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AQUEOUS SOLUTION CONTAINING HYDROPHILIC  
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# DISPERSION AND FLOCCULATION OF $\alpha$ - $\text{Al}_2\text{O}_3$ IN AQUEOUS SOLUTION CONTAINING HYDROPHILIC POLYMERS

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## Abstract

The effect of polyacrylic acid on the dispersion and flocculation behavior of  $\text{Al}_2\text{O}_3$  in aqueous solution was investigated. The stability of  $\text{Al}_2\text{O}_3$  suspension was evaluated from the measurements of average particle size, turbidity, sedimentation volume and viscosity. The dispersion and flocculation behavior of  $\text{Al}_2\text{O}_3$  was explained by measuring the adsorption amount of the polyacrylic acid and the zeta potential of  $\text{Al}_2\text{O}_3$ . When the adsorption of polyacrylic acid on  $\text{Al}_2\text{O}_3$  is saturated, the dispersion of  $\text{Al}_2\text{O}_3$  is enhanced. It is evident that the conformation of the polymer is a controlling factor in determining the stability of  $\text{Al}_2\text{O}_3$  particles. The addition of polyacrylic acid with a molecular weight of 6000 gives the best dispersion state among the various polyacrylic acids of different molecular weights used in our experiments.

## 1. Introduction

Oxide particles are used in many industrial manufacturing processes: paints, cosmetics, ceramics, electronics, the inorganic chemical industry etc.<sup>1)~4)</sup>. Colloidal stability is a key interfacial parameter that controls the performance of products. Highly dispersed particles are desirable in most of these processes. For the waste water treatment, on the other hand, it is necessary to aid the solid-liquid separation by increasing particle size with flocculation<sup>5)</sup>.

According to the D.L.V.O. theory, dispersion and flocculation of oxide particles is determined by the balance between the repulsive force due to electrical charge and van der Waals attractive force. In general, the surface charge on particles can be changed to control the stability of suspension, because van der Waals attraction energy between particles, which is a universal parameter, is almost

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impossible to be varied. When hydrophilic polymers such as polyacrylic acid and polyacryl amide are added to suspensions, the electrical charge and the steric hindrance effect result in dispersion of particles. The adsorbed layer of polymers would serve to protect from the approach of particles. From the manufacturing viewpoint, the steric stabilized system is more advantageous than the electrostatic stabilized system alone<sup>6)</sup>.

Polymer substances work as dispersants or flocculants, depending on the amount of polymer added and the molecular weight. Whether polymer works as a dispersant or a flocculant is mainly dependent on the structure of the polymers. Though the conformation and orientation of adsorbed polymers on the particles has not been clarified yet, it is important to establish the method to grasp the behavior of polymers.

In this study, the dispersion and flocculation of  $\alpha$ - $\text{Al}_2\text{O}_3$  in aqueous solution was investigated in the presence of polyacrylic acid. The stability of dispersion of the particles in polymer aqueous solution was examined by changing the amount of polymer added, the molecular weight of polymer, and the pH as a parameter. Both the adsorption behavior of polyacrylic acid and the effect of the polymer adsorption layer on  $\alpha$ - $\text{Al}_2\text{O}_3$  were investigated. Various measurements on the physical properties of slurry, such as particle size, light transmittance, sedimentation volume, and viscosity were carried out in order to establish an evaluation method for stability of the slurry.

## 2. Experimental

### 2.1 Reagents

$\alpha$ - $\text{Al}_2\text{O}_3$  (Sumitomo Chemical Ltd.) was selected as the model particle in this study. It has a 0.5  $\mu\text{m}$  mean size with specific surface area (BET) of 7.1  $\text{m}^2/\text{g}$ . Polyacrylic acid (PAA) was used as a surface active reagent, which has molecular weight of 2000, 6000, 20000 and 450000 with straight chains of  $\text{CH}_2\text{CH}(\text{CO}_2\text{H})$ . The PAA chain may have either neutral or negative charge by dissociation according to the following equation:



HCl and NaOH were used to adjust pH, and NaCl was used to maintain ionic strength.

