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Complex Coacervation and Chain Conformations in the System of Partially Sulfated Polyvinyl Alcohol and Partially Aminoacetalyzed Polyvinyl Alcohol

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Complex coacervation in the system of partially sulfated polyvinyl alcohol (PVA–S) and partially aminoacetalyzed polyvinyl alcohol (PVA–AA) was studied in aqueous solutions containing microsalt. By measuring turbidity, conductivity and pH, it was shown that 1: 1 complex was formed at various mixing ratios of polymers. Concentrations of polymer in the coacervate (C_c) and the equilibrium liquid (C_e) were examined as functions of the initial polymer concentration (C_i). The complex showed smaller value of limiting viscosity number than that of single polyelectrolyte in 0.1 M salt solution. Coacervation of the 1: 1 complex was suppressed by the addition of microsalt on account of the change in chain conformations.

INTRODUCTION

When a polyelectrolyte solution is mixed with a solution of the oppositely charged polyelectrolyte on an appropriate condition, the mixed solution separates into two liquid phases. This phase separation of liquid-liquid type was named complex coacervation and has been studied by many workers.[1~6] Recently not only biopolymers but also synthetic polymers[7~9] have been used for the investigation of coacervation and complex-formation. In previous papers,[7,9] we have mentioned some results on coacervation in the system of partially sulfated polyvinyl alcohol (PVA–S) and partially aminoacetalyzed polyvinyl alcohol (PVA–AA) prepared from polyvinyl alcohol (PVA). In this paper, we further study the conformations of polyelectrolytes in coacervation by using these polyelectrolytes.

There are many different terms on the same things and phenomena because coacervation has been studied in such various fields as biology, biochemistry, evolution, colloid chemistry and polymer chemistry. We summarize definitions used in these fields as follows: coacervation=phase separation of the liquid-liquid type; complex coacervation=coacervation of a polyelectrolyte complex, on which electrostatic forces act essentially; coacervate=mixture of coacervate drops and the equilibrium liquid= turbid solution produced by coacervation; coacervate drops=coacervate droplets, which form a concentrated phase; equilibrium liquid=dilute phase produced by coacervation.

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EXPERIMENTAL

PVA–S was prepared by sulfation of parent PVA in a 70% H_2SO_4 aqueous solution at 0°C for 1 hour. Parent PVA was roughly fractionated in *n*-propanol-water system. The reaction mixture was neutralized with Na_2CO_3, dialyzed in water, and deionized through a mixed-bed ion-exchange resin.

PVA–AA was prepared by aminoacetalyzation of parent PVA. 2.5 g of PVA, 2.5 ml of aminoacetal, 5 ml of HCl and 90 ml of H_2O were reacted at 70°C for 2.5 hours. The reaction mixture was precipitated once, dialyzed in water, and deionized through a mixed-bed ion-exchange resin.

Symmetrical coacervation of PVA–S and PVA–AA was examined in the following way. Each 5 ml of same concentration of PVA–S and PVA–AA was mixed at 30°C. The coacervate was kept at 30°C for 10 minutes and centrifuged at 800 × g for 10 minutes. By centrifugation coacervate drops were precipitated at the bottom of the vessel. The volume of each phase was recorded. Equilibrium liquid was separated from coacervate drops by decantation. Weights of coacervate drops and equilibrium liquid were measured after drying overnight under vaccum in the presence of P_2O_5.

Phenomenon of suppression of coacervation was followed by turbidity measurement. After PVA–S and PVA–AA solution were mixed, turbidity of the mixed solution was measured at 30°C by adding salt solution with stirring. Added volume of salt solution was restricted not so small as to affect the total volume of coacervate.

RESULTS AND DISCUSSION

Characterization of PVA–S and PVA–AA

PVA–S and PVA–AA were used as a polyanion (Q^-) and a polycation (P^+), respectively. Characters of these polyelectrolytes were summarized in Table I. It was assumed that no degradation of polymer chains took place during replacement reactions of parent PVA. Molecular weights of which were estimated from the limiting viscosity number $[\eta]$ by using the equation[10]; $[\eta] = 6.66 \times 10^{-4} \times M^{0.64}$ Degrees of sulfation and aminoacetalyzation were determined by conductometric titration method (Figure 1).

