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ORIGINAL CONTRIBUTION

Electrochemically induced aggregation of intra-particle cationic nanogel complexes with a stoichiometric amount of bound polyanions

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Abstract The present study aimed to see the effect of an applied electric field on the stability of a colloid system in which overall electroneutrality is maintained in a metastable state. We employed two polyelectrolyte nanogels (PENG) based on *N*,*N*′-methylenebisacrylamide (MBA)-cross-linked terpolymer composed of *N*-isopropylacrylamide (NIPA), acrylic acid (AAc) and 1-vinylimidazole (VI) and MBA-cross-linked copolymer of NIPA and VI. The complexes of these PENG particles with potassium poly(vinyl alcohol) sulfate (KPVS) were formed in an aqueous HCl solution (1 mM, pH 3) which allows a complete ionization of the PENG-fixed imidazole groups. The amount of KPVS anions was adjusted so as to become equivalent to that of PENG-fixed cations. The complex dispersion was electrolyzed in a simple cell made of a glass tube. A fine platinum wire was used as an electrode for both cathode and anode. It was suggested that the electrochemically induced increase in pH in the cathodic side causes the aggregation of the complex particles due to a partial dissociation of the bound polyanions from the complex.

Keywords Polyelectrolyte nanogel complexes · Metastable charge-neutral colloid · Electrolysis · Electrochemically induced aggregation · Generated pH gradient · Partial polyion dissociation

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Introduction

Ionic colloids such as proteins and charged polymer latexes, often referred to as a ‘hard’ colloid, have charges only on the surface of a particle. In contrast to these colloids, the nanoparticles composed of a lightly cross-linked polyelectrolyte gel network (i.e., polyelectrolyte nanogel, abbreviated herein as PENG) have charges both on the surfaces and within the bodies themselves. Therefore, the PENG particles undergo a large change in the size depending on its ionization state (for examples, see [1, 2]), as observed in the corresponding polyelectrolyte bulk gels ([3] and other references therein).

Our previous study [4] has dealt with the polyelectrolyte complex formation of a positively charged PENG particle with a linear polyanion in aqueous solutions. We paid a special attention to the effect of the concentration (C_s) of a simple salt (KCl), as well as of the mixing ratio (r_m) based on moles of the anion charges to the cation charges which are respectively bound to the polymer and the network. It has become apparent that there is a critical mixing ratio (cmr) at which both size and molar mass of the resulting particles abruptly increase, indicating the formation of an “interparticle” complex. The cmr value at $C_s \leq 0.01$ M (=mol/l) was observed to be at r_m around unity. At $r_m < \text{cmr}$, the measured molar mass of the complex agreed with that of a PENG particle to which the calculated amount of the polyanion is bound. This means the formation of an “intraparticle” complex ($G^{m+} \cdot (P^{n-})_a$), according to the stoichiometry of the reaction,

$$G^{m+} + aP^{n-} \rightarrow G^{m+} \cdot (P^{n-})_a \quad (1)$$

where G^{m+} denotes a PENG particle with $+m$ charges, P^{n-} is a polyanion chain with $-n$ charges, and $a = (m/n) r_m$.

During the process of intraparticle complex formation, both hydrodynamic radius (R_h), by dynamic light scattering (DLS), and mean square radius of gyration (R_g), by static light scattering (SLS), were found to decrease with an increase in r_m and become minimum at $r_m=1$, the point at which a stoichiometric amount (a moles) of P^{n-} ions was added to the dispersion of G^{m+} particles. These mean the gel collapse due to the neutralization of its network charges in the complexation with polyanion P^{n-}. At $r_m=1$, however, the mobility (U) of a stoichiometric $G^{m+}\cdot(P^{n-})_a$ complex was positive but not zero when the complex formation process was studied by electrophoretic light scattering (ELS) [5]. Attempting to resolve this contradiction, we assumed that (a) electroneutrality is maintained in the complex particle with the aid of counterions, but (b) the complex is highly polarizable, and hence (c) during ELS the polyanions would dissociate in part from the complex. This hypothesis was supported by the following results: (1) Mixing the $G^{m+}\cdot(P^{n-})_a$ complex with α moles of the uncomplexed G^{m+} brings about an increase in R_h and a decrease in the light scattering intensity of the complex at the same time, suggesting a polyelectrolyte exchange reaction:

$$\mathrm{G}^{m+}\cdot(\mathrm{P}^{n-})_a+\alpha\mathrm{G}^{m+} \rightarrow (1+\alpha)\left[\mathrm{G}^{m+}\cdot(\mathrm{P}^{n-})_{a/(1+\alpha)}\right]^{x+} \quad (2)$$

where $\mathrm{G}^{m+}\cdot(\mathrm{P}^{n-})_{a/(1+\alpha)}$ is a complex having positive x charges $(=m-[na/(1+\alpha)])$ due to transferring $a\alpha/(1+\alpha)$ moles of P^{n-}. (2) The same phenomenon is seen when β mole of polycation $P^{\gamma+}$ is added to the dispersion of stoichiometric $G^{m+}\cdot(P^{n-})_a$ complex, meaning that the polycation takes out the polyanion from the complex to form a more stable polyelectrolyte complex $(\mathrm{P}^{n-})\cdot(\mathrm{P}^{\gamma+})_\delta$, the reaction of which may be given by Eq. 3 in consideration of a 1:1 stoichiometry:

$$\mathrm{G}^{m+}\cdot(\mathrm{P}^{n-})_a+\beta\mathrm{P}^{\gamma+} \rightarrow \left[\mathrm{G}^{m+}\cdot(\mathrm{P}^{n-})_{a-(\beta\gamma/n)}\right]^{y+} + \beta\gamma/n\left[(\mathrm{P}^{n-})\cdot(\mathrm{P}^{\gamma+})_\delta\right] \quad (3)$$

where $y=\beta\gamma$. Note that this seems to be an indirect evidence for (b) and (c) in our assumption. Moreover, (3) upon addition of KCl, the complex undergoes little change in R_h at $C_s \leq 0.02$ M; aggregates with each other at C_s from 0.03 to 0.2 M; and becomes water-soluble at $C_s>0.2$ M. (4) The R_h of the soluble complex at C_s from 0.3 to 0.5 M is larger than that at $C_s<0.02$ M, suggesting dissociation of the P^{n-} ions.

In addition to the above, we have reported that the zero mobility ($U\sim0$) was not observed by ELS for a 'stoichiometrically charge-neutral' complex formed by addition of anionic PENG particles or polyions into the cationic PENG dispersion [6]. These experimental results seemed to be closely related to the results of molecular dynamic simulations [7, 8] in which a 'charge inversion' has been predicted in electrophoresis of a macroion (including a rod macroion such as DNA) in the presence of multivalent counterions [7] and polyelectrolyte counterions [8]. At the present stage, however, there is no attempt to see what changes are in a "metastable" charge-neutral colloid system such as a $G^{m+}\cdot(P^{n-})_a$ complex dispersion under an applied electric field; therefore, we focused on this subject in terms of a phenomenon and its mechanism.

Experimental

Materials We used two cationic PENG samples [4–6] in the preparation of their complexes. One is a PENG of *N*,*N*′-methylenebisacrylamide (MBA)-cross-linked terpolymer [4, 5] composed of *N*-isopropylacrylamide (NIPA), acrylic acid (AAc), and 1-vinylimidazole (VI), abbreviated as poly(NIPA/VI/AAc). The other PENG is composed of MBA-cross-linked copolymer [6] of NIPA and VI, poly(NIPA/VI). The imidazole group in the VI unit of both PENG particles are completely protonated at pH 3 (see Fig. 3 in [5]); therefore, the complex was formed at this pH and in the absence of salt by titration of PENG with potassium poly(vinyl alcohol) sulfate (KPVS) having a weight-average molar mass (M_w) ~4.19×10^5, using an automatic titrator (Hirama, model ART-3) employed in turbidimetric titration in our previous studies [4–6]. The amount of KPVS-bound anions was then given in moles of sulfate groups and adjusted so as to become equivalent to that of cationic groups bound to a PENG particle. As a result, we obtained an aqueous dispersion containing two complexes: i.e., poly(NIPA/VI/AAc) and poly(NIPA/VI)-based PENG particles, which are referred herein as complexes A and B, respectively. Several significant data of both PENG samples and of the corresponding complexes are shown in Table 1, from which it is obvious that both complexes A and B are a intraparticle and charge-neutral complex; i.e., $G^{m+}\cdot(P^{n-})_a$ where $a=(m/n)$ in consideration of Eq. 1.

Electrolytic experiments Effect of an applied electric field on the complex dispersion was studied by use of a simple setup as shown in Fig. 1. An electrolytic cell was made by a glass tube with an inner diameter of 7 mm, and a platinum wire of 1 mm in diameter was used as an electrode for both cathode and anode. The distance between the electrodes was fixed at 12 cm. The aqueous complex dispersion (5.6 ml; pH 3;

Table 1 Properties of Polyelectrolyte Nanogels (PENG) and their complexes

Sample	Charge density (mmol/g)		10^{-7} M_{w} (g/mol)	R_{h} (nm)
	Imidazole	Carboxyl		
Poly(NIPA/VI/AAc)-based PENG	1.12	1.36	1.49	158±11
Poly(NIPA/VI)-based PENG	1.74	0	1.17	156±11
Complex A			1.80[a]	67±5
Complex B			1.49[a]	70±5

Methods and conditions for measurements are the charge density by potentiometric titration using an aqueous KCl solution (C_{s}=0.5 M) as a dispersing medium; molar mass (M_{w}) by SLS in an aqueous KCl solution (C_{s}=0.1 M) at pH 5.3 (isoelectric point) and at 25 °C for poly(NIPA/VI/AAc)-based PENG and in an aqueous NaCl solution (C_{s}=0.2 M) at pH 11 for poly(NIPA/VI)-based PENG; R_{h} by DLS in an aqueous HCl solution (pH 3) at 25 °C for the all (i.e., the same condition as used in the complex preparation). Complexes A and B were prepared using poly (NIPA/VI/AAc) and poly(NIPA/VI)-based PENG particles, respectively.