## 2.2 Experimental method

0.4 g of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was added to 20 ml of water in a centrifuge tube with a glass stopper, the suspension of a certain pH value was prepared and the tube was shaken for 30 min. A definite amount, 20 ml of PAA solution, which has the same pH value of the Al<sub>2</sub>O<sub>3</sub> suspension already prepared, was added to the Al<sub>2</sub>O<sub>3</sub> suspension in order to maintain the final solid content to be 1 wt%. The mixture was then shaken for 24 hours. A part of the suspension was sampled, and the particle size of Al<sub>2</sub>O<sub>3</sub> was measured by means of a Laser Scattering Particle Size Distribution Analyzer LA-910 (Horiba Ltd.).

Zeta potential measurements of Al<sub>2</sub>O<sub>3</sub> were carried out by using micro-electrophoresis, Zeta-Meter ZM-80, (Zeta Meter Ltd.). The solid content in the slurry was 0.01 wt% for zeta potential measurements.

For the investigation of PAA adsorption on the particles, a suspension with solid content of 10 wt% in the presence of various concentrations of PAA was made to attain equilibrium by using a reciprocal shaker for 24–48 hours. Then it was centrifuged for 1 hour at 3000 rpm. The clear supernatant solution of 20 ml was removed, and then NaCl solution was added to supernatant solution so that the resultant volume was 40 ml. Each sample was adjusted to pH 2.6 with HCl. The amount of PAA remaining was determined by a potentiometric titration.

Turbidity of Al<sub>2</sub>O<sub>3</sub> suspension was measured using 1.0 wt% Al<sub>2</sub>O<sub>3</sub> suspension. The suspension was shaken for 24 hours and left to rest for another 24 hours. The supernatant solution of 6 ml was sampled and measured with a Sphere Method Turbidi Meter, Type SED-PT (Nippon Precision Optical Instrument Co., Ltd.).

Sedimentation volume measurements were performed using 15 wt% Al<sub>2</sub>O<sub>3</sub> suspension after shaking for 24 hours and leaving for another 24 hours.

## 3. Results and Discussion

It is important for certain manufacturing processes to know how to measure and evaluate the extent of dispersion and flocculation of particles. In this study, the stability of an Al<sub>2</sub>O<sub>3</sub> suspension was evaluated by measuring the physical properties of the suspension: an average particle size of Al<sub>2</sub>O<sub>3</sub>, zeta potential, turbidity of Al<sub>2</sub>O<sub>3</sub> suspension, sedimentation volume and apparent viscosity. The results of the measurements are shown in Fig. 1 as a function of pH. The point of zero charge (abbreviated P.Z.C.) of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> used in this study is found at pH 8.3. In both of the higher and lower pH regions than P.Z.C., the absolute value



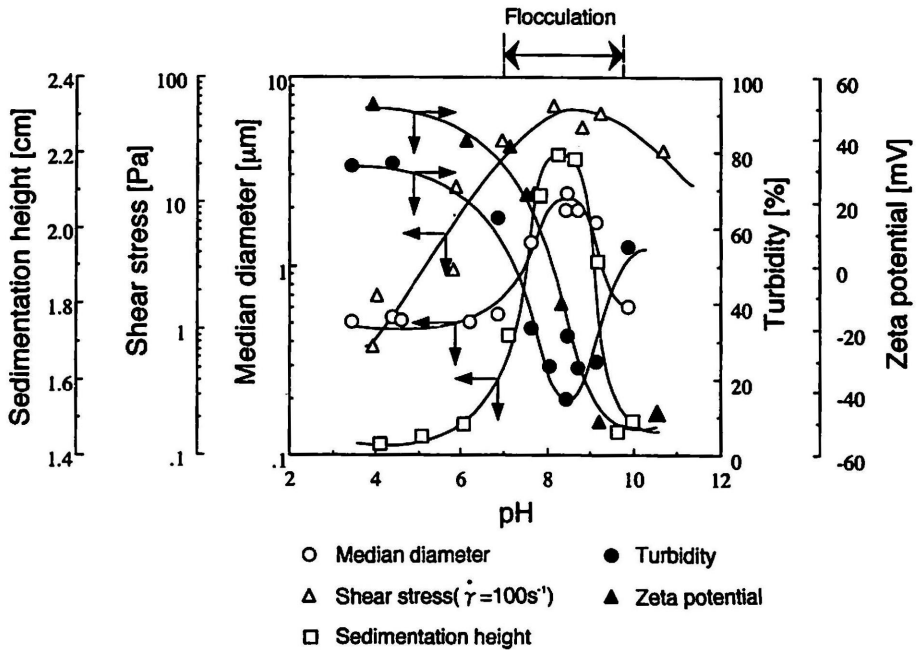


Fig. 1 Evaluation of flocculation and dispersion of  $\alpha\text{-Al}_2\text{O}_3$  slurry by various measurements