Asymmetrical Mixing of PVA–S and PVA–AA

Mixing of PVA–S and PVA–AA led to complex coacervation. Hydrogen exponent pH (a), turbidity τ (b), and conductivity (c) of the coacervate in the system containing $0.1M$ NaCl and 2 mg/ml polyelectrolytes were measured as functions of the mixing ratio (Figure 2).

Maximum turbidity of the coacervate was observed when the same amounts of P^+ and Q^- were mixed. Even in the case of 1: 4 or 4: 1 mixing ratio, the coacervate showed large turbidity. Because the turbidity is mainly attributed to coacervate drops, coacervate drops are formed when P^+ and Q^- are mixed in such asymmetrical ratios.

Increase in conductivity was observed up to a mixing ratio of *ca.* 0.5. As coa-
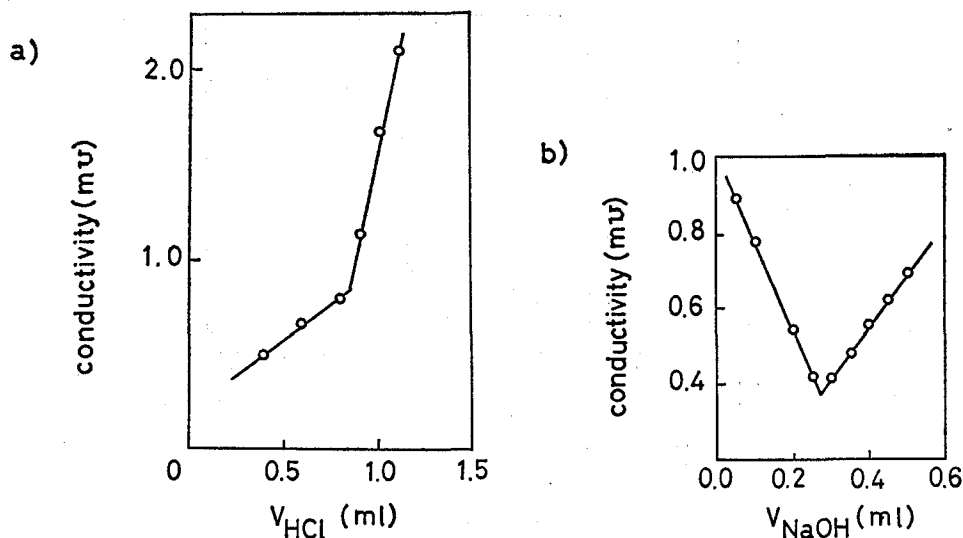
a)

b)

Fig. 1. Conductometric titrations of (a) PVA–AA and (b) PVA–S. Conductivity of solution is plotted against an added volume of a) acid (V_{HCl}) and b) alkali (V_{NaOH}).

Table I.　Characterization of Samples

	PVA–S	Parent PVA	PVA–AA	Parent PVA
M	15200	12700	15900	14300
ρ	10.6	—	11.7	—
$[\eta]$	0.335	0.282	0.360	0.304
α	1.15	1.12	1.17	1.12

M: Molecular weight,　ρ: Degree of substitution, mol %,　$[\eta]$: dl/g, $[\eta]$ and α were measured in 0.1 M NaCl aqueous solution.

cervate drops are formed, counterions of P^+ and Q^- (Cl^- and Na^+, respectively) are released from the polyelectrolytes into the equilibrium liquid, resulting in an increase in conductivity ($P^+Cl^- + Q^-Na^+ = P^+Q^- + Na^+ + Cl^-$). Linear relation between conductivity and the mixing ratio is explained in terms of complete reaction of minor component.

In the case of asymmetrical mixing, the coacervate contains coacervate drops which were formed with equal amounts of P^+ and Q^-, and excess amount of polyelectrolyte of the major component. The latter determines mostly the value of pH of the coacervate. The point of neutralization of P^+ with Q^- locates at the mixing ratio of 0.5. Judging from the results mentioned above, coacervate drops are constructed with equal amounts of P^+ and Q^- (1: 1 complex).

