

Polyelectrolyte Complexes 1.

Ionic Bonding between Sulfated and Aminoacetalized Derivatives of Polyvinyl Alcohol

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Interaction between a pair of poly-ion-compounds, sulfated and aminoacetalized derivatives of polyvinyl alcohol was studied by nephelometry under various conditions. In the turbidity curve of the mixing solution of the poly-ion-compounds, a maximum or minimum was observed at a position nearly equal to the stoichiometric equivalent. It is found that when the mixing proportion differs from the equivalent, the composition of the ion-complex produced somewhat varies according to the rate of stirring. A mechanism of the complex formation under the stirring is proposed.

INTRODUCTION

The early studies of mechanism about the interactions between polyelectrolytes were made by Bungenberg de Jong and co-worker¹⁾ for a system of gelatin and gum alabic. They obtained a composite complex from ionic reaction between the two polyelectrolytes by mixing the aqueous solutions of the polymers, and called it "complex coacervate". It was found that the ionic reaction generally did not proceed stoichiometrically and the composition of the complex depended on the concentration of each polymer solution, pH of the solution and mixing proportion. Fuoss and Sadek²⁾ showed that the yield of the complex formation from polyvinyl methylpridium and sodium polystyrene sulfonate depended on the order of mixing of the solutions. Also, Matsumoto *et al.*³⁾ obtained a similar result for the complex formation between aminoacetal of polyvinyl alcohol and hydrolytes of vinylacetate methyl acrylic acid copolymer. Recently, however, Michaels and co-worker⁴⁻⁶⁾ have reported a different result on the interaction between sodium polystyrene sulfonate and polyvinyl benzyltrimethyl ammonium chloride. They showed that the ionic interaction between those polymers yielded a composite containing essentially stoichiometric equivalents of the component polyions and the reaction was independent of the mixing proportion and order of mixing. Thereupon, why the deviation from the stoichiometric reaction occurs in the content of the composites remains questionable, though the interactions between polyions are the same as regards the ionic bonding.

The ionic reaction may mainly depend on the following two variables; (a) the acidity and basicity of polyions, and (b) inter- and intra-molecular spatial obstruction. When either or both of polyelectrolyte is weak, the interaction should be influenced by the pH. When the aqueous solutions of two polyelectrolytes with opposite signs of charge are mixed, the ionic bonding between the polyions may be taken place through the following progress.

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First, pairing of polyions arises accompanying entanglement of macromolecules. Accordingly, next, small counter ions bound by polyion become free and these mobile ions release from domain of the macromolecules into medium by diffusion. Thus, the ionic bonding becomes perfect and then the polyion complex which is not influenced by those small counter ions is produced. However, when the mixing ratio is not equivalent and inter- and intra-molecular spatial obstruction exist if any, the pairing of the polyions supposedly becomes imperfect to result in a deviation from the stoichiometric equivalent in the reaction. These spatial obstruction may be mainly related to polymer concentration, non-ionic parts of polymer chain and undissociated groups of polyion. When polymer concentration is dense, incomplete pairings of polyions take place as a result of volume exclusion of the macromolecule itself. Consequently the ionic reaction may not be stoichiometric.

Michaels *et al.*⁵⁾ showed that the concentration of polymer solution and an add salt in the stoichiometric reaction were less than 10^{-2} N. Aforementioned disaccordance in the results obtained by Fuoss *et al.* and Michaels *et al.*, may come from a difference in the concentration. When the content of ionized groups of polymers is small, the residual non-ionic part may behave as a spatial obstructor in the reaction. Also, undissociated groups of polyion may have a similar effect. It seems that the disaccordance in the results obtained by Bungenberg de Jong *et al.* and Michaels *et al.* is caused by a difference in these obstructions. The purpose of this work is to elucidate the mechanism of the ionic reaction between polyelectrolytes. The ionic interaction between partially sulfated polyvinyl alcohol and partially aminoacetalized polyvinyl alcohol was studied by nephelometry under various conditions that differ in mixing proportion, order of mixing, pH *etc.* Chemical analysis of the composition of polyion complexes produced was made concerning stoichiometry.

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA) supplied by the Kurare Co. was fractionated by a conventional separation technique with use of isopropyl alcohol-water mixtures at 30°C. A fraction obtained was used as a starting material. The intrinsic viscosity of this fraction was 0.77 in water at 30°C.