of zeta potential increases because of either protonation or deprotonation of the  $\alpha\text{-Al}_2\text{O}_3$  surface. In the pH region where electrical potential shows over  $\pm 25\text{mV}$ , slurry with good dispersion is obtained, in which about  $0.5\mu\text{m}$  of the average particle size of  $\alpha\text{-Al}_2\text{O}_3$  is measured. On the other hand, in the pH region around P.Z.C., the  $\alpha\text{-Al}_2\text{O}_3$  particles are flocculated to give an average particle size of about  $2.5\mu\text{m}$ . It is thought that flocculation might occur, since van der Waals attractive force is stronger than the electrical repulsive force in the pH around P.Z.C.. It is found that physical properties such as particle size, viscosity, turbidity and sedimentation volume, which are chosen as measures for evaluation of the extent of dispersion and flocculation of the slurry, give the same results as to the extent of dispersion and flocculation. When the slurry is in dispersion state, viscosity is seen to be low and turbidity of the slurry to be higher. As the particles are closely packed in the dispersion state, the sedimentation volume has a small value. On the other hand, the viscosity is higher and turbidity lower when the slurry is in the flocculation state. Since the floc is not closely packed, the sedimentation volume has a big value. Thus, some different measurements give

us the same results. These measuring methods were therefore found to be useful for evaluating particle behavior in aqueous solution.

Figure 2 shows the mean particle size of  $\alpha\text{-Al}_2\text{O}_3$  in the suspension as a function of the concentration of PAA2000. In the presence of PAA2000, the flocculation and dispersion of  $\alpha\text{-Al}_2\text{O}_3$  particles are affected greatly by the change in pH value and the amount of added PAA2000. When the concentrations of PAA2000 are as low as 10–70 ppm, the pH value which shows maximum median particle size decreases with an increase in PAA2000 concentration. As compared with the experiments in the absence of PAA2000, the range of pH where  $\alpha\text{-Al}_2\text{O}_3$  particles flocculate is broader and the median diameter of flocculated  $\text{Al}_2\text{O}_3$  particles is three times longer. When the concentration of PAA2000 is more than 100 ppm, a good dispersion of  $\alpha\text{-Al}_2\text{O}_3$  particles of particle size  $0.5\mu\text{m}$  is obtained.

It is important in this study to clarify the effect of repulsive force on the dispersion behavior of  $\alpha\text{-Al}_2\text{O}_3$  particles. The zeta potential of  $\alpha\text{-Al}_2\text{O}_3$  in the presence of PAA2000 is shown in Fig. 3 as a function of pH. In the PAA2000 concentration of 0.01–0.7 ppm, which corresponds to 1.0–70 ppm in Fig. 2, the

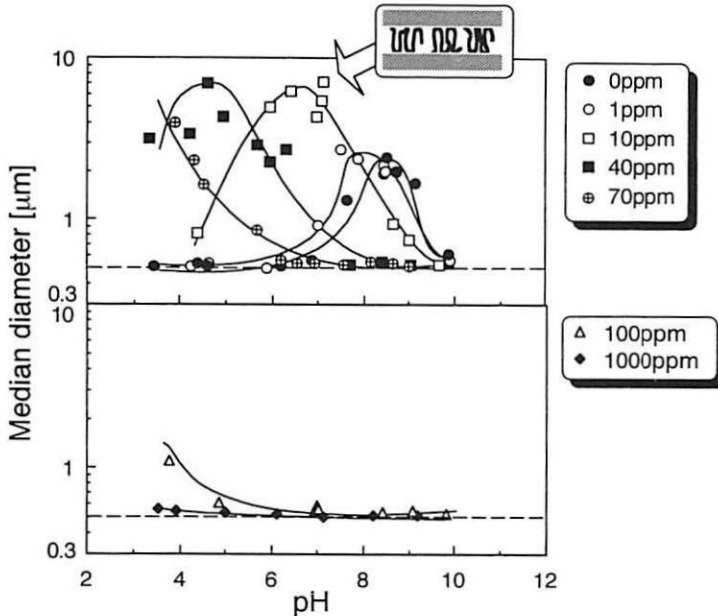


Fig. 2 Dispersion and flocculation of  $\text{Al}_2\text{O}_3$  in the presence of PAA2000 (Solid content 1 wt%)