In our previous paper,[9] the viscosity number at very low polymer concentrations did not show such a high value as observed for polyelectrolytes in aqueous solution. Thus, charges on the polyelectrolytes in the coacervate are neutralized by interaction between polycation and polyanion.
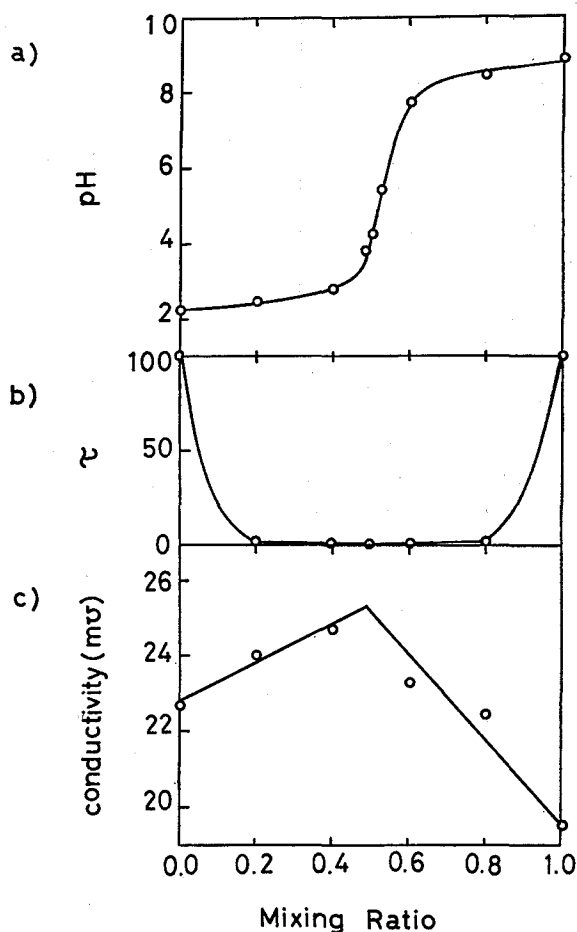
(65)

Fig. 2. Plots of pH (a), turbidity (b) and conductivity (c) of mixed solutions against the mixing ratio. Total concentration of polyelectrolytes is 2 mg/ml in 0.1 M NaCl aqueous solution. Turbidity is given by % transmittance at 450 nm.

Symmetrical Mixing of PVA–S and PVA–AA

Concentration of Coacervate and Equilibrium Liquid — Equal amounts of P+ and Q⁻were mixed (symmetrical mixing). The concentration (C_c) of coacervate drops and that (C_e) of equilibrium liquid were plotted against the initial concentration (C_i) before the mixing, in Figure 3. Both C_c and C_e are not constant but varied with C_i. Dependence of C_c and C_e on C_i were also reported elsewhere.[4,6,9]

Polymer Chain Dimensions in Equilibrium Liquid — In order to study the states of polyelectrolyte in the mixed solution and equilibrium liquid, we measured the viscosities of these solutions, and calculated the chain dimensions from the following equation.[11]