[a] Calculated M_{w} values based on Eq. 1 are 1.76×10^{7} g/mol for complex A and 1.50×10^{7} g/mol for complex B.

concentration=0.816 g/l for complex A and 0.756 g/l for complex B) not containing low molecular-weight salt, other than KCl (about 1 mM) resulted in the complexation, was taken in the cell. A voltage of 90 V was then applied using a voltage stabilizer. Time and position-dependent changes of the complex dispersion during the electrolysis were recorded by a digital camera (Olympus, model E-330). The position-dependent pH change in the cell as a function of time was studied using the dispersing medium (1 mM HCl). A sample (0.5 ml) was sucked up from the cell at four positions at different time and subjected to pH measurements with a micro pH electrode.

Size and turbidity measurements The pH-dependent aggregation of the complex nanoparticles was studied by measuring absorbance of the dispersion at 500 nm using a Hitachi spectrophotometer (model U2800). The R_{h} of the complex particles before and after the electrolysis was estimated by DLS using an Otsuka DLS 7000 apparatus (Osaka, Japan) equipped with a He–Ne laser as the light source. We analyzed the autocorrelation functions with the CONTIN program.

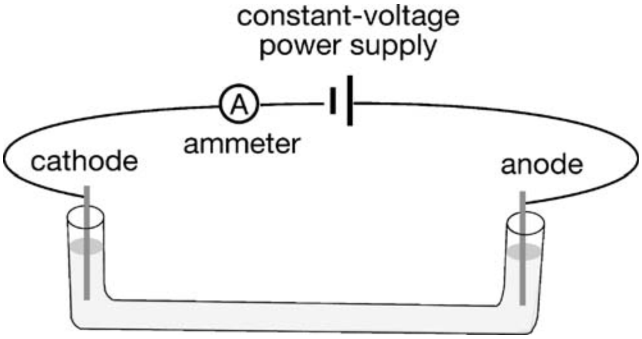


Fig. 1 Setup for electrolytic experiments. Details of each part are described in the text

Results and discussion

Aggregation of complex particles under an applied electric field

Figure 2 shows the aspect of the dispersion of complexes A and B as a function of time when an electric field of 7.5 V/cm was applied between the cathode and anode. Also shown in this figure are the electric current changes observed in the corresponding complex system and in an aqueous HCl solution (1 mM; pH 3) as well as in a KCl–HCl mixture (1 mM both; pH 3). Note that the HCl solution is the dispersing medium used in the complex formation, and the KCl–HCl mixture contains almost the same amount (1 mM) of KCl which should result in the complexation; therefore, both may be regarded as a control sample for our experiments.

As can be seen from Fig. 2, the dispersion near the cathode becomes slightly opaque after 5 min, and at 30 min after, a white precipitate appears during which the turbidity disappears. Upon further electrolysis, the precipitate moves to the anodic side (see 120 min after). Tiny bubbles generated near both anode and cathode upon applying the voltage, and the resulting bubbles dispersed inside the cell as time passed. Qualitative measurements showed that the volume of generated gases was greater at the anode than at the cathode. In addition to these visible changes, a decrease in the current was observed in the electrolysis of both the complex systems as well as of the aqueous HCl solution for 10–50 min during which there were a few changes in the KCl–HCl system.

