

# Formation of Polyelectrolyte Complex and Its Adsorption Properties

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## Synopsis

Polyelectrolyte complex formations between two oppositely charged polyions [ionene, poly(vinylbenzyl trimethylammonium chloride), poly(diallyl dimethylammonium chloride), poly(aminosulfone), potassium poly(vinyl sulfate), sodium poly(styrene sulfonate), poly(acrylic acid)] have been investigated by conductance and turbidity measurements. It was found that the complex formation of these polyelectrolytes formed in stoichiometry. Adsorption isotherms of water, methanol, acetone, and benzene were determined for the resulting complexes at 25°C with a gravimetric adsorption apparatus. The differences in adsorption can be exclusively ascribed to differences in ion site and hydrophobic circumstances around the ion site, since each complex has a low specific surface area (<1 m<sup>2</sup>/g). Amount of adsorption increased in the order of water > methanol > acetone > benzene. This order corresponds to that of the polarity of adsorbate.

## INTRODUCTION

It is well known that insoluble precipitates are formed in an aqueous medium by the electrostatic interaction between two oppositely charged polyelectrolytes. The precipitates are referred to as a polyelectrolyte complex.<sup>1,2</sup> Attention has been devoted to such intermolecular interactions, not only from biochemical interests, but also from physico-chemical aspects.<sup>3,4</sup> Michaels et al.<sup>5</sup> studied the composition and some of the properties of a complex composed of poly(styrene sulfonate) and poly(vinylbenzyl trimethylammonium) and suggested its potential as a new material. However, the majority of the results reported so far related only to the above complex. Very little work has been done on the other complexes. Therefore, in the present article, the complex formation between the other oppositely charged polyelectrolytes and the adsorption properties of complex have been investigated by conductance, turbidity, and vapor adsorption isotherm measurements.

## EXPERIMENTAL

### Materials

Polycation-poly(vinylbenzyl trimethylammonium chloride) (PVBTMA-Cl) with designation of Dow ECR-34 (intrinsic viscosity: 0.3 dl/g in 3N KCl at 30°C, quarternized nitrogen: 80%), poly(diallyl dimethylammonium chloride) (PDADMA-Cl) (Calgon Corporation,  $M_w$ : 50,000–200,000), and ionene with designation of Bubond 60 (Buckman Laboratories, Inc.) were supplied from

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Marusyō Industrial Co., Ltd. Poly(dimethyl diallylammonium chloride-SO<sub>2</sub> copolymer) with designation of PAS-A (polyaminesulfone A,  $\bar{M}_w$ : 270,000–330,000) was supplied from Nittobō Co. Polyanion-polyacrylic acid (PA-H,  $\bar{M}_w$ : 50,000) and sodium poly(styrene sulfonate) (PSS-Na,  $\bar{M}_w$ : 80,000) were commercially obtained from Polyscience Co. Potassium poly(vinyl sulfate) (PVS-K, degree of esterification 98.8%, intrinsic viscosity: 0.40 dl/g in 1N NaCl at 25°C) was commercially obtained from Wakō Pure Chemicals Co. Molecular structure of these polyelectrolytes are represented in Figure 1. The polyelectrolyte was reprecipitated twice from aqueous solution with methanol. Then it was dialyzed for pure water and freeze dried.

### Measurements

The conductance was determined by using the alternation current bridge method. A quartz flask-type cell with lightly platinized electrodes was used. The cell constant was 0.2000 cm<sup>-1</sup>. A slight variation in conductance with frequency was observed. This variation appeared to result from suspended complex, since this was reduced so much as to be negligible after the removal of the suspended complex particles. Measurements were made at 1 kHz and in a thermostat at 25 ± 0.01°C. On the other hand, pH measurements of mixed polyelectrolyte solution were carried out by using Hitachi-Horiba F-7 type pH meter. Turbidity of mixed polyelectrolyte solution was obtained as transmittance. That is, the transmittance of mixed solution at various unit mole ratios was measured 2 hr after mixing by the spectrophotometric method, using a wavelength of 660 nm. The solution used for these measurements was prepared by varying the relative proportion of polyanion and polycation stock solutions. Stock solutions (0.01–0.03 unit mole/liter) were made from the polyelectrolyte by dissolving them in distilled water (in this article, polymer concentrations are represented in unit mole).