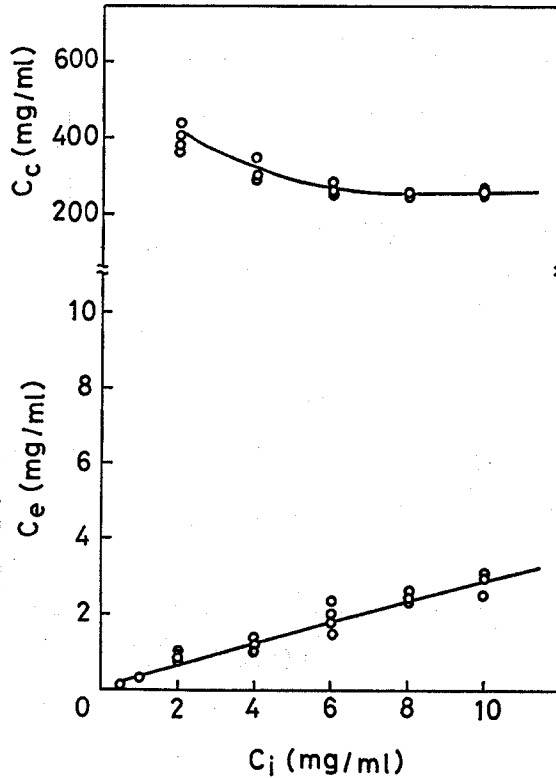$$[\eta] = K M^{1/2} \alpha^3 \tag{1}$$

with

Fig. 3. Plots of concentration of coacervate (C_e) and that of equilibrium liquid (C_e) against initial concentration (C_i) of polymer.

$$K = \Phi(<R_0^2>/M)^{3/2}$$

where, M is the molecular weight of a polymer, α is the expansion factor defined by $\alpha = [<R^2>/<R_0^2>]^{1/2}$, in which R and R_0 are the end-to-end distances of a chain in a solvent and in theta solvent, respectively. The value of $<R>/M$ is independent of the molecular weight of polymer if the polymer is linear homopolymer. At a constant temperature, K is a constant. In this work the following values were assumed.[11, 12]

$$[<R_0^2>/M^{1/2} = 0.950 \times 10^{-8}(\text{cm}), \quad \Phi = 2.1 \times 10^{-21}$$

Thus, one obtains an equation between $[\eta]$ and α.

$$\alpha^3 = \frac{[\eta]}{1.80 \times 10^{-3} \times M^{1/2}} \tag{2}$$

Values of α thus calculated were summarized in Table I (see also Figure 4). The values of α of P$^+$ and Q$^-$ in $0.1M$ NaCl are a little larger than that of the parent PVA. Introduced sulfate and aminoacetal residues may result in some hindrance to the rotation of main chain and increase hydrophilicity of polymers, so that the values of α are increased a little. At any rate, P$^+$ and Q$^-$ have similar chain conformations as that of the parent PVA.

The viscosity numbers in the equilibrium liquid were plotted against polymer
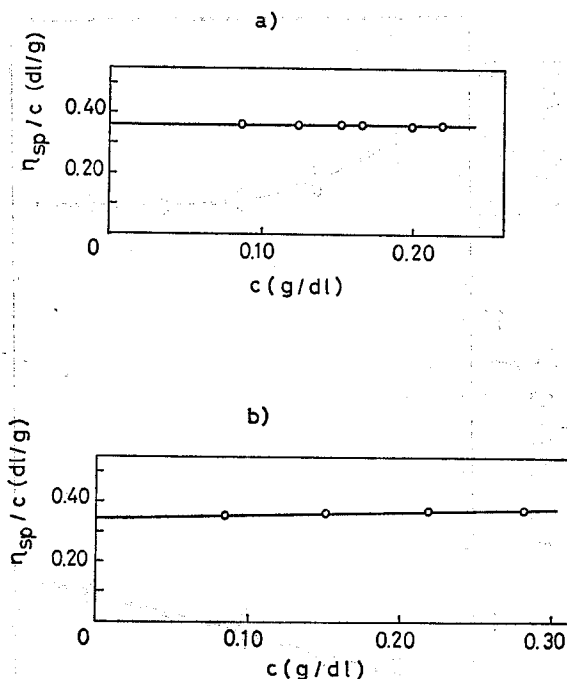
Fig. 4. Viscosity number of a) PVA–AA and b) PVA–S at 30°C in 0.1 M
NaCl aqueous solution.

concentration in Figure 5. Values of $[\eta]$ given in Table II. To calculate the values of α, $M^{1/2}$ was assumed to be the average of $M^{1/2}$'s of P$^+$ and Q$^-$, i.e., $M^{1/2}$ $=125$.

