

ORIGINAL ARTICLE

Colloidal polyion complexation from sodium poly(acrylate) and poly(vinyl ammonium) chloride in aqueous solution

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The colloidal polyion complex formed from sodium poly(acrylate) (NaPA) and poly(vinyl ammonium) chloride (PVACl) is almost stoichiometric but is slightly charged owing to the adsorption of an excess of the polyelectrolyte component onto the neutral complex. The charge stabilizes the colloidal polyacrylate–poly(vinyl ammonium) complex in an aqueous solution of a non-stoichiometric mixture of NaPA and PVACl, and the aggregation number of the colloidal complex increases as the stoichiometric composition is approached. This colloidal polyion complexation is an irreversible process, and the aggregation number depends on the method used to mix the NaPA and PVACl solutions. On the basis of the experimental results, we propose a simple model for colloidal polyion complex formation.

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INTRODUCTION

Polyion complexes formed by a wide variety of polyanions and polycations in aqueous solution have been studied for more than half a century by changing parameters, such as the mixing ratio, ionic strength and pH. Table 1 lists common polyanion–polycation pairs that have been investigated so far; a more comprehensive list can be found in ref. 1. Despite the long research history, the mechanism of polyion complexation is not yet fully understood. Fuoss and Sadek² reported stoichiometric complexation between sodium poly(acrylate) (NaPA) or sodium poly(styrene sulfonate) and poly(4-vinyl-*N*-butylpyridinium) chloride, and other researchers^{3–5} later reported stoichiometric complexation for different polyelectrolyte pairs (Table 1). On the other hand, Tsuchida *et al.*⁶ and Nakajima and his group^{7–9} observed non-stoichiometric complexation of the polyion pairs listed in Table 1. The latter findings indicate that not only the electrostatic attraction but also the hydrophobic interaction among polyion chains has important roles in polyion complexation in aqueous solution.

In dilute solutions, polyion complexes often do not precipitate but become colloidal particles in the same way as hydrophobic colloids of low molar mass salts, such as AgI.¹⁰ Colloidal polyion complexes have also been studied for many years, mainly by viscometry and light scattering. Some colloidal polyion complexes^{3,5,11} were reported to decrease in size with increasing ionic strength, but the opposite ionic strength dependence has also been reported,¹² demonstrating that polyion complexation is not a simple phenomenon. As discussed below, the irreversibility of the complexation makes the phenomenon more complicated.

In this study, we conducted static light scattering measurements on colloidal polyion complexes formed by NaPA and poly(vinyl ammonium) chloride (PVACl) in water of neutral pH. Although PVACl is a polycation of the simplest chemical structure bearing primary amine groups, only a few studies have been performed on polyion complexation of this polycation.^{12,13} This study focuses on the dependences of the colloidal complex structure on the mixing ratio and polymer-chain-length ratio of NaPA and PVACl to elucidate the mechanism of complex formation.

EXPERIMENTAL PROCEDURE

Samples

Free radical polymerization of *N*-vinyl formamide was conducted in a mixed solvent of formamide/2-propanol (1:9, vol/vol) under an argon atmosphere at 70 °C using 2,2'-azobisisobutyronitrile as the initiator. The obtained polymer sample was divided into several fractions by repeated fractional precipitation with water as the solvent and acetone as the precipitant. The weight-average degrees of polymerization n_w and the polydispersity indices M_w/M_n of the three intermediate fractions of poly(*N*-vinyl formamide) were determined by size-exclusion chromatography equipped with an online multi-angle light scattering detector (SEC-MALS; DOWN DSP, Wyatt Technology, Santa Barbara, CA, USA) using 0.1 M aqueous NaCl as the eluent. The results are listed in Table 2.

The three intermediate fractions and an unfractionated sample were hydrolyzed in 1.5 M NaOH solution at 80 °C for 24 h under reflux, dialyzed against water for a week, and neutralized with HCl to convert the ions to their hydrochloric salts. For the unfractionated PVACl₉₃₀ sample after hydrolysis, n_w was determined by the batch measurement of static light scattering (see below and Table 2).

Table 1 List of typical polyanion–polycation pairs investigated in aqueous solution

Polyanion	Polycation	Ref.
Sodium polyacrylate, sodium poly(styrene sulfonate)	Poly(4-vinyl- <i>N</i> -butyl-pyridinium) chloride	2
Sodium poly(styrene sulfonate)	Poly(vinylbenzyltrimethyl-ammonium) bromide	3 and 4
Sodium poly(styrene sulfonate)	Integrated-type polycation (3X) ^a	6
Carboxymethyl cellulose	Poly(ethyleneimine)	7
Hyaluronic acid, chondroitin sulfate, heparin, sulfated cellulose	Glycol chitosan	8
Heparin	Partly aminoacetalized Poly(vinyl alcohol)	9 and 11
Sodium poly(acrylate)	Poly(vinyl amine)	13
Sodium poly(styrene sulfonate), sodium poly(methacrylate)	Poly(diallyldimethylammonium chloride)	5
Carboxymethyl cellulose	Poly(vinyl amine)	12

^a3X: [N⁺(CH₃)₂–(CH₂)₃–N⁺(CH₃)₂–CH₂–Ph–CH₂]_n.

