussed in terms of chemical structure (distance between reacting groups, and straight or branched chain), molecular weight, and ionic strength. The ion association at very low concentration protonated polyamines was promoted by the close location of amino groups. When the bound counter ions became close to each other, further ion association was inhibited by counter ions which had already bounded. From the colloidal titration of these polyamines, the stoichiometry could be discussed, especially under the conditions where all amino groups on the polymer are converted into ammonium ions. The results of the colloidal titration indicated that the stability constant for the ion association was drastically increasing near the equivalence point of the colloidal titration.

Colloidal titration[1] due to ion association between polycation and polyanion is a conventional method widely used for the determination and the characterization of polyelectrolytes. The colloidal titration method is still viewed with uncertainty, because it has not been studied enough to disscuss the quantitative analysis to be compared with results of acid–base, oxidation–reduction, complexometric, and argentometric titrations.

Many papers[2] has been published about the polycation–polyanion association. Investigations of the ion association between a macroion and the oppositely charged ion, which was a monomer, oligomer or polymer, demonstrated that stability constants of ion association increased with polymerization.[3] Measurements of ion association constants and their kinetic parameters indicated that dehydration was an important process leading to polycation–polyanion complex formation.[4] In most of the studies, however, the constant of ion association was not indicated.

Recently, we reported the ion association complex between glycolchitosan (GCh) and poly(vinyl sulfate) (PVS) obtained by potentiometric titration.[5] The experimental concentrations of their polyelectrolytes were 5×10^{-4} equiv mol dm^{-3}. By use of a flow-though reference electrode and batchwise method, pH measurements which could avoid contamination of sample solution due to inorganic salt leaking from the reference electrode. But the observed constant of the ion association was not enough to explain the accuracy of the colloidal titration. We pointed out that coagulation of polyelectrolyte complex near the equivalence point was important in the colloidal titration. To establish the colloidal titration, accumulation of more data on other polyelectrolyte complex is required. In this study, we selected poly(vinylamine) (PVA) and branched poly(ethylenimine) (PEI) as polyamines with highly ionic density, and measured the equilibrium constants for the association with PVS and dodecylbenzenesulfonate (DBS), in contrast with the low ionic density of GCh. We discuss the effects of microstructure, molecular weight, and ionic strength on the ion association, and speculate about the stoichiometry of colloidal titration.

Experimental

Materials. Two samples of PVA–HCl,[6] prepared by radical polymerization of *N*-vinylformamide followed by acid hydrolysis, were kindly supplied from Mitsubishi Kasei Co. (Tokyo, Japan). Their limiting viscosities in aqueous 0.01 M NaOH–0.1 M NaCl solution (1 M = 1 mol dm^{-3}) were 98 and 695 cm^{-3} g^{-1}, respectively. Viscosity-average molecular weights of these samples are 5.9×10^4 and 5.5×10^5, respectively.[7] The normalities (equiv mol dm^{-3}) of PVA–HCl solutions were measured by acid–base titration with NaOH. The concentration of chloride ion was measured by potentiometric titration with $AgNO_3$ solution, using a silver ion-selective electrode. PEI (average molecular weight approximately 7×10^4) solution was purchased from Wako Pure Chemical Ind., Ltd. (Osaka, Japan), and was dialyzed in dilute aqueous HCl solution before use. The normality of PEI solution was measured by a conventional Kjeldahl method. The ^{13}C NMR spectrum of the PEI (10% H_2O–D_2O solution) had eight peaks corresponding to primary, secondary and tertiary amine groups, indicating the presence of branched structures. The concentration of chloride ions in PEI–HCl solution was determined by the argentometric titration. Potassium PVS and sodium DBS was purchased from Wako Pure Chemical Ind., Ltd. The potassium PVS (esterification above 90%) was converted into sodium PVS by ion-exchange using a sodium form of Amberlite IR-120. The limiting viscosity number was 181 cm^3 g^{-1} in aqueous 0.5 M NaCl, and the viscosity-average molecular weight was 1.6×10^5.[8] The normality of the PVS solution was measured by colloidal titration. The sodium DBS was a standard material (purity above 99%) containing a few percent of isomers,[9] and was used without further purification.