Partial sulfate of PVA (PS) was prepared by reacting the PVA fraction with 80% sulfuric acid at 0°C for one hour. After the reaction, the reaction mixture was neutralized with sodium bicarbonate and dialyzed with a flowing water. After the dialysis, the

Table I. Characterization of PN and PS.

Sample no.	Degree of sulfation (mol. %)	Degree of acetalization (mol. %)	$[\eta]^b$ IN KCl, 30°C
FD-2 ^{a)}	—	—	0.77 ^{c)}
KS-II	15.1	—	0.78
KA-III	—	15.2	0.78

a) Fractionated PVA used as a starting material. The degree of polymerization was 1390.

b) Intrinsic viscosity $[\eta]$ was determined in IN KCl aqueous solution at 30°C.

c) Determined in water at 30°C.

product was further purified through an ion-exchange resin.

Partial aminoacetal of PVA (PN) was prepared by reacting the PVA with aminoacetal at 70°C for 25 hours. The reaction mixture was neutralized and dialyzed, and the product purified in the same manner for PS.

The characterizations of these polyelectrolytes are shown in Table I. The degree of sulfation was determined by a barium sulfate method, and the degree of acetalization was estimated by a conductometry and the Kieldahl nitrogen analysis.

Turbidity Measurements

Apparent turbidity (τ') for the present was defined as

$$\ln I_0/I = \ln(T)^{-1} = \tau l = \tau' \quad (1)$$

Here I_0 and I are incident and emergent intensities of light, respectively, T is the transmission, τ is the turbidity and l is the optical path length in the cell of an apparatus. Transmission measurements were carried out with a photometer, Type SP-20 from Simazu Seisakusho Co.

Dispersion Quotient (DQ)

DQ method^{7,8)} was adopted to estimate the particle size of colloiddally dispersed complexes produced under various conditions. Dispersion quotient (DQ) is defined as

$$DQ = \tau_1' / \tau_2' \quad (2)$$

where τ_1' and τ_2' are apparent turbidity at λ_1 and λ_2 , respectively. When the relative refractive index is given, the radius of the particle can be determined from numerical tables with DQ. The measurements were made with beams of 340, 430, and 600 m μ .

Determination of Degree of Dissociation

The degree of dissociation of the PN in a given concentration at a pH value was determined by the following procedure. An adequate amount of hydrochloric acid was added to control the pH value of test solution to be in a range of between 3 and 5. A given amount of the test solution was potentiometrically titrated with a normalized solution of sodium hydroxide. As a blank titration, an aqueous solution of hydrochloric acid was tested under the same conditions.

The excess volume of sodium hydroxide expended for the test solution than for the blank at a given pH value was determined by comparison between these two potentiometric titration curves. The volume was converted to the degree of dissociation of sample at the pH value. The potentiometric titration was carried out with a Horiba-Hitachi pH meter, model P.

RESULTS

Degree of Dissociation of PN

Figure 1 shows a potentiometric titration curve of PN and that of hydrochloric acid as a blank. Figure 2 shows the degree of dissociation determined by the said method as a function of pH. From Fig. 2, the apparent dissociation constant was estimated as 8.18.

Effect of pH on Formation of Complex

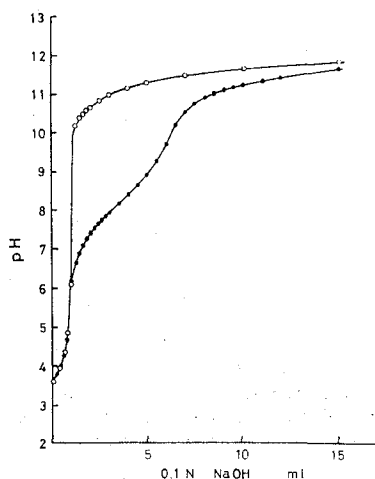


Fig. 1. Potentiometric titration curve.

● PN: 0.0966 g/100cc, ○ HCl aqueous solution, 20°C.

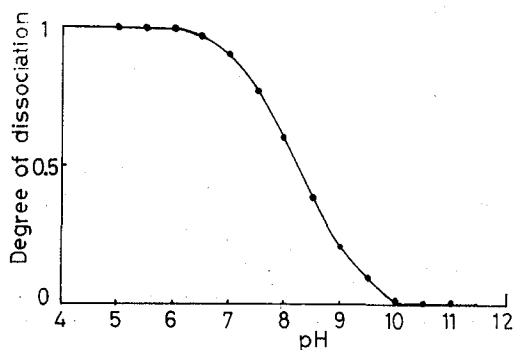


Fig. 2. Dissociation curve of PN.