As is obvious in Figure 3, C_e varies with C_i, but α seems to be unchanged. These α values were smaller than those of P$^+$ and Q$^-$ in solution (see Table I). In the equilibrium liquid, P$^+$ and Q$^-$ are not dissolved separately but formed a 1:1 complex whose charges are neutralized apparently. Charges on their residues force to form the 1:1 complex electrostatically. Decrease in the values of α is attributed to this formation of complexes. Taking the formation of the complex into account, we assumed that the expansion factor α of the complex was equal to that of a polymer whose molecular weight was twice larger than that of P$^+$ or Q$^-$. Thus, α'^3 was $2^{-1/2}$ times larger than α^3. In the case of gelatin coacervation, Veis[4] has assumed the formation of a neutral aggregate, α of which was 0.9, to calculate the free energy of mixing of the equilibrium liquid.

Suppression of Coacervation

Addition of salts suppresses the formation of complexes because these complexes are formed by electrostatic interactions between P$^+$ and Q$^-$. This phenomenon was followed by means of turbidity measurements (Figure 6). Turbidity of the coacervate changed suddenly at the range of 0.4M–0.8M NaCl. Coacervation occurred at the concentration of 0.1M NaCl but did not at 1.0M NaCl. Viscosities of the solution (Figure 7) in 1.0M NaCl showed fairly good correspondence to those of P$^+$ and Q$^-$
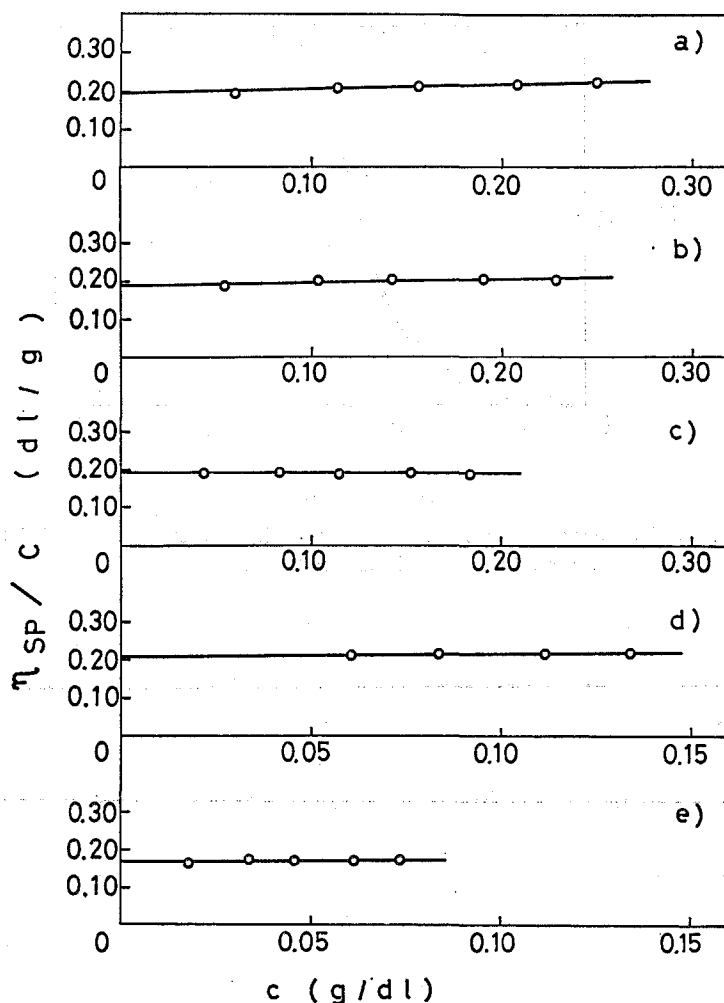
Fig. 5. Viscosity number of polymer in equilibrium liquid at 30°C in 0.1 M NaCl
aqueous solution. Initial concentrations of polymer are varied as follows; a)
10 mg/ml, b) 8 mg/ml, c) 6 mg/ml, d) 4 mg/ml and e) 2 mg/ml, respectively.