Table 2 Molecular characteristics of NaPA and PVACl samples used

Sample	<i>n</i> ₊ , <i>n</i> _–	<i>M</i> _w / <i>M</i> _n
PVACl ₃₉₀	385 ^a	1.18 ^a
PVACl ₆₃₀	626 ^a	1.26 ^a
PVACl ₉₃₀	933 ^b	—
PVACl ₁₁₀₀	1090 ^a	1.22 ^a
NaPA ₁₁₀	111 ^c	1.55 ^c
NaPA ₃₀₀	303 ^d	1.09 ^d
NaPA ₃₇₀	373 ^e	1.03 ^f
NaPA ₆₀₀	603 ^e	1.07 ^f

Abbreviations: NaPA, sodium poly(acrylate); PVACl, poly(vinyl ammonium) chloride; SEC, size-exclusion chromatography.

^aDetermined by SEC before hydrolysis.

^bDetermined by static light scattering.

^cDetermined by SEC.

^dValues reported by the supplier.

^eDetermined by sedimentation equilibrium.¹⁴

^f*M*_n/*M*_w determined by sedimentation equilibrium.¹⁴

The polymer of *tert*-butylacrylate was obtained by the reversible addition-fragmentation chain transfer polymerization in dimethyl formamide under an argon atmosphere at 70 °C, purified by reprecipitation using a methanol/water mixture as the precipitant, and hydrolyzed in 2 M HCl solution at 120 °C for 24 h under reflux. The obtained sample was dialyzed against water for a week and neutralized with NaOH to convert it to the sodium salt. The weight-average degree of polymerization *n*_– and *M*_w/*M*_n of the NaPA sample (NaPA₁₁₀) were determined by SEC-MALS (Table 2). Two stock NaPA samples¹⁴ (NaPA₃₇₀ and NaPA₆₀₀) and an anionically polymerized commercial NaPA sample (NaPA₃₀₀; Polymer Source, Quebec, Canada) were added for the following experiments.

Preparation of test solutions

Freeze-dried samples of NaPA and PVACl were dissolved into pure water separately to make dilute solutions of the same initial concentration *c*₀ at neutral pH. Then, the solutions of NaPA and PVACl with volumes *V*_– and *V*₊, respectively, were mixed at room temperature to form the polyacrylate–poly(vinyl ammonium) (PA–PVA) complex. In the following text, the polymer composition in the mixed solution is expressed in terms of the mole fraction *x*_– of the carboxy group calculated from *x*_– = (*V*_–/*M*_{0,–})/[(*V*_–/*M*_{0,–}) + (*V*₊/*M*_{0,+})], with *M*_{0,–} and *M*_{0,+} representing the molar masses of the NaPA and PVACl monomer units, respectively.

Nuclear magnetic resonance measurements

Two pairs of aqueous NaPA and PVACl solutions with a relatively high concentration (*c*₀ = 5.0 × 10^{–4} g cm^{–3}) were mixed with different *x*_– and kept standing for ~12 h. The mixed solution was slightly turbid and was therefore centrifuged at 9000 r.p.m. for 1.5 h. The obtained precipitate was dried *in vacuo* overnight and dissolved in D₂O with NaOD (pD ≡ –log [D⁺] = 13) to make a

¹H-nuclear magnetic resonance (NMR) measurement at 30 °C using a JEOL JNM EX270 MHz or GSX400 spectrometer (JEOL Ltd, Tokyo, Japan). Chemical shifts were determined using 2,2-dimethyl-2-silapentane-5-sulfonic acid as the internal reference.

Light scattering

When the total polymer concentration *c*₀ was less than 1 × 10^{–4} g cm^{–3} and *x*_– was not close to 0.5, the aqueous NaPA–PVACl mixtures were almost transparent. Static and dynamic light scattering measurements were performed on these mixtures at 25 °C using an ALV/SLS/DLS-5000 light scattering instrument (ALV, Langen, Germany) with an Nd:YAG laser operating at 532 nm or an Otsuka Electronics DLS-7000DL instrument (Otsuka Electronics Co. Ltd, Hirakata, Japan) with an He–Ne laser of 633 nm. Each of the NaPA and PVACl solutions was filtered with a 0.20-μm cellulose acetate membrane filter before mixing. The measurements were performed at least 6 h after mixing, and the scattered light intensity did not change with time.