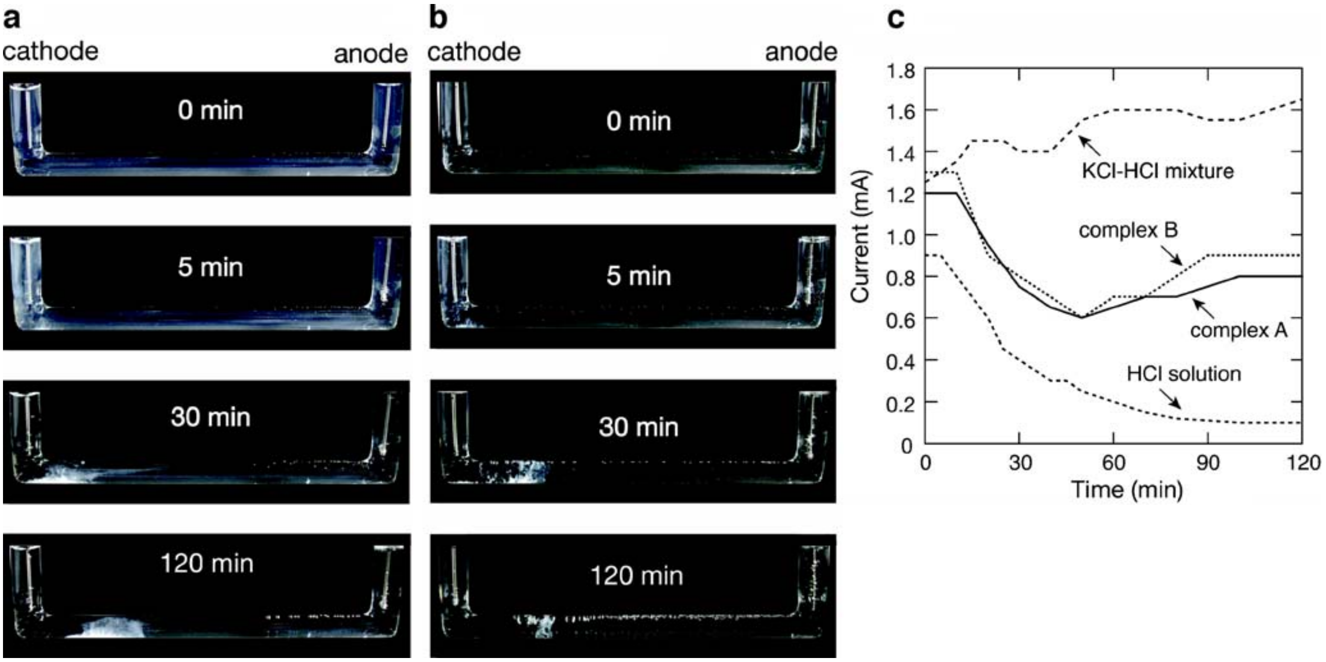
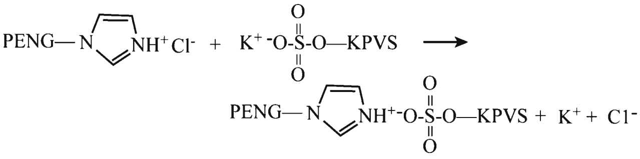


Fig. 2 Pictures (**a** and **b**) as well as current data (**c**) that show the time course of electrolysis at 90 V for aqueous dispersions of complex A (**a**) and complex B (**b**). Also shown in **c** are the current changes of the dispersing medium (1 mM HCl) and a KCl–HCl mixture (1 mM both) as a control sample. Initial complex concentrations are 0.816 g/l for complex A and 0.756 g/l for complex B

For understanding the results in Fig. 2, we should initially consider the electrolysis of the aqueous system containing H^+, K^+, and Cl^- ions. Note that K^+ and Cl^- ions result in the complexation;



(4)

In such a system, the anodic and cathodic reactions would be written as:

$$2Cl^- \rightarrow Cl_2 + 2e^- (\text{anode}) \tag{5a}$$

$$2H^+ + 2e^- \rightarrow H_2 (\text{cathode}) \tag{5b}$$

In addition, from the measurement of generated gas volumes at the anode and cathode, the electrolysis of water would occur at the same time, the reactions of which are written as,

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- (\text{cathode}) \tag{6a}$$

$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^- (\text{anode}) \tag{6b}$$

and summarized as:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{6c}$$

Other than the above, we must consider that the concentration of K^+ ions takes place near the cathode, while a part of the resulting Cl_2 on the anode reacts with water to yield HCl and HClO ($Cl_2+H_2O \rightarrow HCl+HClO$). Therefore, we performed the analysis of free chlorine (hypochlorous acid plus hypochlorite) according to [9]. The samples were then obtained by passing the complex dispersions (1 ml at both the anode and cathode) through a 0.1-μm filter. Free chlorine was detected from all the samples including the KCl–HCl mixture and the dispersing medium (1 mM HCl): e.g., 1.5 mg/l (anodic side) and 0 mg/l (cathodic side) for complex B after 120 min; and 6.0 mg/l (anodic side) and trace amount (cathodic side) for the KCl–HCl mixture (1 mM both). As a result, we may consider the generation of a pH gradient in the cell during the electrolysis (this is proved in the next section).

Taking the above into account, we may discuss the time course of electric current during the electrolysis (Fig. 2c). A marked difference between the HCl solution and the KCl–HCl mixture should be due to a difference in the concentration of K^+ and Cl^- ions between both systems. The complex dispersion, however, should contain almost the same amounts of both K^+ and Cl^- ions as existed in the KCl–HCl mixture; thus, one might not expect to be the difference as observed between the complex and KCl–HCl systems. Then, we consider that a part of K^+ and Cl^- ions other than those consumed during the electrolysis would be absorbed in the aggregated complex, the matter of which will be discussed later.

Position dependence of pH in the cell on time

To confirm the generation of a pH gradient during the electrolysis, the dispersion medium (1 mM HCl) was electrolyzed and subjected to the pH measurement (see “Experimental”). As can be seen from Fig. 3, there are increases in pH from 3.0 to 6.3 around the cathode and a decrease in pH from 3.0 to 2.6 around the anode. It was not possible to perform the same measurement for the complex dispersion because the complex precipitated during the electrolysis. This result is, however, an indication of the generation of a pH gradient during the electrolysis, which varies depending upon time.