Measurements. A flow-through type pH meter (model No. IM-40 and FAR-201A, TOA Electronics Co., Tokyo, Japan) was used to measure the pH in a glove box in an argon atmosphere. The flow-through pH meter was effective in avoiding contamination of sample solution due to KCl leaking from the reference electrode and enabled stable measurements of pH even at very low concentrations of electrolytes.

As the titration was done batchwise, a series of sample solutions had to be prepared for measuring the association constants (K_i) and the acid dissociation constants (K_a). Different amounts of NaOH solution were added to the solutions containing adequate amounts of NaCl and polyamine–HCl. After the solution was diluted to about 40 cm^3 with deionized water, the amount of PVS or DBS equivalent to the polyamine was added. The volume of mixture was finally brought to 50 cm^3. The ionic strength (μ) was adjusted by adding appropriate amounts of NaCl. The preparation of each solution was carried out in a glove box in a CO$_2$-free argon atmosphere. Each mixture was equilibrated by standing for 2 h in a water bath maintained at 25±0.1°C.

Results

Relationship between pH and Degree of Neutralization (*B*). Figure 1 shows typical titration curves of PVA–HCl in the absence (a) presence (b) of sodium PVS. Curve a is similar to that for an acid–base titration of simple weak bases. The shape of curve a was related with the acid dissociation constants, K_a of PVA. The K$_a$ is described as follows:

$$PVAH^+ \rightleftharpoons PVA + H^+, \qquad K_a = \frac{\{PVA\}[H^+]}{\{PVAH^+\}} \tag{1}$$

The bracket, [*i*], indicates molarity (mol dm^{-3}) of *i* and the brace, {*j*}, normality (equiv mol dm^{-3}) of *j*.

The apparent values of K_a vary at each value of neutralization *B*. The value of *B* is described as follows:

$$B = (\{PVA\}_t + [Na^+]_{base} - [Cl^-]_{acid})/\{PVA\}_t \tag{2}$$

where $\{PVA\}_t$ is total concentration of amine groups for PVA (or PEI), and $[Na^+]_{base}$ is concentration according to the addition of NaOH, and $[Cl^-]_{acid}$ is concentration according to the addition of PVA–HCl. By taking into account the mass balance condition of PVA: $\{PVA\}_t=\{PVAH^+\}+\{PVA\}$, charge balance condition: $\{PVAH^+\}+[Na^+]+[H^+]=[Cl^-]+[OH^-]$ and ion product of water (K_w), Eq. 3 for K_a is obtained:

$$K_a = \frac{[H^+]^2 + B\{PVA\}_t[H^+] - K_w}{(1-B)\{PVA\}_t - [H^+] + K_w/[H^+]} \tag{3}$$

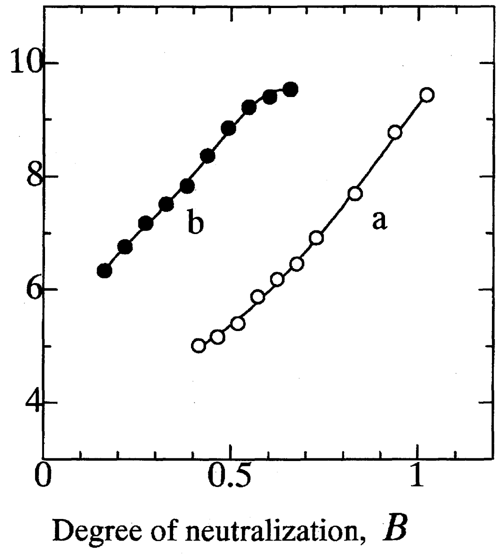

Fig. 1. Potentiometric titration curves of PVA–HCl (5×10^{-4} equiv mol dm^{-3}) solution. $\mu = 1\times10^{-3}$ (NaCl); a: NaPVS absent, b: 5×10^{-4} equiv mol dm^{-3} NaPVS present.

