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Title: Compaction of TiO$_2$ suspension by using dual ionic thermosensitive polymers

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Abstract

The compaction of TiO$_2$ suspension as a negatively charged model suspension by using dual ionic thermosensitive polymers was investigated. First, a cationic thermosensitive polymer, poly(*N*-isopropylacrylamide-*co*-N,N-dimethylaminopropylacrylamide) was added to the TiO$_2$ suspension, followed by an anionic thermosensitive polymer, poly(*N*-isopropyl-acrylamide-*co*-acrylic acid). By adding the latter, a polymer complex with the cationic thermosensitive polymer adsorbed on the particle is formed, and charge neutralization occurs to decrease the transition temperature of the polymer adsorbed on the TiO$_2$ particles. As a result, the compaction of the TiO$_2$ suspended particles due to the hydrophobic interaction of the adsorbed polymers occurs at a relatively low temperature by applying an adequate mechanical force with a plunger. In order to initiate the compaction, it was necessary to cover the surface of the TiO$_2$ particles sufficiently by the cationic thermosensitive polymer molecules, and the optimum dosage of the anionic thermosensitive polymer was observed. The transition temperature of the polymer complex adsorbed on the TiO$_2$ particles was dependent on the ratio of the dosages of the cationic and anionic thermosensitive polymers.

1. Introduction

Polymeric flocculants with high molecular weights have been widely used in the flocculation of suspended particles and sludge dewatering. It is well known that the function of the polymeric flocculants is bridging between the suspended particles to form flocs. However, the flocs formed are usually bulky and contain a large amount of water. This is attributed to the hydrophilicity of the solid surface and polymer molecules. It is difficult to effectively remove this large amount of water by the conventional mechanical dewatering method.

In order to alleviate this problem, the authors proposed a novel compaction method using thermosensitive polymers [1,2]. Thermosensitive polymers are soluble in water at low temperatures; however, they are insoluble above the intrinsic temperature of the polymer because they become hydrophobic [3,4]. The hydrophilic/hydrophobic transition of a thermosensitive polymer is reversible. This intrinsic temperature is referred to as the lower critical solution temperature (LCST) or transition temperature; it depends on the side-chain structure of the polymer [3]. Poly(*N*-isopropylacrylamide) (poly(NIPAM)) is a representative nonionic thermosensitive polymer with a transition temperature of approximately 32°C [3].

The compaction method proposed by the authors is as follows: First, by mixing the suspended particles with the thermosensitive polymer below its transition temperature, the surface of the former is sufficiently covered with the adsorbed polymer molecules. Similar to the excess dosage condition in the conventional flocculation process using polymeric

flocculants, these particles are stably dispersed. When this suspension was heated above the transition temperature, the polymer molecules adsorbed on the particles become hydrophobic. As a result, the surface of the suspended particles also becomes hydrophobic. The particles aggregate, and flocs are formed due to these hydrophobic interactions. The subsequent application of an adequate mechanical force to the flocs induces the particles in the flocs to rearrange, thereby discharging the water molecules from them and leading to compaction. The mechanism for the formation of flocs by hydrophobic interactions is basically the same as that proposed by Zhu and Napper [5], except for the rearrangement of the particles in the floc by applying an adequate mechanical force.

We previously reported that by using kaolin-nonionic poly(NIPAM), a compacted kaolin sludge could be conveniently obtained by utilizing the hydrophilic/hydrophobic transition of poly(NIPAM) [1,2]. Furthermore, this method was applied to the dewatering of the activated sludge, and a lower water content in the dewatered cake compared with that in commercial flocculants was achieved [6]. However, it was found that the use of nonionic poly(NIPAM) has limitations, and that the ionic thermosensitive polymers are effective for the compaction of suspended particles with a high surface charge, such as the activated sludge and TiO_2 suspension [7]. However, a serious problem exists; the transition temperature of the ionic thermosensitive polymer is high compared with that of the nonionic poly(NIPAM). In order to solve this problem, in this paper, we propose the use of dual ionic thermosensitive polymers—cationic and anionic thermosensitive polymers—for TiO_2 suspended particles as a negatively charged model suspension. By using the anionic thermosensitive polymer in

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combination with the cationic thermosensitive polymer, a polymer complex forms. In other words, charge neutralization occurs. As a result, it can be expected that the transition temperature of the polymer adsorbed on the TiO_2 particles decreases, and that the hydrophobic interaction appears at a temperature relatively lower than the transition temperature of the cationic thermosensitive polymer [8].

Many researches on flocculation using dual polymeric flocculants have been published, and the dual polymer system has usually been used to produce large flocs [9,10]. Our concept of the use of dual ionic thermosensitive polymers is different from the numerous previous researches, as mentioned above.