Figures 3,4,5, and 6 show the turbidity of mixtures of PN and PS solutions as a function of the mixing proportion ($\text{PN} \times 100 / (\text{PN} + \text{PS})$, vol. %) at various pH values. (Hereinafter, the curve is called as turbidity curve)

The experiments were carried out as follows. The PS solution at a given pH was added titrimetrically to the PN solution at the same pH under slow stirring. The pH value of the solution was adjusted with hydrochloric acid or sodium hydroxide or veronal buffer. Both concentrations of PN and PS were less than 10^{-3} N. The turbidity was determined mainly with light beam of 430 $\text{m}\mu$ for one day after mixing.

Figures 3 and 4 show turbidity curves at pH 3 and pH 6, respectively. It is observed that both positions of maxima of two turbidity curves are nearly equal to 46.0 (vol. %). On the other hand, the equivalent ratio ($\text{PN} \times 100 / (\text{PN} + \text{PS})$, vol. %) calculated from the degree of sulfation of PS and the degree of acetalization of PN is evaluated to be 45.8 (vol. %) from the consideration that PS is a strongly acidic polyelectrolyte and PN behaves like a strongly basic one at the pH less than 6 as shown in Fig. 2. It was proved that the mixing proportion at the maxima of the turbidity curve was equal to the equivalent in such a range of pH.

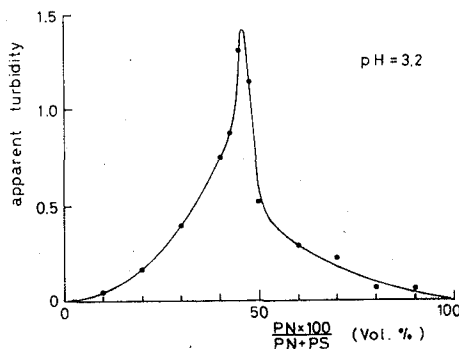


Fig. 3. Turbidity curve at pH 3.2.
PN: 0.0460 g/100cc, pH 3.18, PS: 0.0461 g/100cc, pH 3.21.
Order of mixing: PS solution was added to PN solution (PS $\rightarrow$ PN)
under slow stirring. Measured at 23°C, 1 day after the mixing.

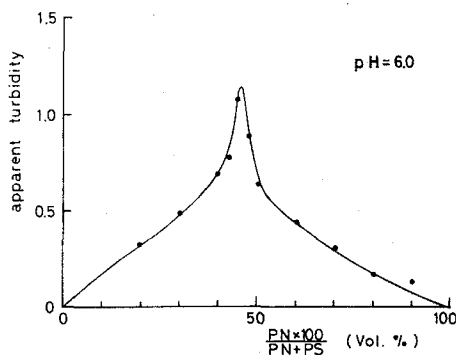


Fig. 4. Turbidity curve at pH 6.0,
PN: 0.0460 g/100cc, pH 5.84, PS: 0.0461 g/100cc, pH 6.21.
Order of mixing: PS $\rightarrow$ PN, slow stirring, 1 day after the mixing.
Measured at 23°C.

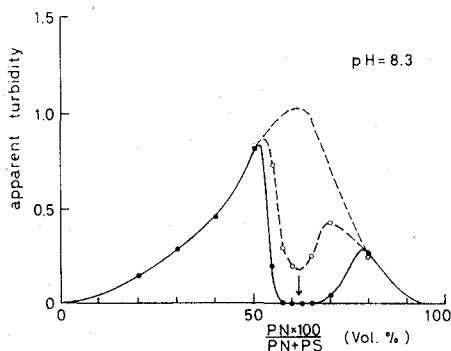


Fig. 5. Turbidity curve at pH 8.3.
PN: 0.0138 g/100cc, pH 8.26, PS: 0.0137 g/100cc, pH 8.35.
Order of mixing: PS $\rightarrow$ PN, slow stirring. —○— 3 hours after the
mixing, and —●— 1 day after mixing. Both measured at 23°C.