Therefore, apparent K_a values at various pH's can be calculated by *B* and pH.

On curve b, the values of *B* are always smaller in the presence of sodium PVS than in the absence at the same values of pH. This shows that hydrogen ions are consumed when *PVA* combines with PVS^-.

$$PVA + H^+ + PVS^- \rightarrow PVAH{\cdot}PVS \tag{4}$$

Therefore, the analysis of curve b leads to determination of the apparent ion association constant of the *PVAH·PVS* complex.

The ion association constant, K_i, between $PVAH^+$ (or $PEIH^+$) and PVS^- is described as follows:

$$K_i = \frac{\{PVAH{\cdot}PVS\}}{\{PVAH^+\}\{PVS^-\}} \tag{5}$$

In the solution of curve b, the charge balance condition requires:

$$\{PVAH^+\} + [H^+] + [Na^+] = \{PVS^-\} + [OH^-] + [Cl^-] \tag{6}$$

Since $[Na^+]$ is the sum of the addition of NaOH ($[Na^+]_{base}$), NaPVS and NaCl, and $[Cl^-]$ is the sum of the addition of PVA–HCl ($[Cl^-]_{acid}$) and NaCl, Eq. 6 is converted into Eq. 7.

$$[Na^+]_{base} - [Cl^-]_{acid} = \{PVS^-\} + [OH^-] - \{PVS\}_t - \{PVAH^+\} - [H^+] \tag{7}$$

From Eq. 7, by taking into account Eq. 2 of *B* and mass balance conditions of PVA and PVS; $\{PVA\}_t=\{PVA\}+\{PVAH^+\}+\{PVAH{\cdot}PVS\}$ and $\{PVS\}_t=\{PVS^-\}+\{PVAH{\cdot}PVS\}$, respectively, Eq. 8 is obtained:

$$\{PVA\} = B\{PVA\}_t - K_w/[H^+] + [H^+] \tag{8}$$

When Eq. 8 is substituted in Eq. 1, then:

$$\{PVAH^+\} = (B\{PVA\}_t - K_w/[H^+] + [H^+])[H^+]/K_a \tag{9}$$

By taking into account Eqs. 8 and 9, and the mass balance conditions of PVA and PVS, Eqs. 10 and 11 for $\{PVAH{\cdot}PVS\}$ and $\{PVS^-\}$ are obtained:

$$\{PVAH{\cdot}PVS\} = \{PVA\}_t - (1 + [H^+]/K_a)(B\{PVA\}_t - K_w/[H^+] + [H^+]) \tag{10}$$

$$\{PVS^-\} = \{PVS\}_t - \{PVA\}_t + (1 + [H^+]/K_a)(B\{PVA\}_t - K_w/[H^+] + [H^+]) \tag{11}$$

Therefore, when Eqs. 9, 10, and 11 are substituted in Eq. 5, K_i can be dissolved by giving pH, B, and K_a.

For polyelectrolytes, however, since K_a varies with pH, B, and the forming ratio of ion association complex, the calculation of K_i must be given an adequate value of K_a for each point on the curve. We first examined the value of K_a of each polyamine, and then estimated the value of K_i.

Dissociation Constants. Figure 2 shows the dependence of the value of pK_a on the degree of ionization ($\alpha=\{PVAH^+\}/\{PVA\}_t$) for the two kinds of PVA. The apparent values of pK_a increased with increasing ionic strength, showing that amino groups were easily ionized at high ionic strength. Although GCh, having a low density of amino groups, showed relatively constant pK_a values at $\mu=1$,[5] PVA does not give constant values of pK_a at any ionic strength, as shown in Fig. 2. Such behavior results from a higher density of ionic groups on PVA than on GCh.