2. Experimental

2.1. Preparation of cationic and anionic thermosensitive polymers

The cationic thermosensitive polymer was synthesized by copolymerizing the cationic component, *N,N*-dimethylaminopropylacrylamide (DMAPAA, Kohjin Co., Ltd., Japan) with NIPAM (Kohjin Co., Ltd., Japan). On the other hand, the anionic thermosensitive polymer was synthesized by copolymerizing acrylic acid (AAC, Katayama Chemical, Japan) with NIPAM. The mole fractions of DMAPAA and AAC in the syntheses of these copolymers were 0.1. These cationic and anionic thermosensitive polymers, poly(NIPAM-*co*-DMAPAA) and poly(NIPAM-*co*-AAC), are denoted as CP-10 and AP-10, respectively. Nonionic

poly(NIPAM) was also prepared for use as a control. These polymers were synthesized by radical polymerization by using *N,N,N′,N′*-tetramethylethylenediamine (Kanto Chem. Inc., Japan) and ammonium peroxodisulfate (Kanto Chem. Inc., Japan) as the polymerization accelerator and initiator, respectively. The procedures previously reported were used to prepare these polymers [7]. The synthesis conditions are listed in Table 1.

The molecular weights of CP-10 and AP-10 were not measured, but that of poly(NIPAM) was measured in the previous study, and it was approximately 4×10^6 [7].

The contents of the DMAPAA and AAC groups in these copolymers were analyzed using a colloidal titration method with 1/400 N potassium polyvinyl sulfate (PVSK, Wako Pure Chem. Ind., Ltd., Japan) by a procedure same as that reported in the previous paper [7]. The contents of DMAPAA and AAC in these copolymers were 10.1% and 12.6%, respectively.

2.2. Measurement of the transition temperatures of CP-10 and AP-10

The aqueous solution of a thermosensitive polymer is transparent below its transition temperature because the polymer molecules are hydrophilic and water soluble. However, the solution becomes milky white upon heating above the transition temperature because the polymer molecules become hydrophobic, and thus water insoluble. Therefore, the transition temperature can be estimated by a change in the transmittance through the polymer solution with temperature. The measurement procedure of the transmittance was the same as that used in the previous paper [7]. An aqueous polymer solution of 5 kg/m^3 was used, and the

transmittance was measured at 600 nm using a spectrophotometer equipped with a temperature-control system (V-530, Japan Spectroscopy Co., Ltd.). The measurements were performed under various pH conditions because it is well known that the transition temperatures of ionic thermosensitive polymers are pH dependent.

2.3. Measurement of zeta potential of TiO_2 particle

The zeta potentials of TiO_2 suspended particles (average particle size: 2.1 μm, Sigma-Aldrich Japan Co.) prepared under various pH conditions were measured using a streaming potential analyzer (ZP-20, Shimazu Co., Japan). The measurements were carried out in the presence of an electrolyte (0.01 M KCl), similar to the previous study [7]. An isoelectric point was observed at approximately pH 6; this was in good agreement with the value reported by Deng et al [11]. Since the zeta potential above pH 6 was negative, it was expected that CP-10 was effective for the flocculation and/or compaction of the TiO_2 suspension under neutral or weak alkaline conditions.

2.4. Compaction experiments

A highly concentrated TiO_2 suspension (250 kg/m^3) was used in order to clearly visualize the compaction. The pH of the suspension was adjusted to 8 with sodium hydroxide. The compaction experiment was carried out according to the method previously reported [1,7].

First, 60 ml of the TiO$_2$ suspension was stirred in a beaker using a magnetic stirrer at room temperature. Then, 20 ml of the CP-10 solution of the desired concentration was added to the suspension, and the mixture was stirred vigorously for several minutes. Subsequently, 20 ml of AP-10 solution of the desired concentration was added, and the mixture was stirred for several more minutes. The mixture was then transferred to a 100-ml cylinder, which was immersed in a water bath adjusted to the desired temperature. After the temperature of the mixture in the cylinder reached the desired value, a plunger was thrust into the mixture repeatedly at a constant speed (approximately 20 strokes/min) for 10 min. An acrylic resin bar of 10 mm in diameter was used as the plunger. The cylinder was allowed to stand for 30 min, and the sediment volume or volume of the compacted sludge was recorded. In this experimental range, the interface between the supernatant and the sediment sludge was clear.