NMR analyses indicated that the NaPA and PVACl solutions formed a stoichiometric complex consisting of equal numbers of PA and PVA monomer units in the aqueous solution of the NaPA–PVACl mixture with any *x*_–. Therefore, the mixture solution contains the (almost) neutral PA–PVA complex (component 2) and the excess component (that is, PVACl at *x*_– < 0.5 and NaPA at *x*_– > 0.5; component 1). Light scattering theory gives us the following equation for the dilute ternary solution:¹⁵

$$\frac{Kc}{R_\theta} = \frac{1}{w_2 M_2 P_2(\theta)} + 2c \left[A_{2,22} + \frac{2w_1 M_1 P_1(\theta) \gamma_1}{w_2 M_2 P_2(\theta) \gamma_2} A_{2,12} \right]. \quad (1)$$

On the left-hand side, *K* is the optical constant, *c* is the total polymer mass concentration and *R*_θ is the excess Rayleigh ratio at the scattering angle *θ* of the mixture solution over that of the solution containing only the excess component. On the right-hand side, *w*_{*i*}, *M*_{*i*}, *P*_{*i*}(*θ*) and *γ*_{*i*} are the weight fraction (of the total polymer), molar mass, particle scattering function and refractive index increment of species *i* (= 1, 2), respectively, and *A*_{2,*ij*} is the second virial coefficient between species *i* and *j*. If the complex (component 2) is stoichiometric, the following equations hold for *w*₂ and *γ*₂:

$$w_2 = \begin{cases} \frac{x_-(M_{0,-} + M_{0,+})}{x_- M_{0,-} + (1-x_-) M_{0,+}} & (x_- < 0.5) \\ \frac{(1-x_-)(M_{0,-} + M_{0,+})}{x_- M_{0,-} + (1-x_-) M_{0,+}} & (x_- > 0.5) \end{cases}, \quad \gamma_2 = \frac{M_{0,-} \gamma_- + M_{0,+} \gamma_+}{M_{0,-} + M_{0,+}}. \quad (2)$$

By differential refractometry, *γ*_– of NaPA and *γ*₊ of PVACl were determined to be 0.185 cm³ g^{–1} and 0.234 cm³ g^{–1}, respectively, and *γ*₂ was calculated to be 0.207 cm³ g^{–1} from equation (2), which was used to calculate the optical constant *K* in equation (1).

The scattering intensity was enhanced by mixing the NaPA and PVACl solutions to such a degree that *R*_θ in equation (1) was approximated by the excess Rayleigh ratio of the mixture solution over that of the solvent, and the *A*_{2,12} term in parentheses on the right-hand side of equation (1) was neglected.

For polydisperse colloidal solutions, M_2 and $P_2(\theta)$ should be regarded as the weight-average value and z-average function, respectively. In what follows, M_2 and the radius of gyration obtained from $P_2(\theta)$ are denoted as M_w and $\langle S^2 \rangle_z^{1/2}$, respectively, and $A_{2,22}$ simply as A_2 .

Dynamic light scattering provides the intensity autocorrelation function $g^{(2)}(t)$. The first cumulant Γ and the hydrodynamic radius R_H were determined from $g^{(2)}(t)$ using the equations

$$\Gamma = \frac{1}{2} \lim_{t \rightarrow 0} \frac{d \ln[g^{(2)}(t) - 1]}{dt}, \quad R_H = \frac{k_B T}{6\pi\eta_0} \left(\lim_{k, c \rightarrow 0} \Gamma/k^2 \right)^{-1}, \quad (4)$$

where $k_B T$ is the Boltzmann constant multiplied by the absolute temperature, and η_0 is the solvent viscosity.

Electrophoretic light scattering measurements on some NaPA–PVAcI mixture solutions ($c_0 = c = 1 \times 10^{-4} \text{ g cm}^{-3}$) were conducted using an Otsuka Electronics zeta-potential analyzer ELSZ-2 (Otsuka Electronics Co. Ltd). From the Doppler shift frequency, $\Delta\omega$, obtained by electrophoretic light scattering, the apparent electrophoretic mobility, U_{app} , was estimated using the equation

$$U_{\text{app}} = \Delta\omega/Ek, \quad (5)$$

where E is the strength of the applied electric field and k is the magnitude of the scattering vector. The true electrophoretic mobility U was obtained after correcting for the electro-osmotic effect.¹⁶

The zeta potential of the colloid surface was calculated using the Smoluchowski equation¹⁷

$$\psi_\zeta = \frac{\eta_0}{\varepsilon_0 \varepsilon_r} U, \quad (6)$$

where ε_0 is the electric constant and ε_r is the relative permittivity of the solvent. The Fujita–Hermans theory¹⁸ gives us the following equation for the electrophoretic mobility U of spherical particles

$$U = \frac{n_C e}{4\pi\eta_0 R_H} \frac{1 + e^{-2\kappa R_H}}{3 + (\kappa R_H)^2}, \quad (7)$$

where n_C , e and κ are the total charge number of a spherical particle, the elementary charge and the inverse of the Debye length, respectively.