For two kinds of PVA, nearly identical pK_a vs. α curves were obtained at $\mu=10^{-3}$, while the pK_a values of the high-molecular-weight PVA for $\mu=5\times10^{-3}$, 5×10^{-2}, and 1 were different from the pK_a values of the low-molecular-weight PVA. The pK_a va. α curves of the high-molecular-weight PVA have an inflection point near p$K_a=7$. The inflection becomes clearer as the ionic strength increases.

Figure 3 shows the effect of α on the value of pK_a of PEI. The shape of pK_a vs. α curves was similar to that reported by Bloys and Staverman.[10] Although the behavior of the pK_a of PEI resulted from the high density of the charge just like PVA, the values of pK_a of PEI were significantly smaller than those of PVA. The difference between the values of pK_a was attributed to the difference of ionizing groups. PVA consists of only primary amine units, but PEI has primary, secondary, and tertiary amine groups.

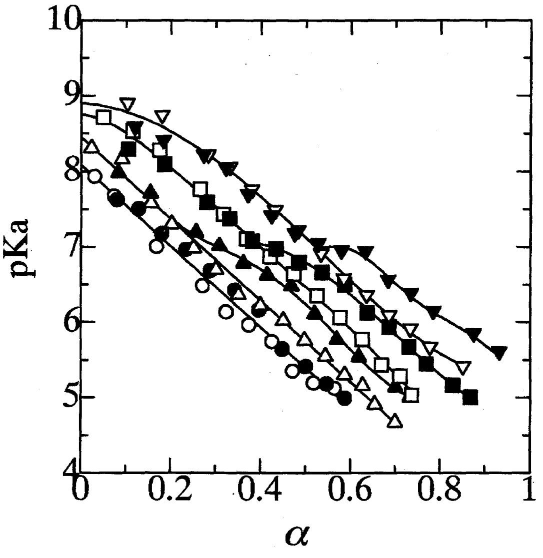

Fig. 2. Apparent pK_a of PVA at various α. Open signs are for the low molecular-weight PVA, and closed signs are for the high molecular-weight PVA. ○ and ●: $\mu=1\times10^{-3}$, △ and ▲: $\mu=5\times10^{-3}$, □ and ■: $\mu=5\times10^{-2}$, ▽ and ▼: $\mu=1$ (NaCl).

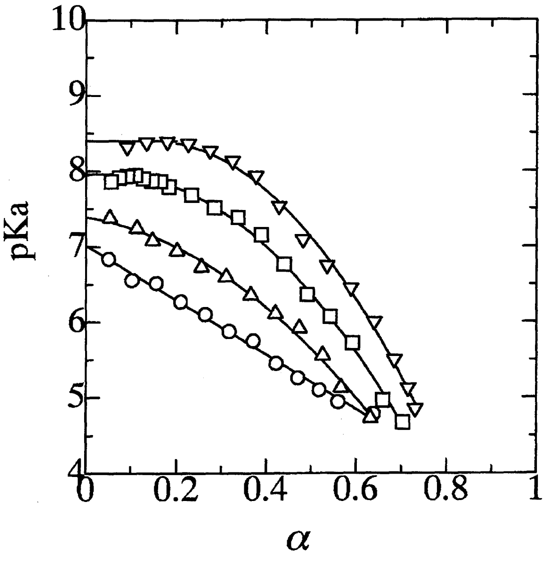

Fig. 3. Apparent pK_a of PEI at various α. ○: $\mu=1\times10^{-3}$, △: $\mu=5\times10^{-3}$, □: $\mu=5\times10^{-2}$, ▽: $\mu=1$ (NaCl).