2.5. Measurement of residual amount of CP-10 in the solution

In order to clarify the compaction mechanism of the TiO$_2$ suspension by using CP-10 or AP-10 in combination with CP-10, the residual amount of CP-10 in the solution was measured. The TiO$_2$ suspension was mixed well with the CP-10 and/or AP-10 solution of the desired concentration. Then, the mixture was centrifuged for 30 min at 4000 rpm, and the residual amount of CP-10 in the supernatant was measured by colloidal titration with 1/400 N PVSK solution.

3. Results and discussion

3.1. Transition temperatures of CP-10 and AP-10

Fig. 1 shows the change in the transmittance with temperature for the aqueous solutions of CP-10 and AP-10 under various pH conditions. The result for the nonionic poly(NIPAM) solution is also shown for comparison. The transmittance of the poly(NIPAM) solution changes drastically at around 32°C, the transition temperature of poly(NIPAM). The transition temperature of poly(NIPAM) was weakly dependent on the pH of the solution, though it is not shown here. On the other hand, the transition temperatures of CP-10 and AP-10 were strongly dependent on the pH of the solution. The transition temperature of CP-10 decreased with an increase in the pH of the solution, while that of AP-10 increased. The transition temperatures of these polymers were considerably high in the neutral pH region.

3.2. Effect of CP-10 dosage on sediment volume of TiO_2 suspension

Fig. 2 shows the effect of the dosage of CP-10 on the sediment volume at 30°C and 60°C. These temperatures are lower than the transition temperature of CP-10 at pH 8, as shown in Fig. 1. Therefore, at these temperatures, CP-10 is hydrophilic, and behaves like common polymeric flocculants. The sediment volume decreased with an increase in the dosage, and increased again with a further increase in the dosage. The optimum dosage was observed as

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similar as common polymeric flocculants. The decrease in the sediment volume was attributed to the formation of flocs, but no compaction of the TiO_2 particles was observed. A higher temperature is required for the compaction due to the hydrophobic transition of CP-10.

3.3. Effect of addition of AP-10 in combination with CP-10 on compaction of TiO_2 suspension

Fig. 3 shows the change in the sediment volume by the addition of AP-10 in combination with CP-10. The experiments were carried out at 60°C for three different initial dosages of CP-10—0.003, 0.005, and 0.01 kg/kg-TiO_2. The horizontal axis shows the sum of dosage of CP-10 and AP-10. The fine broken line in the figure shows the result obtained by using CP-10 only (see Fig. 2). When the initial dosage of CP-10 was 0.003 kg/kg-TiO_2, which is close to the optimum dosage of CP-10, the sediment volume increased due to the addition of AP-10. In other words, dispersion was encouraged by the addition of the anionic polymer. When the dosage of CP-10 was 0.005 kg/kg-TiO_2, which is an excess dosage, the sediment volume decreased by the addition of AP-10 and increased again with further addition. The optimum dosage of AP-10 was observed. Although the sediment volume at the optimum dosage of AP-10 was smaller than that obtained by using CP-10 only, no compaction was observed. In other words, the hard aggregate was not formed when a plunger was thrust. On the other hand, when the dosage of CP-10 was 0.01 kg/kg-TiO_2, the sediment volume decreased drastically by the addition of more than 0.003 kg/kg-TiO_2 of AP-10, and reached a minimum at around 0.005 kg/kg-TiO_2. By adding more AP-10, the sediment volume increased again. At the

minimum sedimentation volume, a very hard aggregate was obtained. In other words, the compaction was observed.

3.4. Residual amount of CP-10 in the solution

In order to elucidate the mechanism of compaction by adding AP-10 in combination with CP-10, the adsorption behaviors of CP-10 on the TiO_2 particles and/or interaction of CP-10 and AP-10 was examined. Fig. 4 shows the residual concentration of CP-10 in the solution. The broken line in the figure shows the relationship between the dosage of CP-10 and the residual concentration of CP-10 in the solution. As the dosage of CP-10 exceeded 0.003 kg/kg-TiO_2, residual CP-10 was observed in the solution. When the initial dosage of CP-10 was 0.01 kg/kg-TiO_2, the residual concentration of CP-10 in the solution was approximately 1.5 kg/m^3. At this point, the adsorbed amount of CP-10 on the TiO_2 particles estimated from the mass balance of CP-10 was approximately 0.0043 kg/kg-TiO_2. On the other hand, the solid line shows the change in the residual concentration of CP-10 in the solution by adding AP-10 in combination with CP-10, whose dosage was 0.01 kg/kg-TiO_2. By adding AP-10 the concentration of residual CP-10 decreased linearly. When the dosage of AP-10 was 0.005 kg/kg-TiO_2, the concentration of residual CP-10 became almost zero. Upon comparing with Fig. 3, the sediment volume did not decrease until the dosage of AP-10 exceeded 0.003 kg/kg-TiO_2. These results suggest that the added AP-10 was consumed to form a polymer complex with the residual CP-10 in the solution until the residual concentration of CP-10 in

the solution became sufficiently low.