RESULTS

Stoichiometry of the PA–PVA complex

Figure 1 shows the ¹H-NMR spectra of the PA–PVA complex precipitated from aqueous solutions of NaPA₆₀₀ and PVAcI₆₃₀ mixtures with different x_- and then dissolved in alkaline D₂O. From the peak areas around $\delta = 1.5$ p.p.m. (methylene group of PA and PVA; A_a), 2.2 p.p.m. (methine group of PA; A_b) and 3.0 p.p.m. (methine group

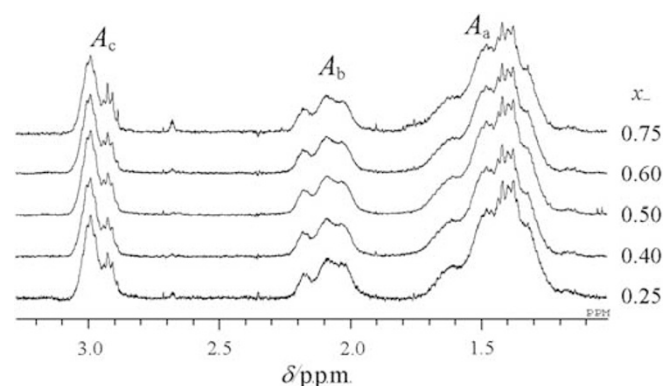


Figure 1 ¹H-nuclear magnetic resonance spectra of polyacrylate–poly(vinyl ammonium) complexes formed in aqueous solutions of NaPA₆₀₀ and PVAcI₆₃₀ mixtures with different x_- values. NaPA, sodium poly(acrylate); PVAcI, poly(vinyl ammonium) chloride.

of PVA; A_c), we have estimated the amounts of the PA and PVA monomers in the precipitated complexes. As shown in Table 3, the PA and PVA monomers are equimolar in the complex irrespective of x_- . The same result was also obtained for the complex formed from NaPA₁₁₀ and PVAcI₉₃₀ mixtures, demonstrating that the PA–PVA complex is stoichiometric, in agreement with the reports for many other polyion complex systems.

Table 4 lists the zeta potential ψ_ζ of colloidal PA–PVA complexes calculated from the electrophoretic mobility U obtained by electrophoretic light scattering at $c_0 = c = 1 \times 10^{-4} \text{ g cm}^{-3}$. The sign of the zeta potential is the same as that of the excess polymer component, indicating that the PA–PVA complex is charged by the excess components from the NaPA–PVAcI mixture solution. This appears to be inconsistent with the ¹H-NMR results listed in Table 2. To check for consistency, we calculated the number of net charges n_C for a polyion complex from equation (7) and the value of $[\text{COO}^-]/[\text{NH}_3^+] = (N_{0,w} - n_C)/(N_{0,w} + n_C)$ contained in a polyion complex from n_C and the total number $N_{0,w}$ of monomer units per polyion complex; $N_{0,w}$ can be calculated from the molar mass M_w of the complex (see below) by $N_{0,w} = 2M_w/(M_{0,-} + M_{0,+})$. The calculated values of $[\text{COO}^-]/[\text{NH}_3^+]$ listed in Table 3 are very close to unity, being consistent with the results of NMR measurements within experimental error. Thus, we conclude that the PA–PVA complex is almost stoichiometric and then neutral, but a tiny amount of the excess polyelectrolyte component is adsorbed on the neutral polyion complex colloids.

Dependence on the method used to prepare polyion complex solutions

Because the polyion complex is formed by mixing NaPA and PVAcI solutions, the mixing method may affect light scattering results. To determine the effect of the mixing method, we prepared the

Table 3 Ratio of carboxy to ammonium groups in precipitates of the PA–PVA complex from aqueous solutions with different n_- , n_+ and x_- , estimated by ¹H-NMR in alkaline D₂O solution

n_-	n_+	x_-	$(A_a + A_b)/A_c$	$[\text{COO}^-]/[\text{NH}_3^+]$
600	630	0.25	5.02	1.00
		0.40	5.08	1.02
		0.50	4.98	1.00
		0.60	4.92	0.98
		0.75	5.11	1.02
110	930	0.25	5.03	1.01
		0.40	5.05	1.01
		0.50	5.07	1.01
		0.60	5.03	1.01
		0.70	5.01	1.00

Abbreviations: NMR, nuclear magnetic resonance; PA–PVA, polyacrylate–poly(vinyl ammonium).