Estimation of Ion Association Constants. When K_i value is to be determined, the apparent K_a value during the complex formation must be known. Moreover, the consideration of non-ion association constant (K_n) between nonprotonated vinylamine (PVA) and vinyl sulfate (PVS^-) is required. Okubo et al.[4] determined simultaneously K_a, K_n, and K_i for the reaction between REI and poly(vinyl sulfonate) at various degrees of ionization of REI. Their results calculated by the three constants, however, were in poor agreement with the experimental titration results. The simultaneous determination of three constants was difficult also for the analysis of the present titration results (Fig. 1b). Since it was expected that the constant of $PVA{\cdot}PVS^-$ was far smaller than the constant of $PVAH{\cdot}PVS$, we neglected the non-ion association of $PVA{\cdot}PVS^-$. Therefore, we determined an apparent K_a value on each titration point by the assumption below. The most important factor of the variation of apparent K_a must be the state of the total charge of PVA itself. During the complexation, the partial chemical species in macromolecules PVA are PVA, $PVAH^+$, and $PVAH{\cdot}PVS$. Since PVA and $PVAH{\cdot}PVS$ are electrically neutral, the only charged species is $PVAH^+$. Therefore, we assumed that the relationship between K_a and $\{PVAH^+\}/\{PVA\}_t$ in the presence of PVS was equal to that in the absence of PVS.

When the amount of $PVAH{\cdot}PVS$ is far less than the total amount of amine groups of PVA, the value of K_i corresponding to each point on curve b in Fig. 1 can be calculated by using the values of K_a obtained from curve a for a same pH. But the amount of $PVAH{\cdot}PVS$ was not neglected in comparison with the total amount of amine. The value of K_i should be calculated using the value of K_a calculated by taking into account the concentration of $PVAH{\cdot}PVS$. Therefore we determined K_i in the following way. For one point on curve b in Fig. 1, by use of all values of the K_a shown in Fig. 2 at 0.01 intervals of α, many sets of K_i and $\{PVAH^+\}/\{PVA\}_t$ were calculated. Among the calculated data, one set of data, for which the calculated value of $\{PVAH^+\}/\{PVA\}_t$ matched with the value of α for the values of K_a used (Fig. 2), was sought. By this process for determination of apparent K_i, we can also simultaneously obtain $\{PVAH^+\}$ and $\{PVAH{\cdot}PVS\}$ at each pH.

Ion Association Constants of PVA and PEI. Figure 4 shows the values of K_i obtained at various pH's for PVA–PVS. K_i gradually decreases with increasing ionic strength and decreasing pH. Although the association constants of low molecular-weight PVA are slightly larger than those of the high molecular-weight PVA at $\mu=5\times10^{-2}$, they have nearly identical values of K_i at low ionic strength. The magnitude of K_i is not strongly affected by molecular weight in contrast to K_a. Figure 5 shows the relationship between $\{PVAH{\cdot}PVS\}/\{PVA\}_t$ ratio (β) and $\log\{PVAH^+\}$. Since the variation in $\{PVAH^+\}$ is directly related to K_i in Eq. 5, the constant values of β is equivalent to decreasing K_i. The constant values of β indicated that the ion association was inhibited by neighbor counter ions which had already bounded; this was called anti-cooperating binding in a statistical mechanical treatment of binding phenomena.[11] According to the statistical mechanical treatment, binding phenomena were classified into three types: cooperating binding (positive effect between binding sites), non-cooperating binding (no effect between binding sites) and anti-cooperating binding (negative effect between binding sites).

All values of K_i of PVAH–DBS were less than 10^6 dm^3 (equiv mol)$^{-1}$ and the K_i vs. pH curves were almost the same as those for PVAH–PVS. The value of K_i for PVAH–DBS was slightly larger than that for PVAH–PVS at the same pH. Figure 6 shows β vs. $\log\{PVAH^+\}$ curves of PVAH–DBS. The β curve for DBS also displays an anti-cooperating binding. The value of β of PVAH–DBS is slightly larger than that of PVAH–PVS.