3.5. Effect of residual CP-10 on sediment volume obtained by adding AP-10 in combination with CP-10

In order to clarify the effect of the residual CP-10 on the sediment volume by adding AP-10 in combination with CP-10, the residual CP-10 in the solution was removed, and then AP-10 was added. The removal of the residual CP-10 in the solution was carried out as follows: The TiO_2 suspension mixed with CP-10 was centrifuged for 30 min at 4000 rpm, and the supernatant containing the residual CP-10 was removed. The sedimented TiO_2 particles were dispersed again in an aqueous solution of pH 8. This procedure was repeated 2~3 times until no residual polymer was detected in the supernatant. The amount of CP-10 adsorbed on the TiO_2 particles before centrifugation was almost the same as that after the removal of CP-10 in the solution, which were estimated from the mass balance of CP-10 between the dosage and the detected amount of CP-10 in the solution. From this result, it was confirmed that the adsorbed polymer scarcely desorbed from the TiO_2 particles.

The results are shown by the solid line in Fig. 5. The initial dosage of CP-10 was 0.01 kg/kg-TiO_2. The broken line in the figure is the same as that shown in Fig. 3. By removing the residual CP-10, the sediment volume could be decreased drastically by adding a small amount of AP-10. These results support the above consideration. In other words, it is considered that the added AP-10 interacts directly with the CP-10 adsorbed on the TiO_2 particles, resulting in

a decrease in the optimum dosage of AP-10.

3.6. Change in zeta potential by adding AP-10 in combination with CP-10

Fig. 6 shows the relationship between the zeta potential and the polymer dosage. While measuring the zeta potential by the streaming potential method, a packed bed of TiO_2 particles was prepared by using the TiO_2 suspension from which the residual CP-10 was removed. The solid line in the figure shows the results obtained by adding CP-10 only. The zeta potential changed from a negative value to a positive value. On the other hand, the broken line in the figure shows the results obtained by adding AP-10 in combination with CP-10 (initial dosage of 0.01 kg/kg-TiO_2). The positive zeta potential now again became negative. The isoelectric point was obtained when the dosage of AP-10 was between 0.0005 and 0.001 kg/kg-TiO_2 (sum of dosage: 0.0105 and 0.011 kg/kg-TiO_2), which is smaller than the amount of CP-10 adsorbed on the TiO_2 particles, 0.0043 kg/kg-TiO_2 (see Sec. 3.4). This dosage corresponds to the optimum dosage of AP-10 shown in Fig. 4. In other words, the compaction occurs most effectively at the isoelectric point.

3.7. Effect of temperature on compaction by adding AP-10 in combination with CP-10

Fig. 7 shows the effect of temperature on the compaction by adding AP-10 in combination with CP-10. The initial dosage of CP-10 was 0.01 kg/kg-TiO_2, and the residual CP-10 in the

TiO$_2$ suspension was removed by the method mentioned above. Two different dosages of AP-10, i.e., 0.001 and 0.005 kg/kg-TiO$_2$, were used. The sediment volume decreased drastically at a certain temperature, which could be the transition temperature of the polymer complex of CP-10 and AP-10 adsorbed on the TiO$_2$ particles. These results support that the transition temperature of a cationic thermosensitive polymer decreases due to the formation of a polymer complex with an anionic thermosensitive polymer. The transition temperature for the AP-10 dosage of 0.005 kg/kg-TiO$_2$ was lower than that for the AP-10 dosage of 0.001 kg/kg-TiO$_2$ which corresponds to the isoelectric point as mentioned in Sec. 3.6. The transition temperature of the adsorbed polymer complex might be dependent on the pH of the suspension in addition to the ratio of CP-10 and AP-10 in the complex, because the pH of the suspension lowered to approximately 5 by adding 0.005 kg/kg-TiO$_2$ of AP-10.

4. Conclusions

The compaction method of the TiO$_2$ model suspension having a negative surface charge by using dual ionic themosensitive polymers was investigated. First, a cationic thermosensitive polymer, poly(NIPAM-*co*-DMAPAA) was added, followed by an anionic thermosensitive polymer, poly(NIPAM-*co*-AAC). By adding the anionic polymer, the compaction occurred through the formation of polymer complex of the cationic and anionic polymers at a relatively low temperature. In other words, the hard aggregate was obtained. However, in order to initiate the compaction, it was necessary to cover the surface of the TiO$_2$

particles sufficiently by the cationic polymer. This implies the cationic polymer residues in the solution. The anionic polymer added subsequently was consumed in neutralizing the residual cationic polymer in the solution. Therefore, the anionic polymer is more essential than the residual cationic polymer. The optimum dosage of the anionic polymer where the zeta potential of the TiO_2 particles covered with the polymer complex was almost zero was also observed. Furthermore, the transition temperature of the polymer complex adsorbed on the TiO_2 particles depended on the ratio of the dosages of the cationic and anionic polymers.