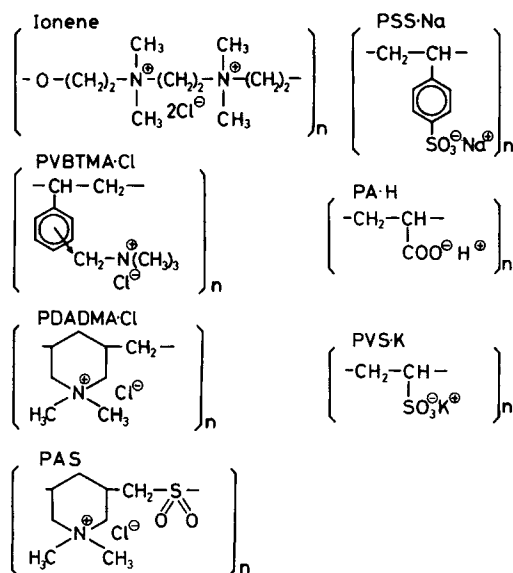


Fig. 1. Molecular structure of the polyelectrolyte.

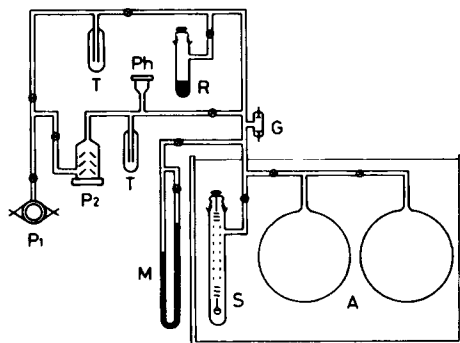


Fig. 2. Adsorption apparatus. (A) Vapor reservoir; ( $P_1, P_2$ ) rotary and diffusion pumps; (G) Geisler tube; (M) manometer; (Ph) Philips vacuum gauge; (S) sample tube; (T) trap.

Aqueous polycation solution (1 wt %) was added dropwise to aqueous polyanion solution (1 wt %) under rapid stirring in approximately equal proportions, resulting in the formation of a precipitate, a so-called polyelectrolyte complex. After being allowed to stand, the precipitate was separated from the solution by means of a centrifuge or filtration. It was washed with water to remove microions and unreacted polyions, and then dried *in vacuo*. The complex was obtained in the form of fine powder. The apparatus of adsorption measurements is shown in Figure 2. A quartz basket in which 0.1–0.3 g of complex powder was placed was suspended on a sensitive spring balance (4.76 mg/mm) in a chamber S, to which the large vapor reservoirs A were attached to eliminate a measurable change in the pressure of adsorption of vapor. The tube R is a water reservoir for giving the vapor of known pressure admitted into chambers A and S. The entire apparatus was immersed in a large thermostat at  $25 \pm 0.1^\circ\text{C}$ . To remove residual water or other sorbed materials, the complex sample was pretreated prior to adsorption measurement by evacuation to  $10^{-5}$  torr and heated at  $80^\circ\text{C}$ . The take-up of the vapor was followed by measuring the extension of the spring balance with a cathetometer to 0.05 mm. Equilibrium adsorption was generally reached within 5–6 hr. No attempt was made to obtain quantitative adsorption rate data, since the extension of the spring balance owing to adsorption was not significant.

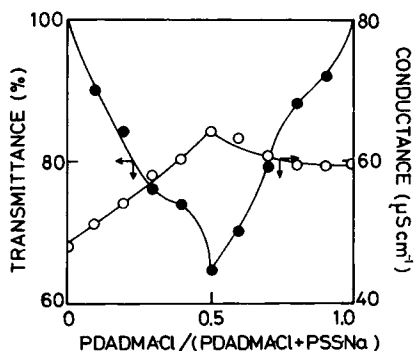


Fig. 3. Conductance and turbidity against unit mole fraction of polycation for PSS-Na-PDADMA-Cl system.

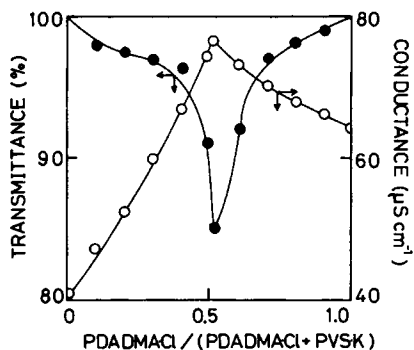


Fig. 4. Conductance and turbidity against unit mole fraction of polycation for PVS-K-PDADMA-Cl system.