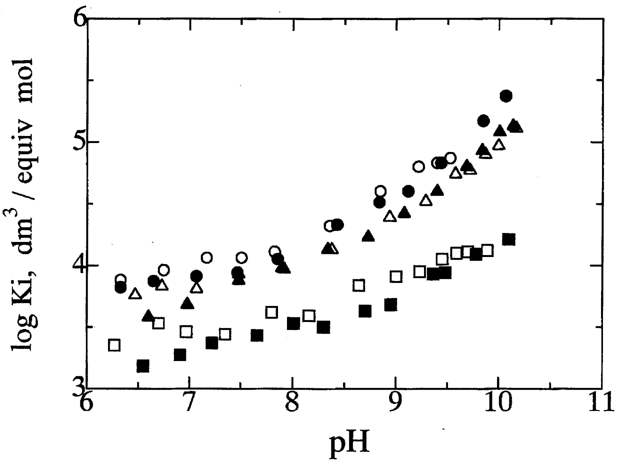

Fig. 4. Apparent ion association constants of PVAH–PVS at various pH. Open signs are for the low molecular-weight PVA, and closed signs are for the high molecular-weight PVA. ○ and ●: $\mu=1\times10^{-3}$, △ and ▲: $\mu=5\times10^{-3}$, □ and ■: $\mu=5\times10^{-2}$ (NaCl).

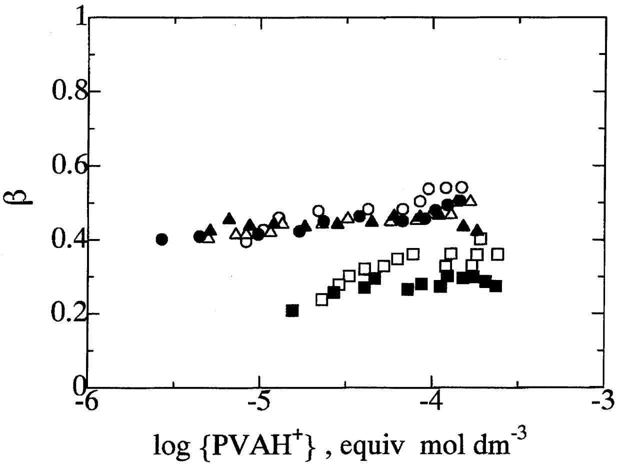

Fig. 5. Binding isotherms of PVAH$^+$ and PVS$^-$. Open signs are for the low molecular-weight PVA, and closed signs are for the high molecular-weight PVA. ○ and ●: $\mu=1\times10^{-3}$, △ and ▲: $\mu=5\times10^{-3}$, □ and ■: $\mu=5\times10^{-2}$ (NaCl).

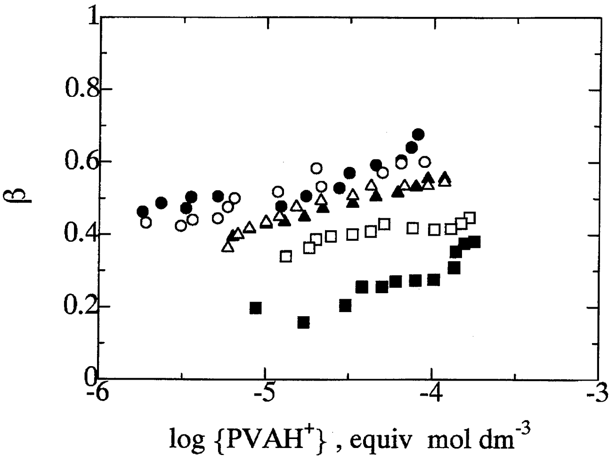

Fig. 6. Binding isotherms of PVAH$^+$ and DBS$^-$. Open signs are for the low molecular-weight PVA, and closed signs are for the high molecular-weight PVA. ○ and ●: $\mu=1\times10^{-3}$, △ and ▲: $\mu=5\times10^{-3}$, □ and ■: $\mu=5\times10^{-2}$ (NaCl).

All values of K_i of PEIH–PVS and PEIH–DBS were also less than 10^6 dm^3 (equiv mol)$^{-1}$, and the K_i vs. pH curves were almost the same as those for PVAH–PVS and PVAH–DBS. They also decreased with increment of pH and ionic strength. The values of K_i of PEIH–PVS and PEIH–DBS were quite similar to each other, in contrast with the PVAH complex. Figure 7 show β vs. $\log\{PEIH^+\}$ curves of PEIH–PVS and PEIH–DBS. The β curve of PEI also displays an anti-cooperating binding. The effect of the addition salt on β is small when compared with the result of the PVAH complex.