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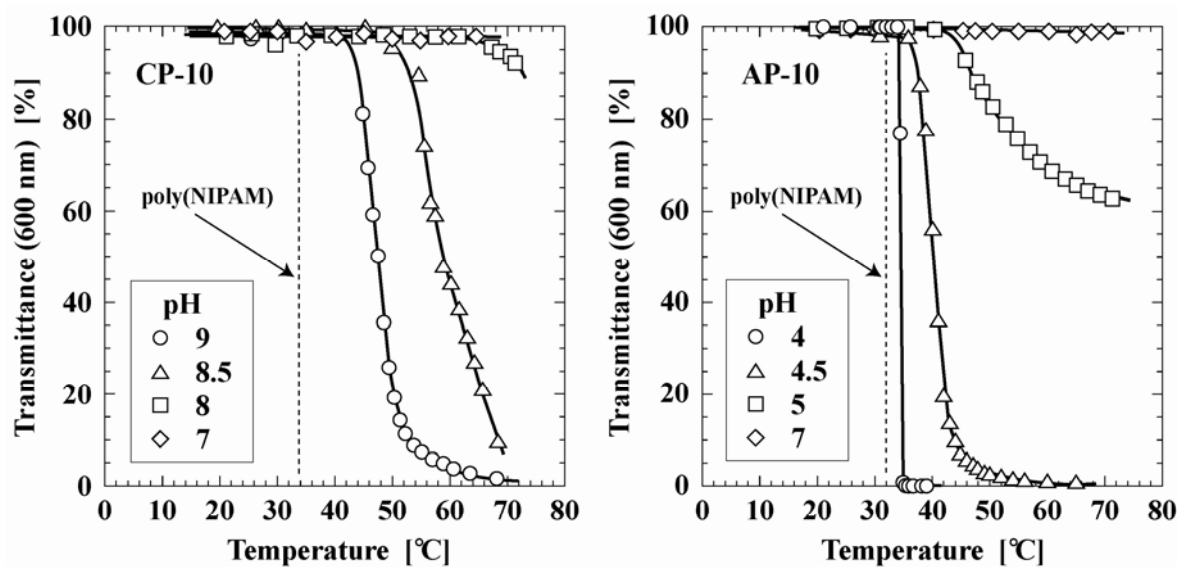
Figure captions

Fig. 1. Temperature dependence of transmittance for aqueous solutions of CP-10 and AP-10 at
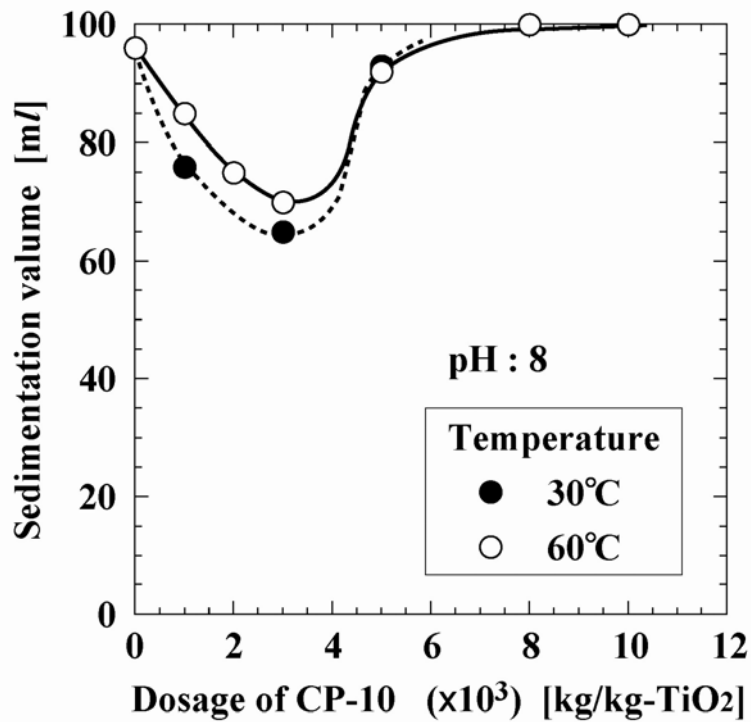
various pH.