Table 4 Electrophoretic light scattering results for colloidal complexes formed from NaPA₁₁₀ and PVAcI₉₃₀ at $c_0 (=c) = 1 \times 10^{-4} \text{ g cm}^{-3}$

x_C	ψ_ζ/mV	$[\text{COO}^-]/[\text{NH}_3^+]$
0.226	38	0.93
0.596	−47	1.01
0.715	−60	1.02

Abbreviations: NaPA, sodium poly(acrylate); PVAcI, poly(vinyl ammonium) chloride.

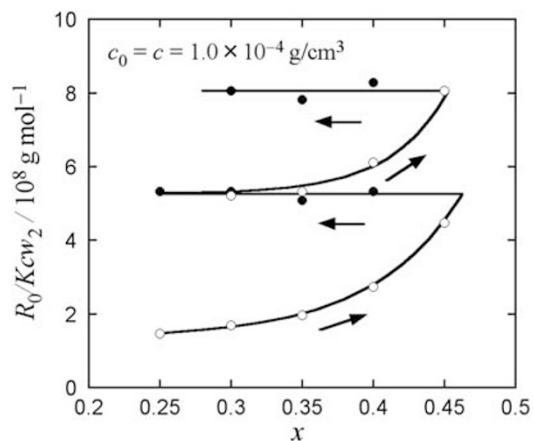


Figure 2 Change in the R_0/Kc value for solutions of NaPA₁₁₀ and PVACl₉₃₀ with increasing and decreasing x_- . NaPA, sodium poly(acrylate); PVACl, poly(vinyl ammonium) chloride.

complex solutions using the following two methods prior to light scattering measurements:

Method 1: A NaPA solution was added dropwise into a PVACl solution rapidly (during ~ 20 s) to prepare test solutions, and the mixture was stirred vigorously for ~ 1 h.

Method 2: A NaPA solution was poured gently on a PVACl solution in a light scattering cell from the cell wall, and the layered solution was kept standing for 24 h before stirring.

Light scattering measurements were performed several times on test solutions prepared using Methods 1 and 2 ($c_0=c=3.0 \times 10^{-5} \text{ g cm}^{-3}$, $x_- \approx 0.3$). $R_0/Kc w_2$ values were $(0.94 \pm 0.19) \times 10^8 \text{ g mol}^{-1}$ and $(15.5 \pm 11) \times 10^8 \text{ g mol}^{-1}$ for solutions prepared using Methods 1 and 2, respectively, where R_0 is the value of R_θ extrapolated to the zero θ and $R_0/Kc w_2$ is approximately equal to the weight-average molar mass M_w in dilute solution. Although variance of the results were rather large for solutions prepared using Method 2, it is clear that Method 2 produces larger colloidal polyion complexes than Method 1. In Method 2, the solution is more heterogeneous, so that polyion complexes formed during the early stage may travel through the PA-rich and PVA-rich regions in the solution many times, growing by adsorbing PA and PVA chains each time.

Figure 2 presents light scattering results for solutions of NaPA₁₁₀ and PVACl₉₃₀ ($c_0=c=1.0 \times 10^{-4} \text{ g cm}^{-3}$) prepared using Method 1, with x_- initially set to 0.25 and then changed between 0.25 and 0.45 by iterative additions of NaPA and PVACl solutions of the same polymer concentration c_0 . When the NaPA solution was added (unfilled circles), $R_0/Kc w_2$ increased and colloidal particles grew, but when the PVACl solution was added (filled circles), no colloidal growth was observed. The results shown in Table 4 show that the colloidal polyion complex is positively charged at $x_- < 0.5$, so that the complex can only adsorb the anionic PA added to grow and does not dissociate on PVACl addition.

The results of the above two light scattering experiments indicate the irreversibility of the PA–PVA complexation and the importance of the method used to prepare the test solution.

Characteristics of the PA–PVA complex colloid

Taking into account the results mentioned above, we performed light scattering on test solutions prepared using Method 1 ($c_0=3.0 \times 10^{-5} \text{ g cm}^{-3}$) by adding NaPA solution to PVACl solution for $x_- < 0.5$ and adding PVACl solution into the NaPA solution for

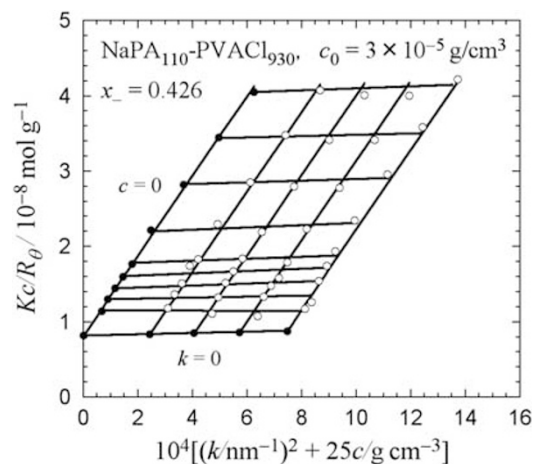


Figure 3 Zimm plot for colloidal polyion complexes formed by mixing aqueous solutions of NaPA₁₁₀ and PVACl₉₃₀ of $c_0=3 \times 10^{-5} \text{ g cm}^{-3}$ with $x_- = 0.426$. NaPA, sodium poly(acrylate); PVACl, poly(vinyl ammonium) chloride.

