Technical Paper

Studies of Polyelectrolyte Complexes (II) Stoichiometry of the Reaction and Properties of Reaction Products between Polycations and Polyanions

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The stoichiometry of the reactions of polyanions (polyaminesulfone, polyvinylbenzyltrimethyl ammonium, ionene and protonated polyethyleneimine) and polyanions (polyacrylate, polyvinylsulfate and polystylenesulfonate) were investigated by conductometric measurements and elementary analysis. Some properties of the complexes composed of polyanions and polycations were investigated by means of X-ray diffraction and water vapor adsorption. It is shown that the complexes had some crystallinity order and water adsorptivity.

1 Introduction

It was previously found that the electrostatic interaction between polyelectrolytes with opposite signs formed a precipitate, so-called a polyelectrolyte complex (PEC)^{1)~3)}. Michaels et al. studied the composition and some of the properties of the complex composed of polystylenesulfonate and polyvinylbenzyltrimethyl ammonium. Bailey et al. also reported that the reaction of polyethylene oxide with polycarboxylic acid yielded a complex in which the ether oxygen and the carboxylic group are hydrogen-bonded⁴⁾.

This reaction is a sort of coacervation phenomena, so-called complex coacervation, and is of an interest because of the similarity in a biological systems^{5),7)}. The complex coacervation is a sort of phase separation in which two liquid phases are formed; one containing a high concentration of polyions and the other a low concentration. At the present time, the investigations and applications of PEC are in relatively early stage^{8),9)}. The PEC is mainly used for membrane, battery separators and biological materials. In the previous report in this series, the authors investigated the complexes composed of polyethyleneimine and polyacrylate or polyvinylsulfate¹⁾. In this report, further investigations have been carried out on complexes prepared from other polyelectrolytes.

2 Experimental

2.1 Reagents

Polyelectrolytes except potassium polystylenesulfonate

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Polycation

Polyanion

Fig. 1 Molecular structure of polyelectrolyte

were commercially obtained, polyaminesulfone from Nittōbō with designation of PAS-A, polyvinylbenzyltrimethyl ammonium chloride (PVBtMA·Cl) from Dow Chemicals with designation of Dow-ECR-34, ionene from Buckman Laboratories with designation of Bubond 60, polyethyleneimine (PEI) from Nakarai Kagaku Co and polyacrylic acid (PA·H) and potassium polyvinylsulfate (PVS·K) from Wakō Jyunyaku

Co. Protonated polyethyleneimine was made by dissolving polyethyleneimine of a reagent grade in distilled water, and by neutralizing with hydrochloric acid solution with bromthymol blue as indicator. Potassium polystylenesulfonate (PSS · K) was synthesized from corresponding stylenemonomer (potassium *p*-stylenesulfonate) by the use of potassium persulfate and sodium bisulfite as initiator under a nitrogen atmosphere at 45°C, according to Wiley et al.^{10).}

The solution containing the monomer and the initiator was placed in a flask, and stirred under a nitrogen atmosphere for 6 hours. The pH of the solution was adjusted to 7–8 by dropping dilute potassium hydroxide solution. These polyelectrolyte reagents were used without fractionation.

2.2 Procedure

To ascertain the stoichiometry of the reaction, the conductance of polyelectrolytes mixture solutions were measured by using the bridge method, and pH values of the solution were also determined with a pH meter (Hitachi Ltd. EHP-2 type). The procedure essentially the same as that previously described^{1).}

A quartz flask type cell with platinized electrodes was obtained. A slight variation was observed in conductance with frequency.

This variation appeared to result from suspended PEC particles, since it was reduced to a negligible extent after removal of the suspended particles. The pH of mixture solution was measured without removal of the suspended particles. The solutions used for these measurements were prepared by mixing the relative proportion of polyanion and polycation stock solutions (0.03–0.08 *N*). Stock solutions were made from a reagent of polyelectrolyte by dissolving it in distilled water. The concentration of each stock solution was determined by colloid titration or neutralization is applicable to the present system by reference to the results of Senjū and Tōei^{11), 12).}

The colloid titration is based on the reaction between positively charged colloid and negatively charged ones. Dilute aqueous polycation solution was titrated with 1/400 *N* potassium polyvinylsulfate solution using toluidine blue as indicator. In titration of polyanion solution, 1/200 *N* glycolchitosan solution was added in excess to the polycation solution and the excess amount of glycolchitosan was titrated with 1/400 *N* potassium polyvinylsulfate solution by using toluidine blue as indicator. However, in the cases of PEI and PA · H, aqueous PEI solution was titrated with a standard HCl solution against phenolphthalein end point, and aqueous PA · H solution with a standard NaOH solution against bromthymol blue end point. Colloid titration reagents were all commercially obtained from Wakō Jyunyaku Co.

Aqueous polycation solution (1 wt%) was added dropwise to aqueous polyanion solution (1 wt%) in approximately equal proportions, resulting in the formation of precipitate, so-called PEC. After being allowed to stand, the precipitate was filtered, washed with water to remove microions and unreacted polyions, and then dried in vacuo. The physical properties of resultant PEC have been investigated by water vapor sorption and X-ray diffractometer.

Water Vapor isotherms were determined according to the method previously described^{13).} The weight of PEC as a function of R.H. was followed by measuring the extension of spring balance with a cathetometer to 0.05 mm (sensitivity of balance: 0.1043 g/cm).