Fig. 2. Effect of CP-10 dosage on sedimentation volume at 30°C and 60°C.
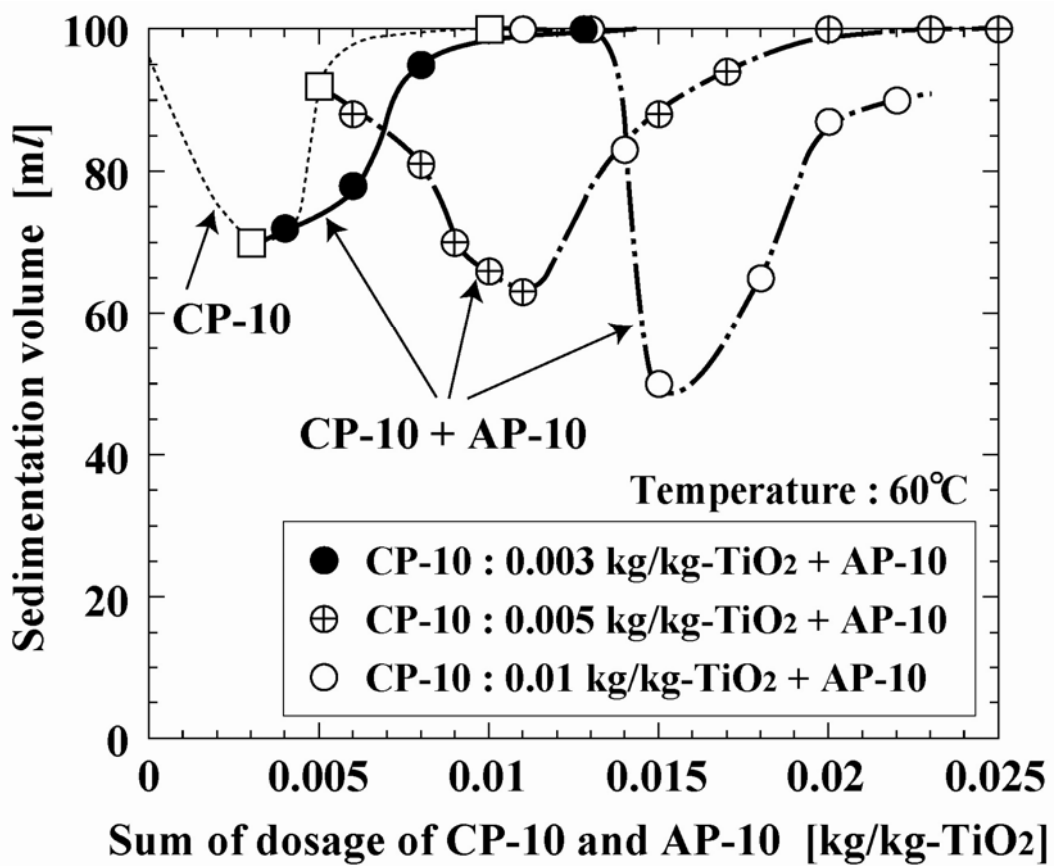
Fig. 3. Sedimentation volume by using AP-10 in combination with CP-10.

Fig. 4. Change in residual concentration of CP-10 in the solution.

Fig. 5. Compaction of TiO_2 suspensions with and without the residual CP-10.

Fig. 6. Change in ζ-potential of TiO_2 particles by adsorbing CP-10 and/or AP-10.

Fig. 7. Effect of temperature on compaction of TiO_2 suspension by adding AP-10 in

combination with CP-10.

Table

Table 1　Synthesis composition of poly(NIPAM), CP-10 and AP-10

		poly(NIPAM)	CP-10	AP-10
Monomer	： *N*-isopropylacrylamide (NIPAM)	1500	750	750
Co-monomer	： *N*,*N*-dimethylaminopropylacrylamide (DMAPAA)	—	82	—
	： Acrylic acid (AAC)	—	—	82
Accelerator	： *N*,*N*,*N′*,*N′*-tetramethylethylenediamine	6	6	6
Initiator	： Ammonium peroxodisulfate	2	2	2

Values are in mol/m^3, Temperature: 25°C

Figure

Fig. 1. Temperature dependence of transmittance through aqueous solutions of CP-10 and AP-10 at various pH.

Fig. 2. Effect of CP-10 dosage on sedimentation volume at 30℃ and 60℃.