Also, Figures 5 and 6 show turbidity curve at pH 8 and 9, respectively. In these figures, it is seen that each curve has a minimum. This decrease in turbidity comes from the precipitation of the colloidal complex suspended in medium. Actually, it was observed

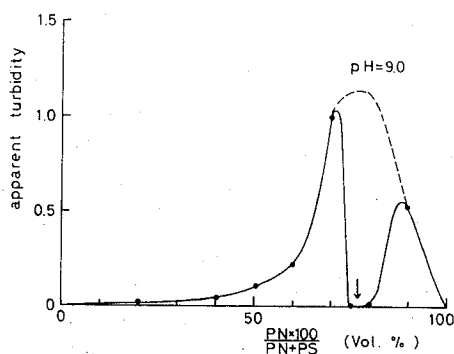


Fig. 6. Turbidity curve at pH 9.0.

PN: 0.0460 g/100cc, pH 8.98, PS: 0.0462 g/100cc, pH 8.91
 Order of mixing: PS $\rightarrow$ PN, slow stirring. Measured at 20°C,
 1 day after the mixing.

that some precipitates separated out from the mixture as a thin layer on the bottom of a vessel used. Therefore, the minima in Fig. 5 and Fig. 6 should correspond to the maxima in Fig. 3 and Fig. 4.

The mixing proportion expressed in $\text{PN} \times 100 / (\text{PN} + \text{PS})$ vol. %, was 62.0 in Fig. 5 and 77.0 in Fig. 6, respectively. On the other hand, the equivalent ratio expressed in the same scale, calculated from the degree of sulfation of PS and the degree of dissociation of PN obtained from Fig. 2 at a given pH value, was 66.0 at pH 8.3 and 78.5 at pH 9.0. Agreement between the observed and calculated values is reasonable.

Effect of Order of Mixing on Formation of Complex

Figure 7 shows a turbidity curve (solid line) where the order of mixing is opposite in contrast with one as shown in Fig. 3 (broken line).

From the comparison between two curves, it is seen that no change in the position of the maxima occurs by the order of mixing and that these shapes are nearly symmetrical with each other as to vertical axis at the position of maximum.

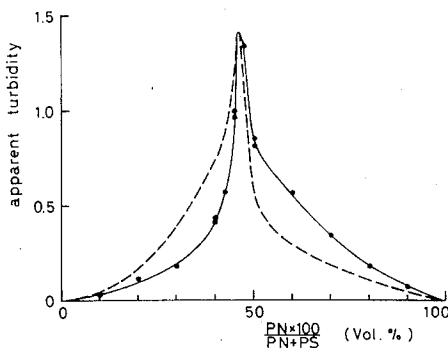


Fig. 7. Effect of order of mixing on turbidity curve.

PN: 0.0460 g/100cc, pH 3.17, PS: 0.0461 g/100cc, pH 3.21.
 Mixed under slow stirring. Measured at 21°C, 1 day after mixing,
 —●— PN $\rightarrow$ PS, ——— PS $\rightarrow$ PN.

Effect of Stirring on Formation of Complex

All turbidity curves shown hereto, have been concerned with the mixture produced under slow stirring. Figures 8 and 9 show turbidity curves which are observed for the mixture produced under vigorous stirring and no stirring, respectively. In each figure, a turbidity curve under slow stirring is shown by a broken line for comparison.

Figure 8 shows that when the mixing proportion ($\text{PN} \times 100 / (\text{PN} + \text{PS})$, vol. %) is larger than the equivalent, the turbidity is very small in comparison with that under slow stirring, and shows that when the mixing proportion is smaller than the equivalent, the turbidity is larger than that under slow stirring.

Figure 9 shows a turbidity curve under no stirring. The mixture was prepared by dropping the PS solution on the different positions of the liquid surface on the PN solution under no stirring. When PS was dropt to PN, the complex was formed as a cloud. When the mixing proportion was nearly equal to the equivalent, some precipitates frequently seperated out from the mixture after mixing. However, in other cases, no precipitate separated out. From Fig. 9, it is seen that the relation between mixing proportion and turbidity can be expressed by two straight lines in the range except the neighborhood in

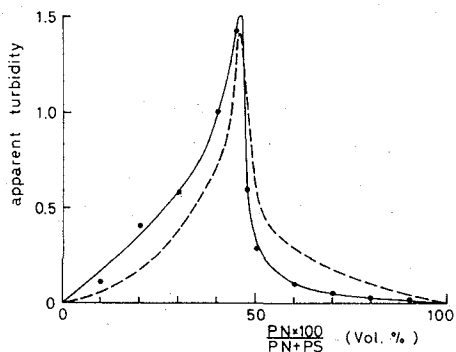


Fig. 8. Turbidity curve under vigorous stirring.