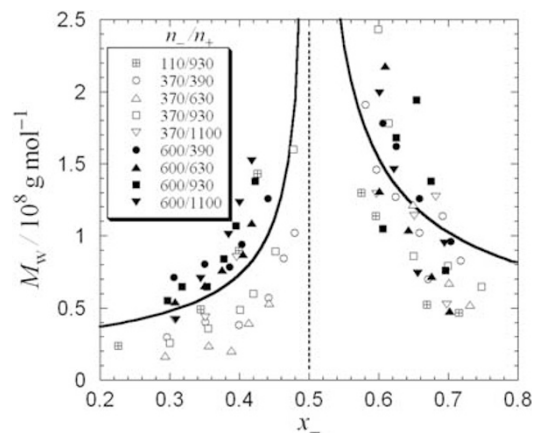


Figure 4 Dependence of the weight-average molar mass on the composition of different pairs of sodium poly(acrylate) and poly(vinyl ammonium) chloride samples. Curves indicate values calculated by equation (11) using $M_N=0$ and $\Lambda=3 \times 10^{10} (\text{g mol}^{-1})^{2/3}$ at $x_- < 0.5$ and $\Lambda=1 \times 10^{11} (\text{g mol}^{-1})^{2/3}$ at $x_- > 0.5$.

$x_- > 0.5$ and diluted with pure water to obtain different total polymer mass concentrations c . Figure 3 shows an example of the Zimm plot for a colloidal PA–PVA complex in aqueous solution. Similar Zimm plots were obtained for other mixtures of NaPA and PVACl samples with different compositions. The common intercept and slopes of the plots at $c=0$ and $k=0$ indicate the weight-average molar mass M_w , the z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ and the second virial coefficient A_2 (cf. equation (1)).

In Figure 4, the results of M_w obtained for different pairs of NaPA and PVACl samples are plotted against the composition x_- . The total aggregation numbers of the polymer chains calculated from M_w by $M_w(n_-^{-1}+n_+^{-1})/(M_{0,-}+M_{0,+})$ range from 400 to 8000, indicating that polyion complexes consist of a large number of polymer chains.

For all the pairs of NaPA and PVACl samples investigated, M_w mostly increases as x_- approaches 0.5 from both sides. PA–PVA complexes formed in solutions with x_- very close to 0.5 precipitated, and light scattering measurements were impossible. This is similar to

hydrophobic colloids of low molar mass salts such as AgI, which precipitates in an equimolar reaction of AgNO₃ and KI in water.¹⁰

The dependence of the M_w of the PA–PVA complex on composition seems to be asymmetric at $x_- = 0.5$ in Figure 4. We will discuss this asymmetry in the next section. On the other hand, the dependence of M_w on the degrees of polymerization n_- and n_+ is less clear than the dependence on composition. The PA–PVA complex consists of so many polyelectrolyte chains that the molecular characteristics of the component polyelectrolytes may not have a major role in the complexation.

Dautzenberg⁵ reported a similar composition dependence of M_w for the mixture of sodium poly(methacrylate) and poly(diallyl-dimethylammonium chloride) in water, but the opposite dependence for the mixture of sodium poly(styrene sulfonate) and poly(diallyl-dimethylammonium chloride) in water. The opposite dependence for the latter system appears to be inconsistent with his observation of macroscopic flocculation in stoichiometric mixtures of both systems (at $x_- = 0.5$). He prepared test solutions for static light scattering measurements by adding the polyanion or polycation solution into the counterpart solution slowly and stepwise approaching an x_- value of 0.5. During the stepwise dosage, the free chain concentration of the excess polyelectrolyte component decreases, and highly aggregated polyion complexes might form at the first dosage for the more hydrophobic sodium poly(styrene sulfonate) and poly(diallyl-dimethylammonium chloride) system.