## RESULTS AND DISCUSSION

Complex formation between oppositely charged polyelectrolytes was followed by measuring turbidity and conductance. A strong repulsion can be expected in a lower concentration range because the charges on polyion repulse each other to stretch it out. When two oppositely charged polyions are mixed in the open extended conformation of polyions, the polyelectrolytes may sufficiently interact through Coulombic forces. The precipitation reaction must be entropic since the process appears to be nearly athermal.<sup>5</sup> The movement of microion in polyelectrolyte solution is restricted to some extent because of the ionic site binding to the polyions. After a precipitate is formed, the microion is no longer restricted, and its entropy is thereby increased as a result of the reaction. The conductances and turbidities of reaction mixtures are shown in Figure 3 for PSS-Na-PDADMA-Cl, Figure 4 for PVS-K-PDADMA-Cl, Figure 5 for PSS-Na-PVBTMA-Cl, and Figure 6 for PSS-Na-ionene. The pH and turbidity of the mixture for PA-PAS are shown in Figure 7. In each figure, the abscissa denotes the ratio of the unit mole of polycation to the total unit moles 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. On the other hand, in Figure 7 there is a decrease of pH, since the release of protons occurs by accompanying complex formation. As shown in the figure, a sharp maximum in conductance (or an inflection point in pH) is found

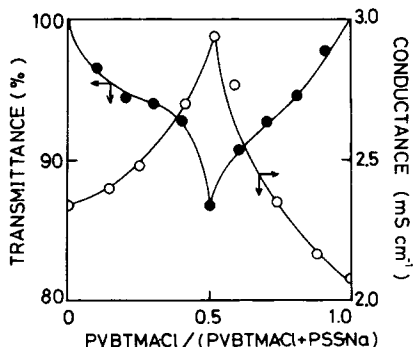


Fig. 5. Conductance and turbidity against unit mole fraction of polycation for PSS-Na-PVBTMA-Cl system.

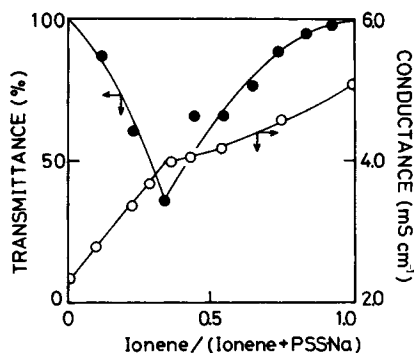


Fig. 6. Conductance and turbidity against unit mole fraction of polycation for PSS-Na-ionene system.

at the ratio of 0.5 for each system except the PSS-Na-ionene system. Transmittance of the mixed solution as a measure of turbidity decreases with increasing polycation up to 0.5, and then it increases. A maximum in conductance (or inflection point in pH) corresponds accurately to the maximum in turbidity. For PSS-Na-ionene system, the maximum shifts to the left and is observed at a ratio of 0.33. However, taking into consideration that ionene contains two cation sites per unit mole, one cation site corresponds accurately to one anion site. These indicate that a one-to-one pairing of ionic site reaction occurs, namely, the reaction is stoichiometric. It seems reasonable to postulate that the quantitative pairing of ionic sites depends on the ability of long portions of oppositely charged polyion chains to come into juxtaposition, on the rearrangement of rotational conformation to bring the reacting ion site close enough to form stable links. Behavior such as the one-to-one pairing observed above may be attributed to the chain flexibility and approximately equal distance between neighboring ion sites of the present component polyions. Presumably, electrostatic interactions between the polyions are diffuse and take place randomly between ionic sites of opposite sign. Michaels proposed a scrambled salt structure for these polyion complexes.<sup>5</sup> However, experimental details were not given. The resulting complexes are insoluble in water and organic solvents. After the precipitate (complex) was separated by filtration and dried *in vacuo*, elemental analysis was made. Observed values were in good agreement with theoretical values calculated by assuming that the complex is composed of the equimolar component polyions.

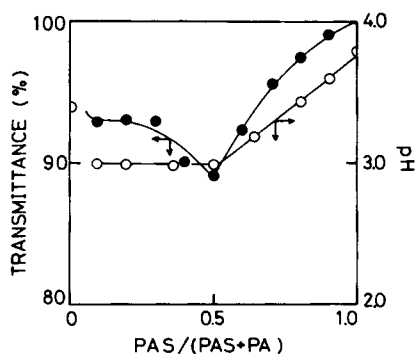


Fig. 7. pH and turbidity against unit mole fraction of polycation for PAS-PA system.