PN: 0.0460 g/100cc, pH 3.16, PS: 0.0458 g/100cc, pH 3.21.
Order of mixing: PS $\rightarrow$ PN, Measured at 19°C, 1 day after mixing,
—●— vigorous stirring, ——— slow stirring.

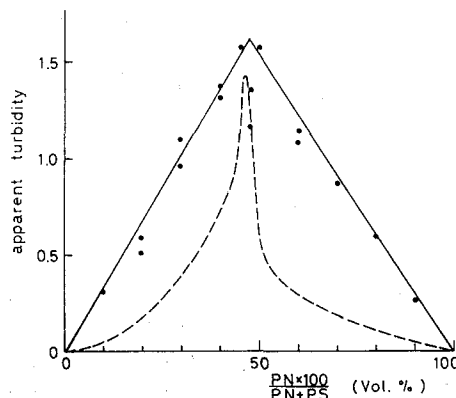


Fig. 9. Turbidity curve under no stirring.

PN: 0.0460 g/100cc, pH 3.16, PS: 0.0459 g/100cc, pH 3.21.
Order of mixing: PS $\rightarrow$ PN. Measured at 19°C, 1 day after mixing,
—●— no stirring, ——— slow stirring.

the equivalent. This suggests that the formation of complex under such a condition is stoichiometric.

Change of DQ Value by Stirring

Dispersion quotient (DQ) called by Teorell⁹⁾ is a function only of the radius of the particle and the relative refractive index, when the refractive index of surrounding medium is known and two different wavelengths of light beam used for turbidity measurements are given.⁷⁾ Consequently, if no significant change in the refractive index occurs in a given system, DQ value can be used as a parameter which indicates the particle size. Table II shows the relative refractive index estimated by turbidity measurements with light beam of three different wavelengths; 340, 430, and 600 m μ .^{7,8)} There, PS was added to PN under slow stirring and after one day the mixture was measured at 20°C.

The results in Table II show that the change of *m* is not so large in the wide range of mixing proportion. Accordingly, change of the particle size was investigated with that of DQ value. Figure 10 shows DQ value as a function of the mixing proportion for the mixture produced under slow stirring with the mixing order PS→PN.

From Fig. 10, it is observed that when a small amount of PS is added to a large amount of PN, DQ value decreases with the decreasing of mixing proportion, namely the particle size becomes larger. When an excess of PS is added to PN, DQ value increases with the decreasing of mixing proportion, namely the particle size becomes smaller.

The fact that the particle size becomes small by adding an excess of PS under stirring, suggests that the formation of the complex does not complete at the end of the adding and that the existence of excess PS as a polyelectrolyte effects on the formation. Consequently,

Table II. Relative Refractive Index(*m*) Estimated by Turbidity Measurements.

Exp. no.	Mixing prop. $\frac{PN \times 100}{PN + PS}$ (vol. %)	<i>m</i>
12-01	30	1.21
12-02	45	1.21
12-03	60	1.20

PN: 0.0426(g/100cc) at pH 3.1

PS: 0.0424(g/100cc) at pH 3.2

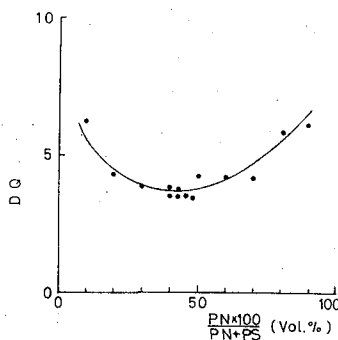


Fig. 10. Change of DQ value under slow stirring. Mixing conditions are the same in Fig. 3.

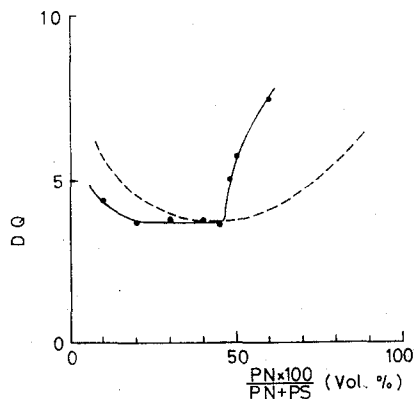


Fig. 11 Change of DQ value under vigorous stirring. Mixing conditions are the same in Fig. 8, ----- from Fig. 10.