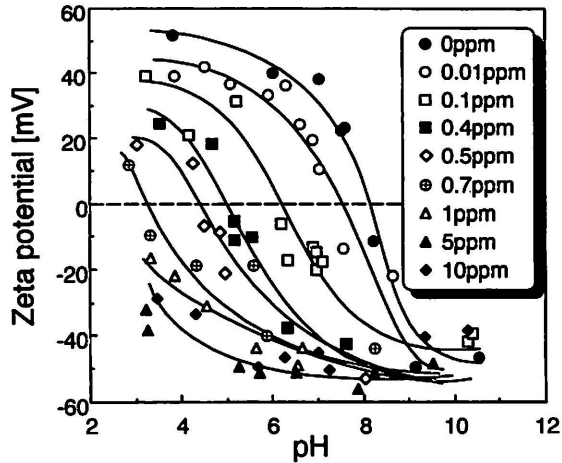
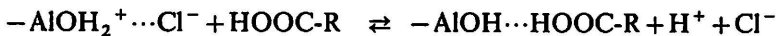


Fig. 3 Zeta potential of  $\text{Al}_2\text{O}_3$  in the presence of PAA2000 (Solid content: 0.01 wt%)

pH of P.Z.C. falls with an increase in the PAA2000 concentration. These results agree well with the results represented in Fig. 2. The decrease in zeta potential is very significant in the acidic pH range where  $\text{Al}_2\text{O}_3$  is positively charged and the polymer is negatively charged. A similar decrease in zeta potential of oxide particles after adsorption of polymer has been reported by Gebhardt et al.<sup>7)~10)</sup>. Because it is considered that this decrease in zeta potential of  $\text{Al}_2\text{O}_3$  is caused by adsorption of PAA on the  $\text{Al}_2\text{O}_3$  surface, the dissolved state of PAA is thought to considerably affect both the zeta potential of  $\text{Al}_2\text{O}_3$  and the adsorption of PAA. The dissolved state of PAA was determined by a potentiometric titration. Figure 4 shows the fraction of dissociated acid group as a function of pH. Carboxylic acid groups of PAA are dissociated at the rate of 50% in pH 5.9. When the dissolved state of PAA is considered, dissociated PAA may interact with surface hydroxyl groups on  $\text{Al}_2\text{O}_3$  as follows,



This reaction can explain the shift of the  $\text{pH}_{\text{P.Z.C.}}$  and the lowering of the positive charge of  $\text{Al}_2\text{O}_3$  obtained in this study. It can be concluded from Figs. 2 and 3 that the small addition of PAA2000 (10–70 ppm) neutralizes the surface charge

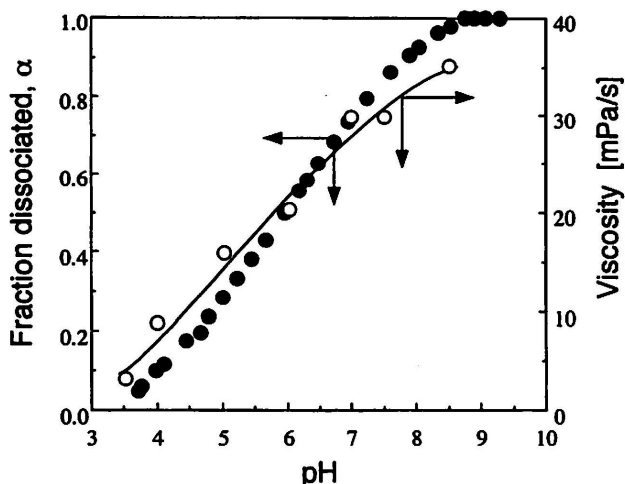


Fig. 4 Dissociated fraction diagram of PAA and viscosity of 0.5 wt% PAA450000 solution as a function of pH