Effect of pH on the complex

We studied the stability of the complex dispersion as a function of pH. It is clear from Fig. 4 that the dispersion of complex A [based on poly(NIPA/VI/AAc)] and complex B [based on poly(NIPA/VI)] undergoes a phase separation over a range of acidic to neutral pH; pH 3.6–5.5 for complex A and pH 4.5–7.3 for complex B. Taking into account this and the above results, we can say that the time-dependent change shown in Fig. 2 is related to the pH gradient during the electrolysis. This also allows us to understand why the cell position at which the precipitation takes place is different between complexes A and B.

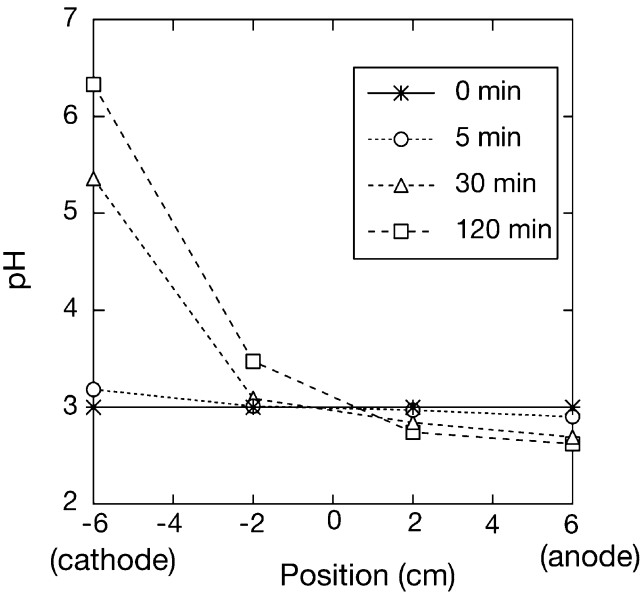


Fig. 3 Position dependence of pH as a function of time during the electrolysis of 1 mM HCl (as the dispersing medium). The zero position denotes the center of the cell shown in Fig. 1. The electrolysis was stopped at the time shown in the figure

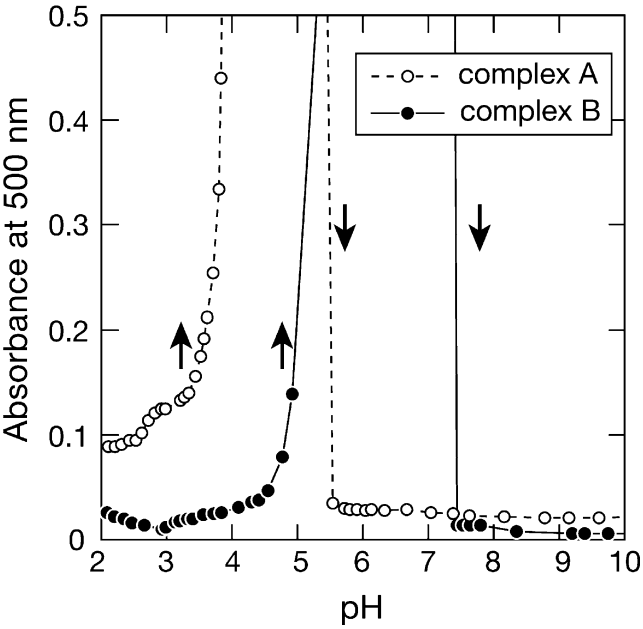


Fig. 4 pH-induced phase separation of complexes A and B. The results are given as pH vs absorbance curve. The *upward and the downward arrow* in the figure show the aggregation and the redispersion, respectively. The complexes were formed at pH 3; thus, the pH adjustment at pH<3 was made with HCl and at pH>3 was with KOH

Now, it would be interesting to see the redispersion of the precipitated complex particles by reversing the anode and the cathode after the electrolysis was performed for 120 min. The results are shown in Fig. 5 (Note that the pictures in this figure before the electrolysis, i.e., time=0 min, are not the same as those in Fig. 2 at 120 min because the data were obtained from the different experiments). We could not redisperse completely the precipitated complex even when the electrolysis was carried out for 47 h; however, the gathering of the complex precipitates falls into fine pieces (like as a cloud), for example, see 15 min after in Fig. 5a. This means an inversion of pH gradient caused by reversing the anode and the cathode.

Whether KPVS dissociates from the complex during electrolysis

It has become apparent that the cationic PENG complexes with a stoichiometric amount of polyanion-fixed charges, i.e., $G^{m+}\cdot(P^{n-})_a$ where $a=(m/n)$ in Eq. 1, aggregate each other under the applied electric field. This is due to the pH change induced by the electrochemical reaction. Then, the question is raised about whether the bound KPVS anions completely or partially dissociate from the complex during the electrolysis. The main purpose of the present study is to answer this question, as mentioned in “Introduction”. We