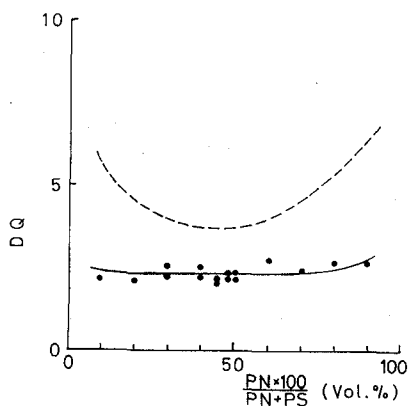


Fig. 12. Change of DQ value under no stirring. Mixing conditions are the same in Fig. 9, ----- from Fig. 10.

it also suggests that the formation may be not stoichiometric. Figure 11 shows the change of DQ value under vigorous stirring (solid line). From the figure, it is observed that when the mixing proportion is larger than the equivalent, a large amount of very small particles is produced due to the stirring, and that when the mixing proportion is smaller than the equivalent, no remarkable change of the DQ occurs in spite of existence of excess PS. This suggests that the formation is more tighter than that under slow stirring. Figure 12 shows the change of DQ value under no stirring. The figure gives an interesting result that DQ value is nearly constant, regardless of the mixing proportion. This fact suggests that formation of the complex may be ideal in such a condition. The radius of the particle produced in the vicinity of the stoichiometric equivalent was nearly 1500 Å under slow or vigorous stirring, and nearly 3200 Å under no stirring. There, they were determined by the DQ method, supposing that the m for water was 1.20.

Composition of Complexes at Variation of Mixing Condition

The composition of complexes was chemically determined as following.

First, 0.34% solution of PS at pH 5.5 was added to 0.40% solution of PN at pH 6.2

Polyelectrolyte Complexes I

Table III. Composition of Precipitates.

Mixing condition		Mixing proportion $\frac{PN \times 100}{PN + PS}$ mole%		
		33.6	50.3	66.9
Vigorous stirring		47.1	—	51.5 ^{a)}
Slow stirring	$\frac{PN \times 100}{PN + PS}$	48.3	49.5	51.8
No stirring	(mole%)	49.6	—	50.7

a) Data at mixing proportion 60.0%

b) Estimated from the composition of equilibrium liquid.

Table IV. Composition of Equilibrium Liquid.

Mixing condition		Mixing proportion $\frac{PN \times 100}{PN + PS}$ mole%		
		33.6	50.3	66.9
Vigorous stirring		16.0	—	—
Slow stirring	$\frac{PN \times 100}{PN + PS}$	23.5	—	75.6
No stirring	(mole%)	21.4	—	84.5

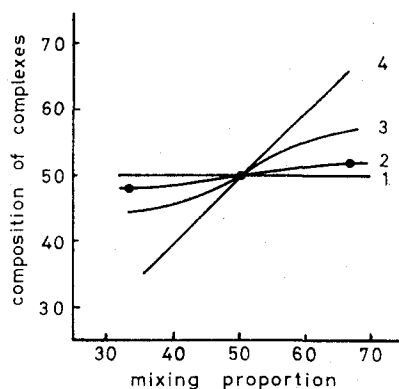


Fig. 13. Relation between composition of complexes and the mixing proportion,

1: Michaels *et al.*,^{4,5)}

2: ours (when slowly stirred),

3: Bungenberg de Jong,¹⁾

4: Matsumoto,³⁾

these data are expressed in fraction of polycation mole%.

under three different conditions, such as vigorous, slow and no stirring. Each concentration of polyelectrolytes was nearly equivalent to 10^{-2} N. Secondly, after these mixtures were kept at 30°C for 5 days, the precipitates were separated by centrifugation at 3500 rpm. for one hour. All equilibrium liquids at a mixing proportion of 50.3 mole% were very clear. But other equilibrium one at other proportions was somewhat cloudy still after centrifuging. Finally, components of the precipitate and the equilibrium liquid were determined by the Kjeldahl method and by barium sulfate method.

The results are shown in Tables III, IV, and Fig. 13. Those composition and mixing

proportion are expressed in mole %. It is found from Table III that the composition of complexes under no stirring is equal to the equivalent regardless of the mixing proportion, although the composition of those under stirrings deviates from the equivalent to some extents. The difference between these compositions will be discussed in the later section.

Figure 13 shows the relation between the composition and the mixing proportion observed in this work, together with that obtained by Bungenberg de Jong *et al.*¹⁾, Matsumoto,²⁾ and Michaels *et al.*^{4,5)} for systems of gelatin-gum alabic, aminoacetalized PVA-hydrolate of vinylacetate acrylic acid copolymer, and polystyrene sulfonate-polyvinylbenzyl-trimethyl ammonium, respectively.