Colloidal Titration. The colloidal titration of three polyamines was carried out at a very low pH value, because the titration was used to determine the total concentration of ionizing groups. For two kinds of PVA, good agreements between the results of acid base titration and colloidal titration were obtained. The result of the titration of PEI, however, did not give the total concentration of the amino groups. On the colloidal titration of PEI in acetic acid solution at pH=2.4,

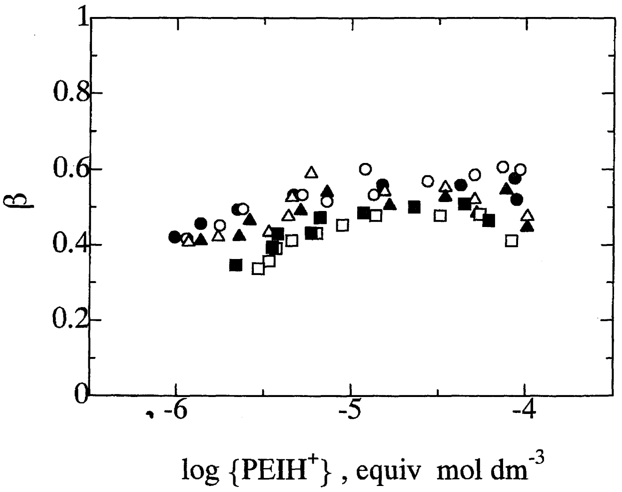

Fig. 7. Binding isotherms of PEIH$^+$ and PVS$^-$ or DBS$^-$. Open signs are for PVS$^-$, and closed signs are for DBS$^-$. ○ and ●: $\mu=1\times10^{-3}$, △ and ▲: $\mu=5\times10^{-3}$, □ and ■: $\mu=5\times10^{-2}$ (NaCl).

the end-point was reached at 87% of equivalence expected from Kjeldahl nitrogen. Since PEI contains tertiary amine groups, all functional groups on PEI can not be completely ionized in the aqueous solution.

Discussion

It was noted that the ion association was inhibited by neighbor counter ions which had already bounded. Such an inhibition was not observed in the ion association between GCh and PVS.[5] The inhibition is considered to be due to the close location of the reacting groups on PVA, that may exert an exclusion effect on the incoming ions. The distance between reacting groups on PVA, however, is matched with the distance between those on PVS. Although the reaction of polymer–polymer ion association with the same distance between reacting groups would form into one of the most compact structures such as a ladder structure,[2a] an expected large stability was not obtained. Such low stability of the polyelectrolyte complex reflected the state of the precipitation. Actually, the precipitation of PVAH–PVS obtained was cotton-like in this experiment. The cotton precipitation may indicate that the ion association complex reaction proceeds without complete dehydration. That is, the effective volume of the reacting groups will become large with the self-hydration.

On the dissociation of the high molecular-weight PVA, the observed inflection may indicate the conformational change. Although the conformational change of PVA was already suggested from estimation of the entropy changes,[12] no clear inflection has ever been reported in the course of acid-base titration.[10,13] The conformational change of PVA before the formation of the polyelectrolyte complex could affect the stability of the polyelectrolyte complex. However, the difference between two PVAs for the ion association was quite small.