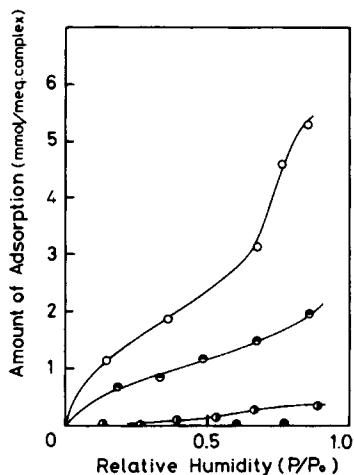


Fig. 8. Adsorption isotherms of (○) water and [(◐) methanol, (◑) acetone, (●) benzene] organic vapors on PSS-PDADMA complex.

Michaels et al.<sup>5</sup> investigated dielectric and permeability properties of a complex prepared from PVB-TMA and PSS, and suggested its availability as an ultrafiltration membrane and medical materials. However, little has been reported about the adsorption properties of such complexes. Consequently, adsorption isotherms of water and a few organic vapors were determined for the complex at 25°C. Vapor adsorption isotherms as a function of  $P/P_0$  are shown in Figure 8 for PSS-PDADMA, Figure 9, for PSS-PVB-TMA, Figure 10 for PSS-ionene, and Figure 11 for PA-PAS. In all cases, the isotherms seem to follow roughly similar trends. That is, each complex shows significant adsorptivity for water and slight adsorptivity for benzene. The adsorptivity increases in the order of water > methyl alcohol > acetone > benzene. This order is in accord with the

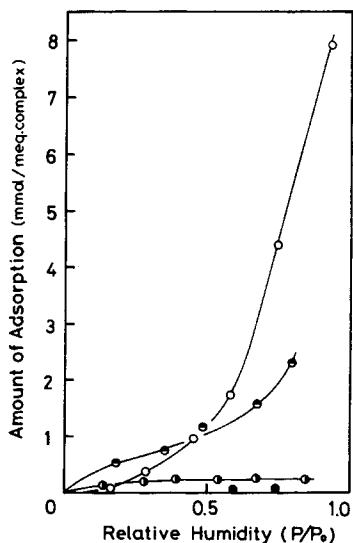


Fig. 9. Adsorption isotherms of water and organic vapors on the PSS-PVB-TMA complex. Symbols are the same as those used in Fig. 8.

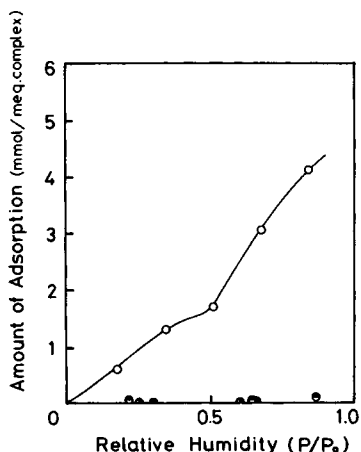


Fig. 10. Adsorption isotherms of water and organic vapors on the PSS-ionene complex. Symbols are the same as those used in Fig. 8.

order of polarity of adsorbate. Specific surface areas determined by the Yuasa-Quntachrome surface area analyzer were as follows: PSS-PDADMA:  $3.6 \text{ m}^2/\text{g}$ , PSS-PVBTMA:  $0.86 \text{ m}^2/\text{g}$ , PSS-ionene:  $0.31 \text{ m}^2/\text{g}$ , PA-PAS:  $0.45 \text{ m}^2/\text{g}$ . The complexes thus are the microreticular type, generally characterized by low surface area (less than  $1 \text{ m}^2/\text{g}$ ). Therefore, the amount adsorbed may not depend primarily on the porosity of the complex structure but on the chemical structure of the complex. It is likely that the difference in isotherms reflects the difference in the chemical structure of the ion site (anion + cation). The PSS-PDADMA system (Fig. 8) composed of component polyelectrolytes having aromatic and cyclic rings shows behavior similar to the PSS-PVBTMA system (Fig. 9) composed of component polyelectrolytes having aromatic rings. It seems that these complexes adsorb both water and organic vapors because of ion site and hydrophobic groups. Adsorption isotherm of water vapor on PSS-PVBTMA is convex towards the  $P/P_0$  axis. This behavior is often observed in hydrophobic materials. The upward curvature of the isotherms at high rel-