DISCUSSION

Turbidity Curve

The turbidity of colloiddally dispersed complex does not directly express the concentration. However, as it was described in the previous papers,^{7,8)} the concentration (c) (g/100 cc) can be estimated by the following equation.

$$c = 3.0701 \times 10^2 \left(\frac{rd}{Kl} \right) \log(T)^{-1} \quad (3)$$

Here, T is the transmission, K is the scattering coefficient, r is the radius of the particle, d is the density and l is the optical path length in the cell.

By Eq. (3), K and r can be easily estimated by DQ method, if the relative refractive index (m) is known. Consequently, the concentration can be appraised with $c \cdot l/d$ in this case. In accordance with this account, turbidity curves shown in Figs. 3, 8, and 9 were transformed into concentration curves, assuming m was 1.20. The results are shown in Figs. 14, 15, and 16. The DQ values in Figs. 10, 11, and 12 were used to estimate K and r . The broken line in Figs. 14 and 15 expresses an ideal relation derived from the supposition that the formation of complex is stoichiometric.

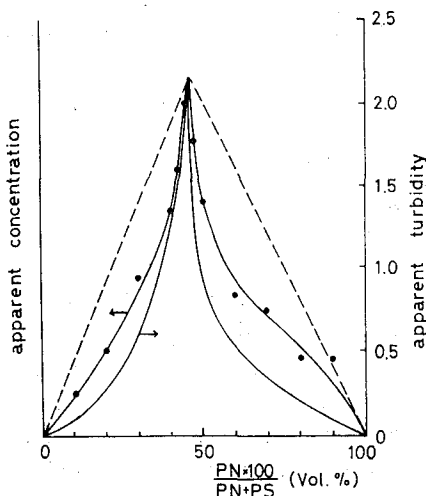


Fig. 14. Concentration of complexes vs. mixing proportion under slow stirring, —●— apparent concentration, — apparent turbidity.

Polyelectrolyte Complexes I

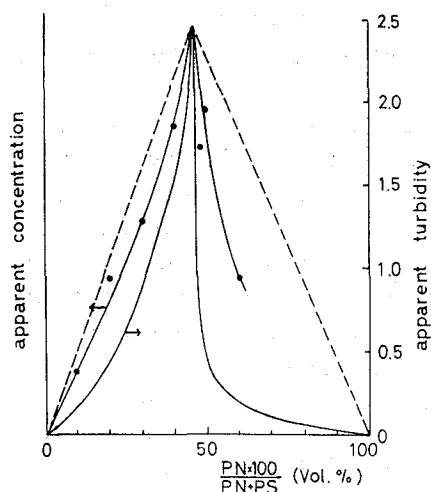


Fig. 15. Concentration of complexes *vs.* mixing proportion under vigorous stirring, —●— apparent concentration, — apparent turbidity.

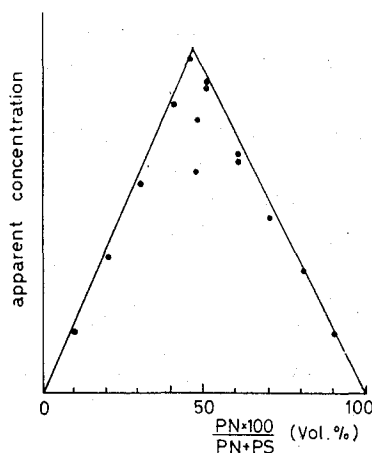


Fig. 16. Concentration of complexes *vs.* mixing proportion under no stirring.

From these figures, it seems that the shape of the concentration curves under stirring considerably differs from the ideal relation and contrary it obeys ideal relation in the case of no stirring.

The difference between Figs. 14 and 15, of course, does not directly mean that the formation of complex is not stoichiometric, because some part of particles produced under stirring may be so small that they are immeasurable with the transmission measurements.

A Mechanism of Complex Formation under Stirring

As seen in Table III and Fig. 13, when the mixing proportion differs from the equivalent, the composition of complexes is somewhat effected by stirring, though two polyelectrolytes with opposite signs of charge dissociate perfectly. On the other hand, the composition of complexes produced under no stirring is nearly equal to the equivalent, regardless of the mixing proportion. Also, effects of stirring appear in the relation between the particle size (or DQ value) and mixing proportion, as shown in Figs. 10, 11,

and 12. These results suggest a mechanism of the complex formation under stirring.