Fig. 3. Sedimentation volume by using AP-10 in combination with CP-10.
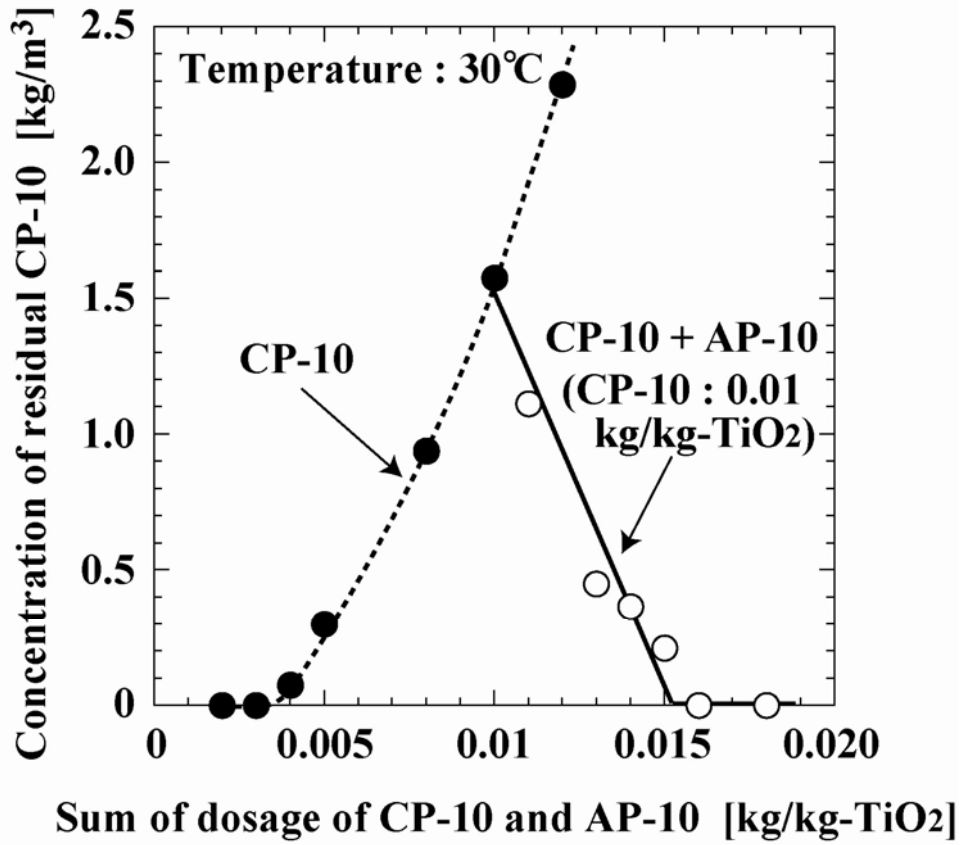
Fig. 4. Change of residual concentration of CP-10 in the solution.
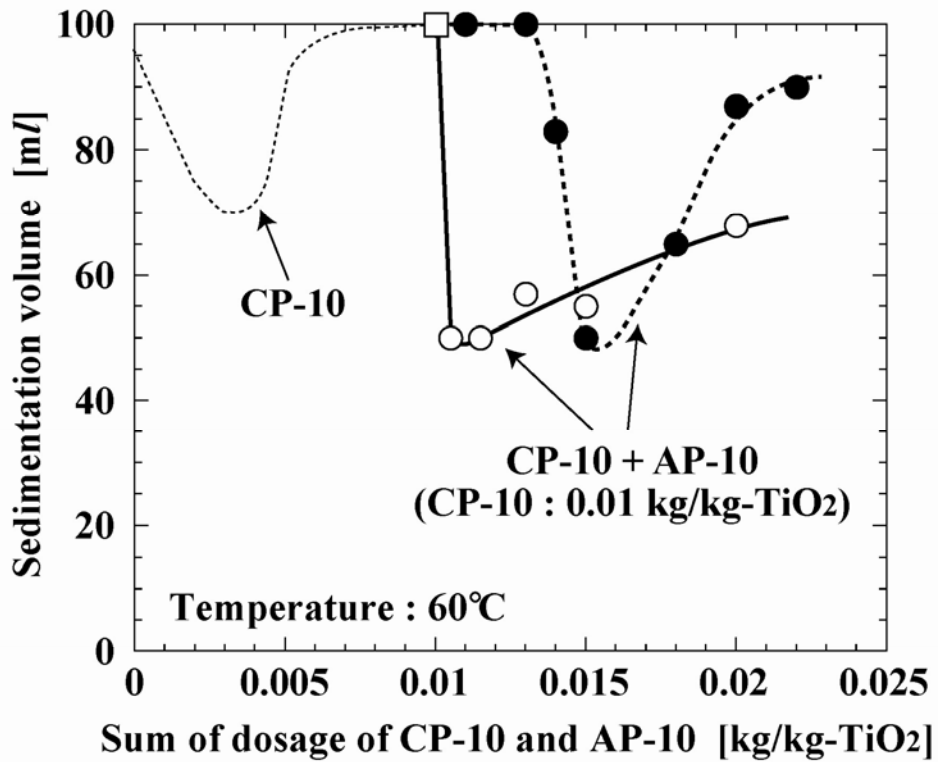