The value of K_i and β of PVAH–DBS were slightly larger than those of PVAH–PVS at same concentration of $PVAH^+$. The large degree of β indicates the relaxation of the inhibition of PVAH–DBS. It has been reported that the values of K_i for GChH–DBS were definitely smaller than those for GChH–PVS at low ionic strengths.[5] GCh did not associate at all with DBS when $\{GChH^+\}$ was lower than $10^{-5.5}$ equiv mol dm^{-3}. For PVAH–DBS, the value of β as large as 0.4 are obtained at $\{PVAH^+\}=10^{-5.5}$ equiv mol dm^{-3} at $\mu=1\times10^{-3}$. It is presumed that the degree of ion association at the initial stage is larger for PVA than for GCh. Unfortunately, we only estimated the values of β in the limited range of $PVAH^+$ concentration from $10^{-5.5}$ equiv mol dm^{-3} to $10^{-4.5}$ equiv mol dm^{-3}because of inaccuracy in measuring pH. The region of cooperative binding,[11] which would be appeared at lower than $10^{-5.5}$ equiv mol dm^{-3} of $\{PVAH^+\}$, can not be observed. The difference in the ion association of DBS between PVA and GCh will also be due to the location of their reacting groups. When only one of DBS reacts with polyamines, the reactivity of the DBS is probably far lower than that of PVS. When many DBSs react with polyamines by cooperating binding, however, the reactivity will become as large as that of PVS. The near location of reacting groups on PVA will easily produce the cooperative binding of DBS in contrast with GCh. On the other hand, the aggregation of DBS is likely more flexible than PVS with firmly chained reactive groups, then the K_i and β of DBS for PVA are slightly larger than those of PVS.

The close location of amino groups of PEI also lead to the exclusion effect and the strong cooperative binding to DBS, like that of PVA. PEIH–PVS and PEIH–DBS have larger values of K_i than PVAH–PVS and PVAH–DBS. Moreover, the effect of ionic strength is small on the values of K_i and β of PEIH–PVS and PEIH–DBS in contrast with PVAH–PVS and PVAH–DBS. The high reactivity and the lower dependency on ionic strength for PEI polyelectrolyte complex may be due to its branched structure.

In the colloidal titration, good agreements between the results of acid base titration and colloidal titration were obtained for two kinds of PVA. Since the high accuracy of colloidal titration must be due to the high complexability of PVA to associate with PVS, large values of K_i were expected for PVAH–PVS. If the reactive ratio for 5×10^{-4} equiv mol dm^{-3} PVA is over 99% at the equivalent point of the colloidal titration, the value of K_i is larger than $10^{7.3}$ dm^3 (equiv mol)$^{-1}$. The calculated values of K_i for PVAH–PVS as mentioned above, however, were far smaller than the $10^{7.3}$ over the wide range of pH. The values of β were smaller than 0.6 even at low pH, because the ion association was inhibited as it proceeded. This discrepancy can be interpreted by taking into account the change of state for the precipitation of the ion association complex near the equivalence point. In the colloidal titration of PVA with PVS, coagulation of PVAH–PVS was observed near the equivalence point. The coagulation was different from the cotton precipitation before the equivalence point. It is assumed that cotton precipitation is still hydrated but coagulation is dehydrated. The release of restrained water from the ion association complex leads to increases in entropy, and total free energy change for the association is increased. Therefore, at the point of the coagulation, a steep increase of the K_i, which is large enough to explain the accuracy of colloidal titration, would be expected. We believe that the coagulation process plays important roles influencing the accuracy of the colloidal titration on PVAH–PVS as well as on GChH–PVS[5,1f)]

Conclusion

At very low concentrations of protonated polyamines, formation constants of PVA and PEI with an amphiphilic singly charged ion, DBS, were larger than those of GCh. The large values of K_i for PVA and PEI resulted from the close location of reacting groups on PVA and PEI. Such near location of reacting groups, however, lost the association selectivity for counter ions. As the ion association proceeded, it was rather inhibited, leading to lower values of K_i. The inhibition may be due to the exclusion effect between the reacting groups. Therefore, even when the ion association was occurred in the polymer–polymer which had the same separation of reacting groups, no large stability due to forming into one of the most compact structures, such as a ladder structure, was observed.

The equilibrium constants for the ion association between PVA and PVS by the present experiment was not large enough to explain the accuracy of colloidal titration. Near the equivalence point of the colloidal titration, when the coagulation occurred, a steep increase of the ion association was expected. The value of ion association constant after the coagulation was considered to become large enough to explain the high accuracy of the colloidal titration.

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