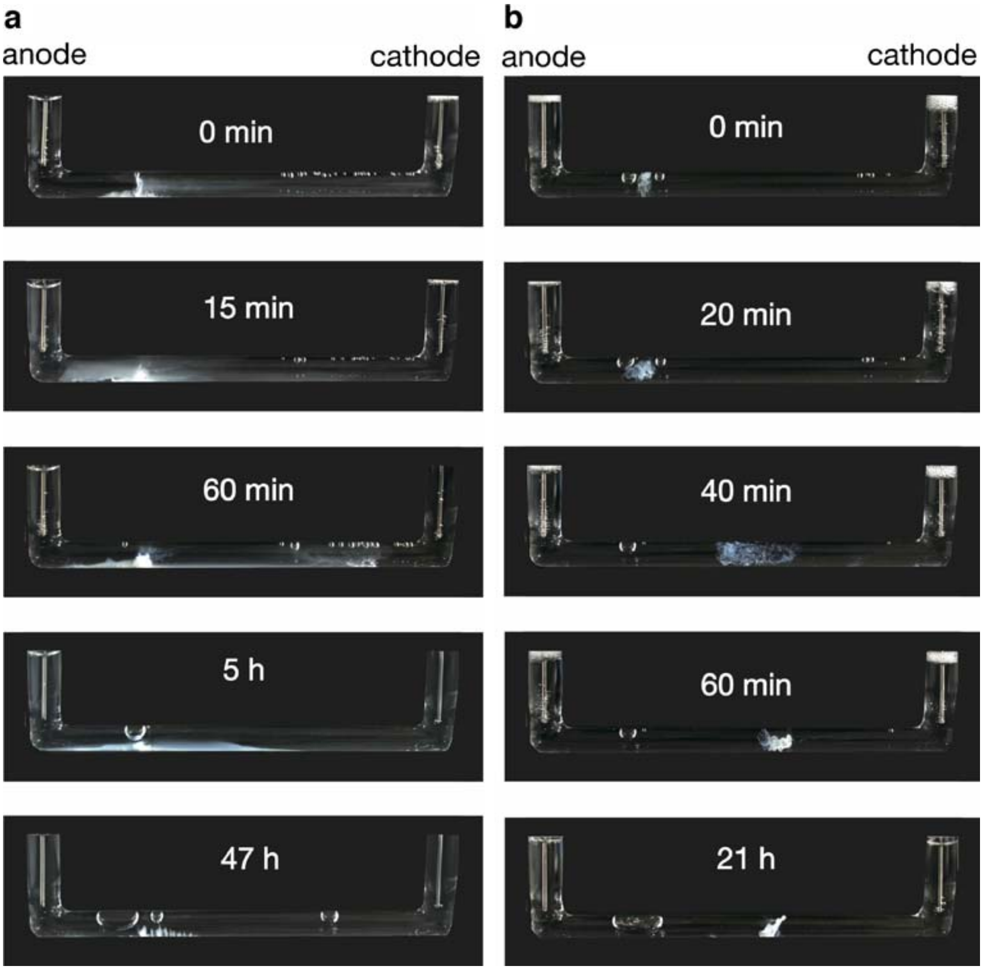


Fig. 5 Pictures showing what happens during the electrolysis of complexes A and B which were electrochemically precipitated. The results of complexes A and B are shown in **a** and **b**, respectively. *White parts* observed on the top of the anodic and the cathodic side (in particular, in the cathodic side in **b**) are the bubble generated in the electrolysis. A considerable volume of gas collected in the cell when the electrolysis was continued for a long time (e.g., longer than 5 h)

thus performed the following experiments: (1) The dispersion (1 ml) in the anodic side was sucked up immediately after the electrolysis for 120 min; (2) the sample dispersion was then passed through a Millipore filter, which permits the passage of KPVS ions, but not of PENG or its complex particles; and (3) the filtrate obtained was examined by colloid titration using a standard poly(diallyldimethylammonium chloride) (PDDA) titrant (0.001 mol/l).

As can be seen from Fig. 6, the free KPVS ions was not detectable in the complex dispersion after the electrolysis, indicating no dissociation of the bound KPVS ions from the complex particles. The same conclusion can be obtained from the samples which sucked up from different positions between the precipitate and the anode (data not shown). However, one might argue that there is possibility for the decomposition or depolymerization of the KPVS ions during the electrolysis. Thus, the free KPVS ions, the amount of which is the same as these used for the complexation, are subjected to the electrolysis under the same conditions as for the complex. This control experiment indicates that a complete quantity (99.9%) of KPVS ions was detected after the electrolysis, meaning no decomposition of KPVS.

On the mechanism of electrochemical aggregation followed by precipitation of the complex

From the results reported above, it is certain that the electrochemically induced increase in pH causes the precipitation of complexes A and B. This seems to be due to a ‘partial’ dissociation of KPVS ions from the complex surface, the aspect of which would be pictured in Fig. 7. This dissociation yields a part of free cationic and anionic charges on the surface of the complex particle; therefore, a strong electrostatic attraction between parts with opposite charges leads to an ‘inter-particle’ interaction among the complex particles, through which several complex particles would aggregate each other (see the photograph at 5 min in Fig. 2a and b). However, the aggregates should be polarized and consequently undergo further aggregation to form precipitates. During such changes, it is reasonable to consider that small anions (Cl^-) and cations (K^+) would be absorbed within the aggregate and/or its precipitate. As a result, a decrease in the current was observed as reported in Fig. 2c.