and induces flocculation of  $\text{Al}_2\text{O}_3$ . However, when the concentration of added PAA2000 is as low as 10–70 ppm, flocculation occurs even though the zeta potential is higher than  $\pm 25$  mV. Furthermore, the stronger flocculation of  $\text{Al}_2\text{O}_3$  with PAA2000 can be produced compared with  $\text{Al}_2\text{O}_3$  in the absence of PAA at  $\text{pH}_{\text{P.Z.C.}}$ . The behavior of  $\text{Al}_2\text{O}_3$  shows the effect of the adsorption layer of PAA on  $\text{Al}_2\text{O}_3$  as well as the decrease in zeta potential. The strong flocculation occurs due to the fact that the incomplete adsorption results in polymer bridging formation where two or more particles can be mutually adsorbed in the polymer chain. On the other hand, when the concentration of PAA added is as high as 10 ppm, which corresponds to 1000 ppm in Fig. 2, the zeta potential of  $\text{Al}_2\text{O}_3$  becomes negative enough, about  $-40$  mV, over a wide pH range. These results are caused by the adsorption of dissociated PAA molecules. Compared with Fig. 2, good dispersion of  $\text{Al}_2\text{O}_3$  can be obtained in the region of high concentration of PAA2000. It is assumed that a strong electrical repulsive force in magnitude of  $-40$  mV zeta potential may contribute to this trend.

The adsorption isotherms of PAA2000 on  $\text{Al}_2\text{O}_3$  at various pH values are shown in Fig. 5. The amount of PAA2000 adsorbed increases with increasing polymer concentration and reaches a plateau. The adsorption of PAA on  $\text{Al}_2\text{O}_3$  is strongly dependent on aqueous pH. The amount absorbed increases with a decrease in pH and as the pH of suspension increases, the plateau of adsorption

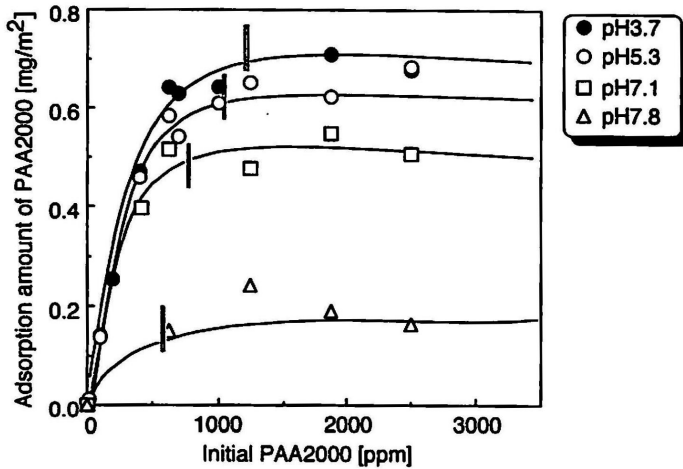


Fig. 5 Adsorption isotherm of PAA2000 on  $\text{Al}_2\text{O}_3$   
(Solid content: 10 wt%)

can be seen at lower concentration of PAA. One of the factors for dependence of the pH of suspension on the amount of adsorbed PAA may be as follows<sup>11),12)</sup>. In considering the relationship between the dissolved state of PAA and the viscosity of PAA solution shown in Fig. 4, we see that the viscosity of PAA solution increases when PAA molecules are dissociated. The viscosity of PAA in stretched state is higher than that in coiled state. As the pH is increased, the negatively-charged sites of PAA also increase, resulting in enhanced intermolecular electrostatic repulsion. The form of PAA stretches more at high pH range. When the pH is decreased and the fraction of dissociated PAA,  $\alpha$ , approaches zero, PAA chains become uncharged and exist in coiled state form, which increases the formation of loops in adsorbed configurations. Thus the projected surface area per adsorbed chain is relatively small.

From the above, we consider that the amount of PAA adsorbed increases at lower pH. It can be found from Figs. 2, 3 and 5 that when the amount of PAA2000 adsorbed on  $\text{Al}_2\text{O}_3$  is unsaturated,  $\text{Al}_2\text{O}_3$  particles flocculate, while saturated adsorption of PAA2000 results in greater stability of  $\text{Al}_2\text{O}_3$  dispersion. It is concluded that there is a close relationship between adsorption of PAA and the stability of  $\text{Al}_2\text{O}_3$  suspension.