Fig. 5. Compaction of TiO2 suspenstions containing and non-containing the residual CP-10.
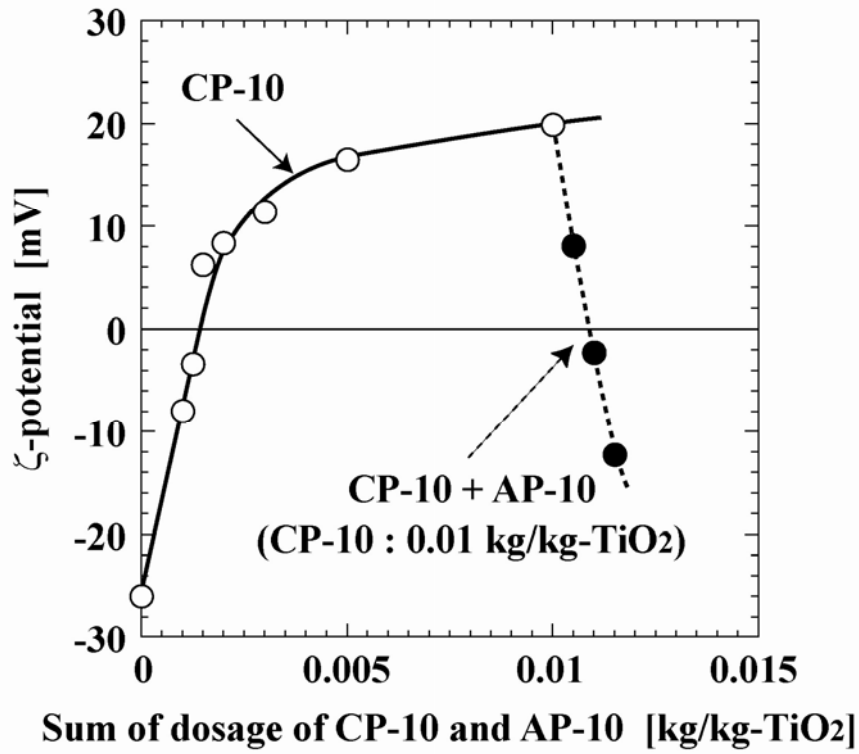
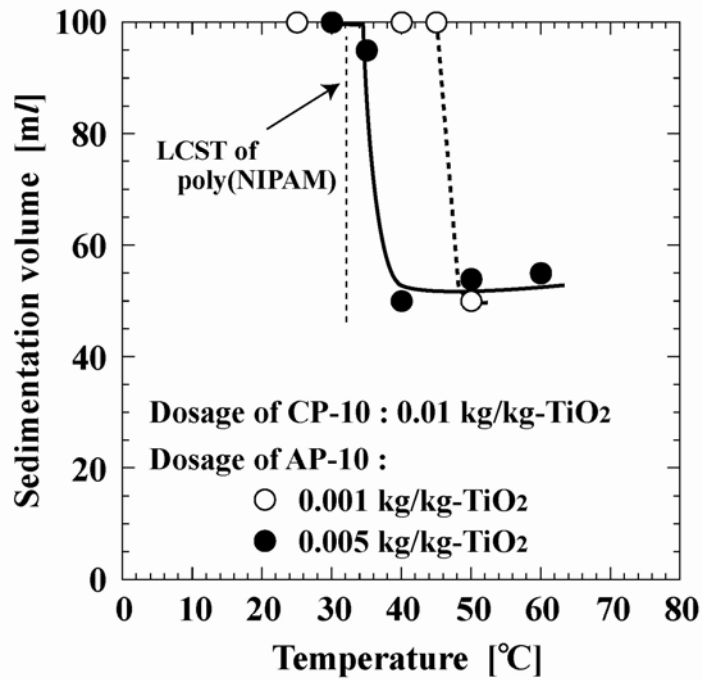Fig. 6. Change of ζ-potenstial of TiO$_2$ particles by adsorbing of CP-10 and/or AP-10.

Fig. 7. Effect of temperature on compaction of TiO$_2$ suspension by adding AP-10 in combination with CP-10