Table II. Expansion Factor α of Chains and the Limiting Viscosity Number
in Equilibrium Liquid

C_i (mg/ml)	2	4	6	8	10
$[\eta]$ (dl/g)	0.17	0.21	0.20	0.19	0.20
α	0.91	0.98	0.96	0.95	0.96
α'	0.81	0.87	0.86	0.84	0.86

solution. P$^+$ and Q$^-$ are not able to form complexes and dissolved individually in
1.0M NaCl aqueous solution. 1.0M NaCl was enough to shield electrostatic interactions between P$^+$ and Q$^-$.
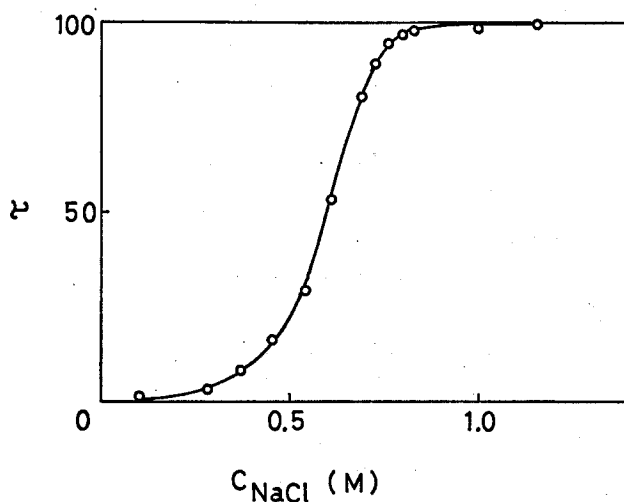   Change of pH is also observed by the addition of salts (Table III). P$^+$ and Q$^-$

Fig. 6. Turbidity (τ) plot against the concentration of NaCl (C_{NaCl}) at 30°C.
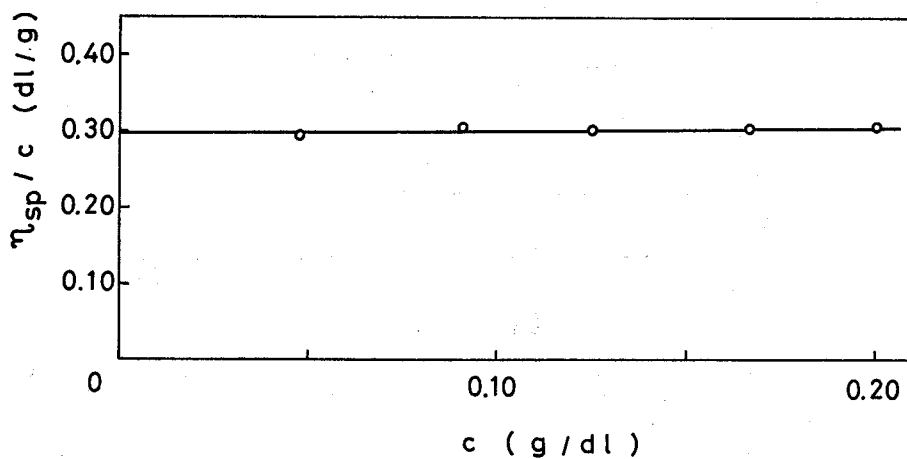Turbidity is given by %transmittance at 450 nm.

Fig. 7. Viscosity number of the mixed solution of P⁺ and Q⁻ in 1.0M NaCl.

Table III. pH of Coacervates

C_i (mg/ml)	pH in 0.1M NaCl	pH in 1.0M NaCl
2	3.70	3.57
6	3.22	3.06

form complexes in 0.1M NaCl aqueous solution and trap some amounts of H⁺ in the domains of the complexes. On addition of salts, however, complexes are dissociated, and separately dissolved into the equilibrium liquid by accompanying the increase in α' value and release of the trapped H⁺.

CONCLUSION

Coacervation of PVA–S and PVA–AA was studied in aqueous solution containing salts. At any ratio of mixing, P^+ and Q^- formed $1:1$ complex, charges of which were neutralized each other. C_e and C_e were dependent on C_i. The expansion factor of the $1:1$ complex in the equilibrium liquid formed by mixing the same amount of P^+ and Q^- was smaller than that of P^+ or Q^- dissolved in the solution individually. Formation of $1:1$ complex was suppressed by addition of salts being accompanied with expansion of polymer.

ACKNOWLEDGMENT

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