As an attempt to support the above discussion, we note the fact that the aggregate of complexes A and B

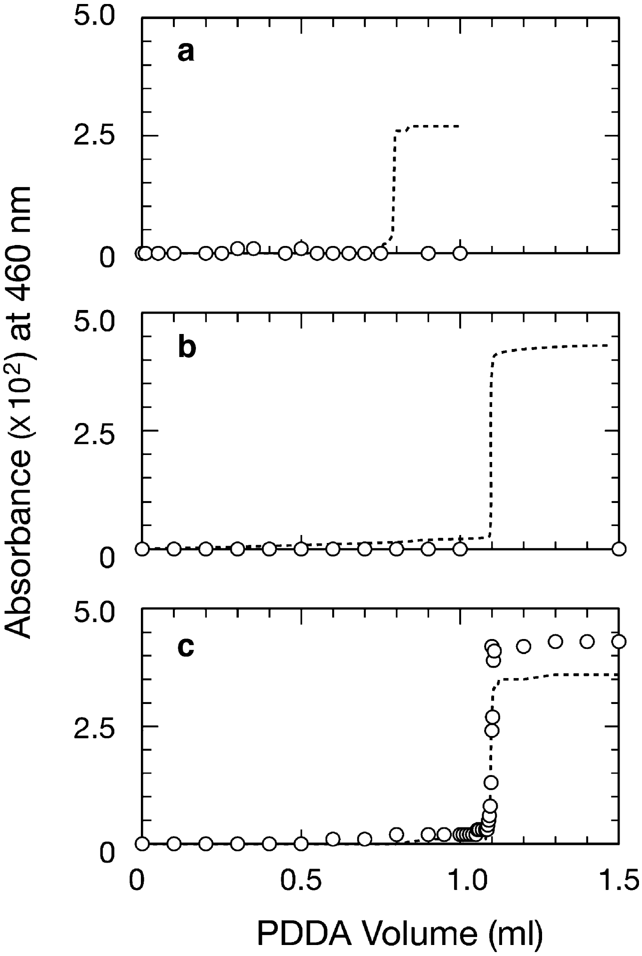
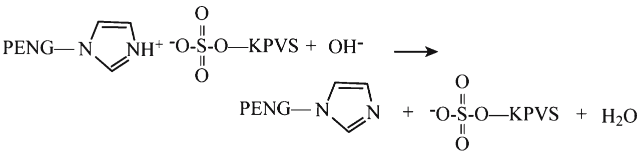


Fig. 6 Effect of an electric field (7.5 V/cm) on the complexed and the free KPVS. Plots (*open circles*) in **a** (complex A) and **b** (complex B) show the colloid titration curves with PDDA (10^{-3} mol/l based on quaternary ammonium ions) for the samples (1 ml) which were separated from the complex dispersion as was mentioned in the text and diluted 30 ml with distilled water. In both **a** and **b**, the *broken line* denotes the titration curves of the free KPVS, the amount of which are the same as that used in the complex formation. Results in **c** are the titration curves of aqueous KPVS solutions (3.3×10^{-5} mol/l based on sulfate groups; 30 ml; and pH 3 with HCl) before and after the electrolysis for 120 min at 90 V: *broken line*, before the electrolysis; and *open circles*, after electrolysis

redisperses with increasing pH (see Fig. 4). This seems to be due to the dissociation of the bound KPVS from the complex; in other words, the breaking of the complex caused by the elimination of positive charges:



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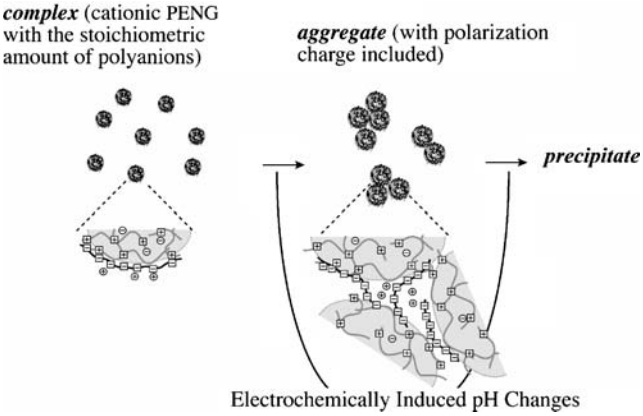

Fig. 7 Schematic illustration for understanding electrochemically induced aggregation and precipitation of intra-particle cationic nanogel complexes with a stoichiometric amount of the bound polyanions