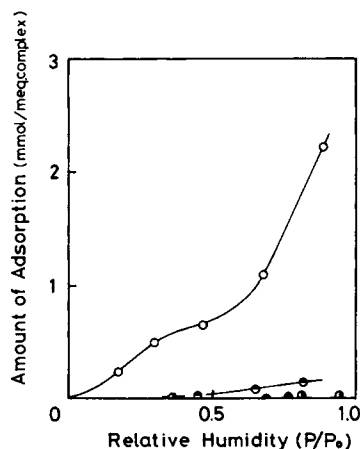


Fig. 11. Adsorption isotherms of water and organic vapors on PAS-PA complex. Symbols are the same as those used in Fig. 8.

ative humidity is, however, suggestive of capillary condensation. The existence of microvoids which bulky hydrophobic group around ion site forms, which fill with water at high relative humidity is quite likely. Since PAS has a  $\text{SO}_2$  group, it is heat stable and hydrophobic compared with other polyelectrolytes. PA is a chain polymer and has few groups that take part in hydrophobic interaction. Hence, as can be seen from Figure 11, the PA-PAS complex adsorbs water but does not absorb organic vapors as much. For the reasons mentioned above, isotherms of the PSS-ionene system may also be similar to those of the PA-PAS system.

The amounts of equilibrium water adsorption at 50% relative humidity correspond to 2.4 water molecules per ion site for PSS-PDADMA, 1.3 for PSS-PVBTMA, 3.4 for PSS-ionene, and 0.7 for PA-PAS. These are undoubtedly far less than the amount of water required to complete the primary ion hydration shell. On the other hand, the equilibrium water sorptions at 100% relative humidity correspond to 7.4 water molecules per ion site for PSS-PDADMA, 9.6 for PSS-PVBTMA, 12.3 for PSS-ionene, and 3.2 for PA-PAS. It thus appears that much of the water adsorbed by the complex probably forms hydration with the ion site. The isotherms of water vapors (except PSS-PVBTMA) show sigmoid type, viz., B.E.T type. Therefore, according to the B.E.T method, specific surface areas were calculated as  $10.5 \text{ \AA}$  of cross section of water. Values calculated were as follows: PSS-PDADMA,  $397 \text{ m}^2/\text{g}$ ; PSS-ionene,  $433 \text{ m}^2/\text{g}$ ; PA-PAS,  $108 \text{ m}^2/\text{g}$ . However, these values are different from those obtained by the Quntachrome surface area analyzer described above. This difference may indicate that water is locally adsorbed on the ion site.

Generally, conventional anion exchange resin adsorbs basic materials, whereas cation exchange resin adsorbs acidic ones.<sup>5,6</sup> It is thus interesting to investigate the extent to which the complex adsorbs acidic or basic materials. As can be seen from Figure 12, the complex, however, adsorbed neither pyridine nor *n*-propylmercaptan. There are some uncertainties in the data which resulted from reading the cathetometer, since the amount of adsorption is slight. The amount of adsorption is nearly equal to the amount of benzene adsorption. It may indicate that an interaction between *n*-propylmercaptan (or pyridine) and the ion site is less appreciable than that between water and ion site, and the accessibility

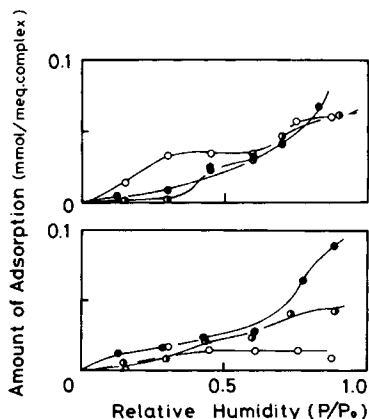


Fig. 12. Adsorption isotherms of (a) pyridine and (b) *n*-propyl mercaptan on complex. (○) PSS-ionene, (●) PSS-PDADMA, (◐) PSS-PVBTMA.



of mercaptan (or pyridine) is low because of existence of the bulky hydrophobic group around the ion site.

Though the mechanism of the adsorption has not been fully elucidated by the present data alone, it seems reasonable to conclude that the differences between isotherms may be attributed to both the chemical structure of the ion site and the circumstance around the ion site, the so-called accessibility of adsorbate to adsorption site.

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