Figure 5a shows the M_w dependences of $\langle S^2 \rangle_z^{1/2}$ of the colloidal PA–PVA complexes prepared for different NaPA and PVACl sample pairs at different x_- values. Although the data points are rather scattered, most seem to follow a common line with a weak slope. The line shown in the figure has a slope of 1/3, expected for uniform density spheres, and yields an internal polymer concentration c_c ($= 3M_w/4\pi N_A(5\langle S^2 \rangle_z/3)^{3/2}$; N_A : the Avogadro constant)

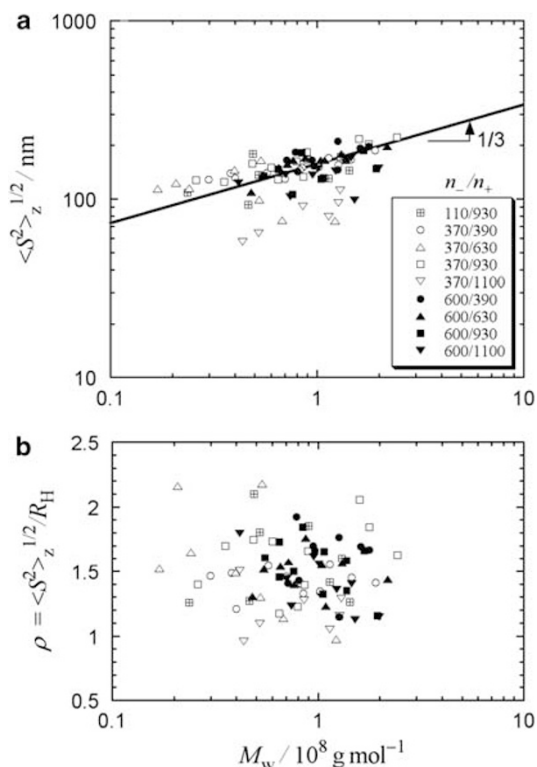


Figure 5 Molar mass dependences of (a) the radius of gyration and (b) the ratio ρ obtained for different sodium poly(acrylate) and poly(vinyl ammonium) chloride sample pairs at different x_- values.

of the spherical colloidal complex of $4.5 \times 10^{-3} \text{ g cm}^{-3}$. Therefore, the PA–PVA complex colloid contains a large amount of water, in sharp contrast to the colloidal complex of sodium poly(styrene sulfonate) and poly(diallyl-dimethylammonium chloride), where c_c is on the order of 0.5 g cm^{-3} .⁵ This contrast may be due to the difference in hydrophobicity between the two polyion complexes.

Figure 5b presents the ratios ρ of $\langle S^2 \rangle_z^{1/2}$ to the hydrodynamic radius R_H obtained by dynamic light scattering. The data points are scattered around 1.5. Although we expect $\rho = 0.775$ for monodisperse uniform-density spheres, polydispersity increases ρ . Spheres with a logarithmic normal distribution of $M_w/M_n = 4$ have a ρ -value of 1.5.¹⁹ Furthermore, a linear Zimm plot as shown in Figure 3 (instead of the Guinier plot) is expected for the polydisperse spherical system of $M_w/M_n = 4$.

Second virial coefficients for the colloidal PA–PVA complexes in aqueous solution ranged from 0 to $1 \times 10^{-4} \text{ cm}^3 \text{ mol g}^{-2}$, irrespective of n_- , n_+ and x_- . These values indicate that the colloidal complexes are almost neutral, consistent with the electrophoretic light scattering results shown in Table 4.

DISCUSSION

In polyion complexation, the electrostatic and hydrophobic interactions among oppositely charged polymer chains interact to give rise to complicated dependences on various experimental conditions. This section uses a simple model schematically illustrated in Figure 6 to interpret the composition dependence of M_w shown in Figure 4. When mixed, polyanion and polycation chains form neutral complexes N , initially due to electrostatic interactions (step 1), followed by the aggregation of neutral complexes due to hydrophobic interactions (step 2). If the system is a non-stoichiometric mixture of polyanions and polycations, then the excess component chain E may adsorb on the growing aggregate N_m to form charged colloids $N_m E_{m_E}$ (step 3), and when the net charge n_C of $N_m E_{m_E}$ attains a critical value n_C^* , the growth of $N_m E_{m_E}$ stops²⁰ (step 4). The value of n_C^* should depend on the strength of the hydrophobic interactions of $N_m E_{m_E}$ and on the ionic strength. Steps 2 and 3 occur simultaneously.

Step 1 may occur rapidly just after mixing the polyanion and polycation solutions. We choose the end of this step to be time $t=0$ and assume N at $t=0$ to be monodisperse spheres of a molar mass M_N . Step 2 may be treated as the rapid coagulation of colloidal particles, which can be explained by the Smoluchowski theory.²¹ This theory gives the time dependence of the weight-average molar mass M_w of colloidal particles N by the equation:

$$M_w = M_N + \frac{4k_B T N_A c_0}{3\eta_0} t, \quad (8)$$

where $k_B T$ is the Boltzmann constant multiplied by the absolute temperature, c_0 is the total polymer mass concentration and η_0 is the solvent viscosity. The radius R of the colloidal particle can be

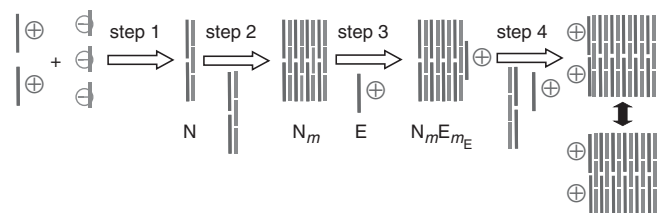


Figure 6 Schematic illustration of the colloidal polyion complexation process. Polyelectrolyte chains and colloidal polyion complexes are symbolically represented as unrealistic segments and rectangular objects, respectively. A full color version of this figure is available at *Polymer Journal* online.

calculated from $4\pi R^3 c_c/3 = M_w/N_A$, where c_c is the polymer mass concentration inside the particle.