In the case of complex A composed of the amphoteric PENG, this process simultaneously accompanies the generation of negative charges via the dissociation of COOH groups. These can be seen by comparing the results of DLS shown in Fig. 8. In our DLS measurements, the three kinds of samples from complexes A and B were used: A, the ‘raw’ complex (i.e., the sample before the electrolysis); B, the complex precipitate resulting from the electrolysis for 120 min; and C, the PENG particle used for the complexation. Because all of the samples for the DLS were adjusted to pH ~11 at which the complex would break into KPVS and PENG, it is presumable that there is no difference among the size distribution curves of the three kinds of samples. Indeed, we obtained the three distribution curves which are very close to each other in both cases of complexes A and B. In addition, it was found that (1) the average R_h values (166±7 nm) of the poly(NIPA/VI/AAc)-based PENG as well as its complexes before and after the electrolysis is larger than those (91±7 nm) of the poly(NIPA/VI)-based PENG and its complex samples; and (2) the R_h values of complexes A and B are smaller at pH 3 than at pH 11 (compare data in Table 1 and Fig. 8). Note that a small peak near $R_h \sim 10$ nm which appeared in all the distribution curves is due to the effect of surface dangling chains (see [10] and other references therein). This is because the free KPVS anion was not detectable by DLS under the conditions used. As a result, the DLS data in Fig. 8 strongly suggest that our discussion mentioned above is reasonable.

General discussion and conclusions

We have studied two polyelectrolyte nanogel complexes as a metastable charge-neutral colloid. The electrolysis, but not the crude moving boundary electrophoresis, was employed as

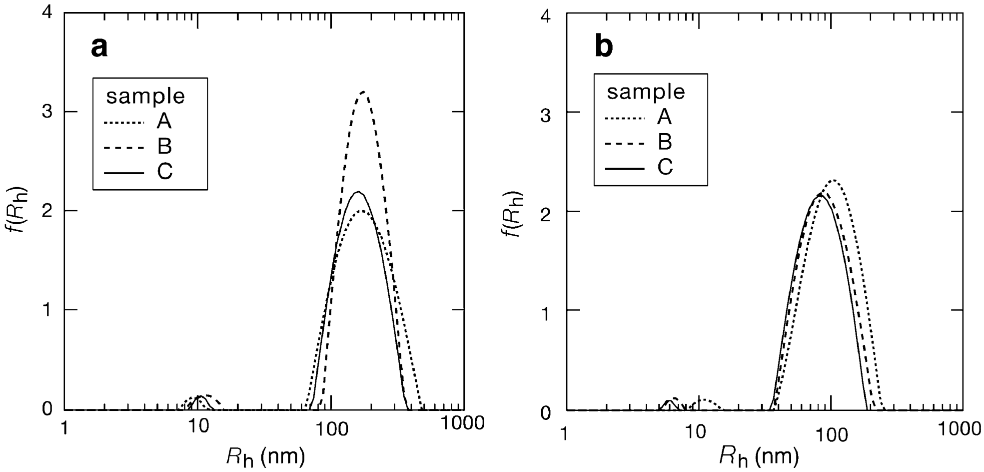

Fig. 8 Comparisons of DLS results for three kinds of samples in aqueous KOH solution (pH 11). Samples: *A*, the complex before the electrolysis; *B*, the electrochemically precipitated complex and then redispersed with the KOH solution; *C*, the PENG sample used for the complexation. The samples in **a** and **b** are the poly(NIPA/VI/AAc)-based system (complex A) and the poly(NIPA/VI)-based system (complex B), respectively. Hydrodynamic radius distributions $f(R_h)$ were normalized by the scattered intensity $\left(I_S \sim \int_0^\infty f(R_h)\, dR_h\right)$ of each sample C. The concentration of each complex was adjusted to provide the same concentration (0.485 g/l) of the corresponding PENG (i.e., sample C) by subtracting the weight of the bound KPVS from the complex weight. The concentration of sample B was determined by evaporating its redispersion to dryness. A maximum deviation is 0.3 au (±15%) in I_s (see **a**) and 14 nm (i.e., ±7 nm) in R_h (see **b**). These values are within experimental errors in our DLS measurements (e.g., see [4–6] and [10])

an experimental method. The electrolytic conditions used here are different from those of ELS experiments in our previous studies [4–6]. Nevertheless, it is known from half a century ago that a pH gradient is generated in an electrophoretic cell under an applied electric field. For example, this aspect was reported in 1948 by Alberty [11] who attempted to look at what is occurring in the cell through calculation using Dole's theory [12]. He showed that there is a slight gradient in the pH (±0.2) even when a barbital buffer solution (pH=8.6; ionic strength=0.05) was employed as a medium. Under these considerations, let us return to the results in Fig. 4. Then, one would learn that a very slight pH change could lead to the aggregation of the complex particles. This means that in the electrophoresis of metastable charge-neutral colloid systems, we must consider an effect of electrochemically induced pH change on the electrophoretic mobility.

In conclusion, we may suggest that the reason why the charge-neutral PENG complex particles reported in our previous papers [4–6] did not exhibit zero mobility in their electrophoresis is due to a pH change which results from an applied electric field. Modern electrophoretic instruments are designed to avoid such pH effects and also heating effects. In the ELS measurements for "metastable" charge-neutral colloids, however, there has been no information about how the mobility varies when a very few pH gradient is generated in an electrophoretic cell.

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