In order to cause a perfect ionic bonding in the complex formation, it is necessary that counter ions bound by polyion become free as a result of the reaction and they remove from domain of these macromolecules. Because, if the small ions didn't remove from the area, the pairing and also the ionic bonding would be imperfect due to the electrostatic screening of these ions. In a natural condition, the removal is achieved by diffusion. Therefore, in this condition, a certain time needs to remove the small ions perfectly from the area. In other words, the occurrence of the pairing (or initial contact between macromolecules) does not mean directly the complete ionic bonding (or complete ionic reaction).

In this diffusion process, if the structure of complex formed by initial contact is thermodynamically unstable due to the random contact and or spatial obstruction between polyions, some "structural rearrangement" into a more stable configuration, as discussed by Michaels *et al.*,⁴⁾ may take place by ionic bond transfer between unreacted and previously reacted polyions in the existence of small salt produced by the reaction. Now, if the removal of salt is effected by another force such as one based on stirring in addition to one based on diffusion, it becomes so fast that the structural rearrangement may insufficiently take place.

Now, first suppose that mixing proportion ($PN \times 100 / (PN + PS)$) is larger than the equivalent and that PS is poured into PN. In this case, random ionic pairing between the polyions may be brought about around the molecules of PS and, therefore, PS may form the nucleus for a particle of polyions which contain more than the stoichiometric equivalent of PN, as pointed out by Fuoss *et al.*²⁾ At this time, if the structural rearrangement insufficiently takes place due to stirring and small salts produced by the reaction rapidly diffuse out from the particle, the composition of the complex may be larger than the stoichiometric equivalent.

Contrary to this, if the mixing is carried out under no stirring and the structural rearrangement sufficiently takes place, the composition of the particle (or complex) may approach to the stoichiometric equivalent. It seems that results given in the forth column of Table III support this idea.

Secondly, suppose that the mixing proportion is smaller than the equivalent and that PS is added to PN. At first, PN is in excess and so the nucleus that contains more than the equivalent of PN is formed. Probably the nucleus have many dangling chain ends of PN. Next, when the mixing proportion becomes smaller than the equivalent by further addition of PS, random ionic pairing arises between PN dangled in the nucleus and added PS, and particles of polyions which contain more than the equivalent of PS are produced. At this time, if the mixing takes place with no stirring, the composition of the complex may approach to the stoichiometric equivalent by the rearrangement of polyions. Contrary to this, if the mixing is carried out under stirring and so the small salts produced rapidly diffuse out on the particle, the composition of the complex may become smaller than stoichiometric equivalent. It seems that results given in the second column of Table III support this conclusion.

An idea is proposed here that the removal of small salts produced as a result of ionic reaction becomes speedy by stirring, in other words, the change of ionic pairing into ionic bonding becomes quick by stirring. Also this may be supported by the result that when the mixing proportion is smaller than the equivalent, the size of particle under vigorous

stirring is larger than that under slow stirring as shown in Fig. 11 with change of DQ values.

Relation between Mixing Proportion at Maxima of Turbidity Curve and pH

Figure 17 shows the relation between mixing proportion at maxima (or minima) of turbidity curve and pH. In this figure, the solid line expresses the relation between the stoichiometric proportion calculated from Fig. 2 and the pH value and the small circles express experimental data by turbidometry. The results show that the experimental data are nearly equal to the calculated values.

However, as can be seen in the figure, these two values are somewhat different in the pH range over 8. It seems that the difference comes from the influence of undissociated groups of polyion. In Fig. 17 the broken line shows a relation between stoichiometric proportion and pH obtained at the concentration 0.0397 g/100 cc for another PN sample (degree of acetalization 13.96 mole %).

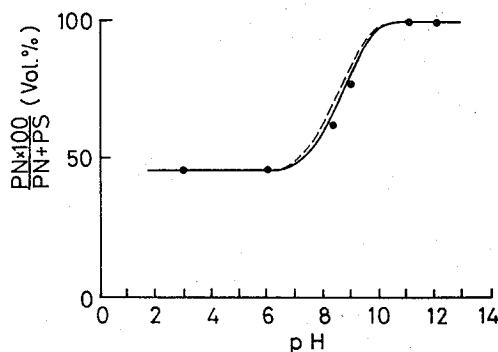


Fig. 17. Relation between mixing proportion at maxima or minima in turbidity curve and stoichiometric rate.

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