The structure of PEC was examined by X-ray diffraction (Rigaku Denki Diffractometer) using Cu-K α radiation (30 kV, 13 mA).

3 Results and Discussion

In the previous report¹⁾, as a rough estimation of the polyion extension, a flow curve of polyion solution was determined in a Couette type rotation viscometer. When two oppositely charged polyelectrolytes were mixed in this concentration range of extension, a precipitate was formed. The precipitate reaction appears to be nearly athermal. The movement of microion in polyelectrolyte solution is restricted to some extent because of ionic interaction of microion with the fixed

Fig. 2 Conductometric titration of aqueous polyanion solution with aqueous polycation solution at 25°C

charge of polyion.

After once precipitates are formed, the microion is no longer restricted, and entropy of microion is thereby increased as a result of the reaction. The conductance of precipitate solution is shown in Fig. 2. In the figure, the abscissa denotes the ratio of the equivalent of polyanion to the total equivalents of polyions in the precipitate solution. There is a marked increase in conductance since the equivalent conductance of the released microion is higher than that of the polyion. As shown in the figure, a sharp maximum in conductance is found at ratio of 0.5 as in the cases of $\text{PEI} \cdot \text{HCl} \cdot \text{PA} \cdot \text{Na}$ and $\text{PEI} \cdot \text{HCl} \cdot \text{PVS} \cdot \text{K}$ previously reported¹⁾. This indicates that a 1:1 pairing of ionic site reaction occurs. The results on elementary analysis of these complexes supported this consideration.

Therefore, the reactions for $\text{PSS} \cdot \text{K}$ -Ionene, $\text{PSS} \cdot \text{K}$ -PVB-TMA $\cdot$ Cl and $\text{PSS} \cdot \text{K}$ -PAS are nearly stoichiometric. On the other hand, in the reactions for $\text{PAS} \cdot \text{PA} \cdot \text{H}$ and $\text{Ionene} \cdot \text{PA} \cdot \text{H}$, there is a decrease in pH mainly due to the release of proton from $\text{PA} \cdot \text{H}$. The pH of precipitate solution vs. the equivalent concentration ratio is shown in Fig. 3.

Fig. 3 pH titration of aqueous polyanion solution with aqueous polycation solution

The pH decreases sharply in the ratio of 0.5 and then remains essentially constant as shown in the figure. This indicates that the reaction is stoichiometric. The results on elementary analysis of these complexes supported this conclusion.

However, in concentrated solution non-stoichiometric complexes were obtained for reactions $\text{PAS} \cdot \text{PA} \cdot \text{H}$ and $\text{Ionene} \cdot \text{PA} \cdot \text{H}$.

The stoichiometric pairing of ionic sites depends on the ability of long portions of the oppositely-charged polyion chains to come into juxtaposition, on the rearrangement of rotational conformations to bring the reacting sites close enough to form stable links.

Therefore, the deviation from the stoichiometry of reaction can be related to the tightly coiled conformation of polyion, and to the stereoregularity of polyion.

X-ray diffraction patterns of PEC are shown in Fig. 4. They are all similar and indicate a common inter-

Fig. 4 X-ray diffraction pattern

molecular order, though the PEC structure has not yet been clarified. Sharp peaks at 31–32 Å for PVB-TMA $\cdot$ Cl, at 10 Å for Ionene-PAS, and at 10 Å for PAS-PSS are not clear. A polyelectrolyte alone has not shown any diffraction pattern, compared with PEC. Therefore, the PEC appears to exhibit physical properties between those of ionic crystallinity and amorphous organic polymers.

Before sorption measurements, the PEC was dried in vacuum for two hours. However, it is likely that some residual water remain in the PEC since infrared spectra indicated weak characteristic water band. Water sorption isotherm as a function of R. H. is shown in Fig. 5. In all cases, the isotherms are convex upward and seem to follow similar trends. This trend is often observed in hygroscopic materials. There is a hysteresis

Fig. 5 Water vapor sorption isotherm at 25°C
1: Ionene-PSS, 2: PVBtMA-PSS, 3: PAS-PA

in the isotherm curve. This suggests some orientation of polyion during the process of sorption or desorption. The equilibrium water sorption at 100% R. H. corresponds to several water molecules per ion site (3 molecules for Ionene-PSS, 4 for PVBtMA-PSS and 4.5 for PAS-PA). It indicates that virtually all the water molecules is probably hydration water of polyion, since the water molecules sorbed corresponds to the amount of water required to form a primary solvation shell.

Below 200°C, PEC was melted and this melt solution was molded as a membrane. The membrane prepared in this manner exhibits a tendency to become hard and brittle, and rubber-like when it is wetted with water. Water may stabilize the PEC as a soft agent. In order to simplify the writing, the polyelectrolytes are expressed by $P^+ \cdot A^-$ and $M^+ \cdot Q^-$ in which P^+ and Q^- are

polyions, and M^+ and A^- are microions, respectively. Then, reaction may be written schematically as

In highly open extended conformation of polyion and appropriate stereoregularity, the reaction may produce PEC of a stoichiometric composition and of a scramble structure (as is proposed by Michaels³⁾). However, in tightly coiled conformation it produces a non-stoichiometric PEC. The non-stoichiometric PEC may be microscopically dispersed into regions of pairing of ionic sites and of unreacted ionic sites. This may behave in simple electrolyte solution as a kind of conventional ion exchange resins. That is, this exchanges counterion readily with ions in the solution.

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