The excess component E adsorbs on the growing colloidal particle surface (step 3). The rate of adsorption dm_E/dt should be proportional to the surface area $4\pi R^2$ of the colloidal particle and to the molar concentration C_E of the E chain:

$$\frac{dm_E}{dt} = 4\pi k_{\text{ads}} R^2 C_E \quad (9)$$

with the rate constant k_{ads} . So little adsorption occurs that the change in C_E over time can be ignored, and the number m_E of E chains adsorbed on a particle can be expressed as

$$m_E = \frac{9(36\pi)^{1/3} \eta_0 k_{\text{ads}} C_E}{20k_B T N_A^{5/3} c_0 c_c^{2/3}} (M_w^{5/3} - M_N^{5/3}). \quad (10)$$

In the late stage, both colloidal growth and E chain adsorption should slow down because of the charging of the colloidal particles (slow coagulation). Although Equation (10) applies to rapid coagulation, we use approximately the same relationship between m_E and M_w for slow coagulation, assuming that the colloidal growth and E chain adsorption decelerate at the same rate. Finally, in step 4, the colloids stop growing when the net charge n_C ($=m_E$ multiplied by the degree of polymerization n_E of the E chain) reaches the critical value n_C^* . The M_w of the stable colloid particle is then given by

$$M_w^{5/3} = M_N^{5/3} + \Lambda \frac{\bar{M}_0}{|1 - 2x_-|}, \quad \Lambda \equiv \frac{k_B T N_A^{5/3} c_c^{2/3} n_C^*}{450(36\pi)^{1/3} \eta_0 k_{\text{ads}}}, \quad (11)$$

where \bar{M}_0 is the average molar mass of the monomer units [$=x_- M_{0,-} + (1-x_-)M_{0,+}$]. We used the relation $C_E n_E = 10^3 |1 - 2x_-| c_0 \bar{M}_0$.

In equation (11), k_{ads} should depend on the affinity between N and E as well as on the diffusivity of the E chain in the solution. That is, k_{ads} may be different at $x_- < 0.5$ (where E is PVA) and > 0.5 (where E is PA) and dependent on n_E . In Figure 4, solid curves indicate values calculated by equation (11) using $M_N = 0$ and $\Lambda = 3 \times 10^{10}$ (g mol^{-1})^{2/3} at $x_- < 0.5$ and $\Lambda = 1 \times 10^{11}$ (g mol^{-1})^{2/3} at $x_- > 0.5$. Although the data points are scattered, the trend of composition dependence is almost reproduced by the curves. The smaller value of Λ at $x_- < 0.5$ implies that PVA has a greater affinity to the neutral complex N than does PA. The lack of importance of M_N in equation (11) indicates that the unit neutral complex N formed in the early stage 1 is much smaller than the final stabilized colloids.

On the other hand, the dependences of M_w on n_- and n_+ are mostly not appreciable within experimental error, but the data points for $(n_-, n_+) = (110, 930)$ (⊕) may be fitted by equation (11) with smaller Λ values than the data points for $(n_-, n_+) = (370, 930)$ (□) and $(600, 930)$ (■) at $x_- > 0.5$. This may result from the high diffusivity of PA with the lowest n_- among the three samples.

CONCLUSION

This study investigated colloidal polyion complexation by mixing aqueous solutions of NaPA and PVAc and characterizing the mixtures by static, dynamic, electrophoretic light scattering and ¹H-NMR. The experimental results obtained here allowed us to propose a simple model for colloidal polyion complexation, illustrated in Figure 6.

The results of ¹H-NMR indicated that the PA-PVA complex is almost stoichiometric, and we assumed that a neutral complex N was formed at the beginning. However, electrophoretic light scattering indicated that the PA-PVA complex is weakly charged by the excess polyelectrolyte component, from which we assumed the adsorption of excess polyelectrolyte chains onto growing colloids. This assumption was consistent with the composition dependence of the molar mass for the final stabilized PA-PVA colloid shown in Figure 4. The molar mass was not sensitive to the degree of polymerization of the constituent polyelectrolytes, and thus, the chain-length ratio of individual polyanions and polycations may not be important in the complexation.

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