An attempt was made to estimate the configuration of adsorbed PAA. The area occupied by one segment of PAA in close-packed monolayer is assumed to be  $26\text{\AA}^2$ <sup>13)</sup>, and a specific surface area of  $\text{Al}_2\text{O}_3$  is measured to be  $7.1\text{ m}^2/\text{g}$ . If

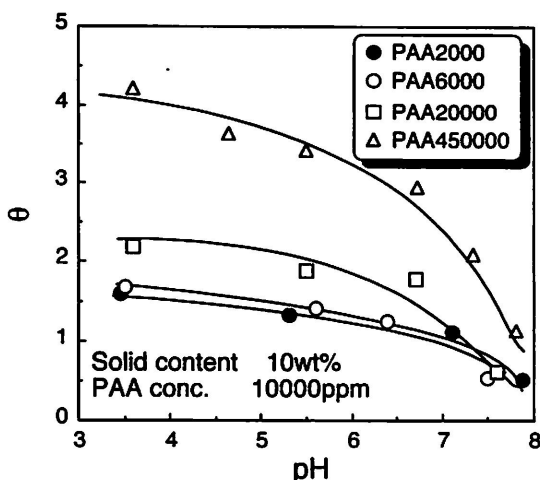


Fig. 6 Relationship between  $\theta$  and molecular weight of PAA as a function of pH

the monolayer adsorption of PAA on  $\text{Al}_2\text{O}_3$  is calculated from these values, the theoretical monolayer adsorption would be  $0.461 \text{ mg/m}^2$ . The value of  $\theta$  is calculated by dividing the experimental adsorption amount of PAA by the theoretical monolayer adsorption,  $0.461 \text{ mg/m}^2$ . The results obtained are represented in Fig. 6. For the system of  $\text{Al}_2\text{O}_3/\text{PAA2000}$ , the value of  $\theta$  is equal to 1.6 at pH 3.8, which suggests that PAA molecules are adsorbed on the  $\text{Al}_2\text{O}_3$  surface in the form of loops and tails. The difference in the amount of adsorbed PAA between a molecular weight of 2000 and other molecular weights is bigger in the acidic pH region. The difference in the adsorbed amount of PAA with each molecular weight is small at higher pH around 8. The results show that the adsorption layer of PAA first forms loops and tails on  $\text{Al}_2\text{O}_3$  and is thickest at pH 4, while an increase in pH to 8 causes the conformation of PAA to change from loops and tails to a flat one: in other words, a more stretched layer. As shown in Fig. 6, the increase in the adsorption amount is observed with increasing molecular weight of PAA. It indicates that the thickness of adsorbed layer is greatest at the same pH as when the molecular weight of PAA increases. Changes in the conformation of adsorbed PAA2000 due to the increase in pH are illustrated in Fig. 7.

The effect of the conformation of PAA on the stability of  $\text{Al}_2\text{O}_3$  is discussed below. The stability of dispersion of  $\text{Al}_2\text{O}_3$  is determined by turbidity measurement of supernatant solution, as shown in Fig. 8. The turbidity of  $\text{Al}_2\text{O}_3$  suspension in the absence of PAA2000 is lowest at a pH around P.Z.C.. This is because the

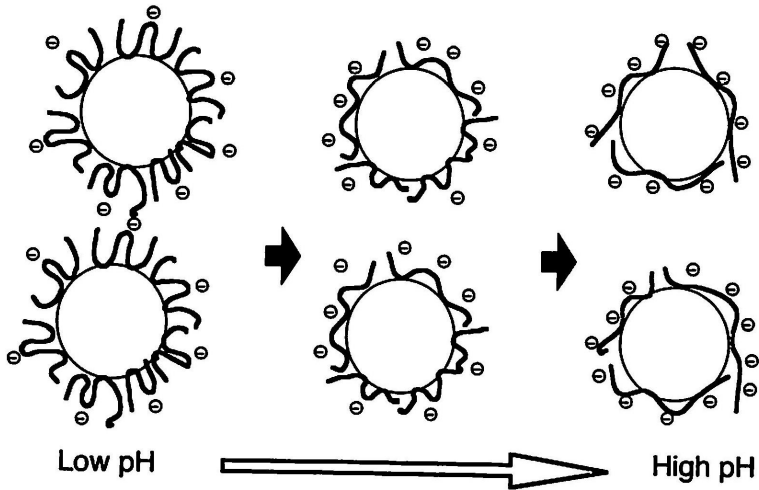


Fig. 7 Adsorption model of PAA2000

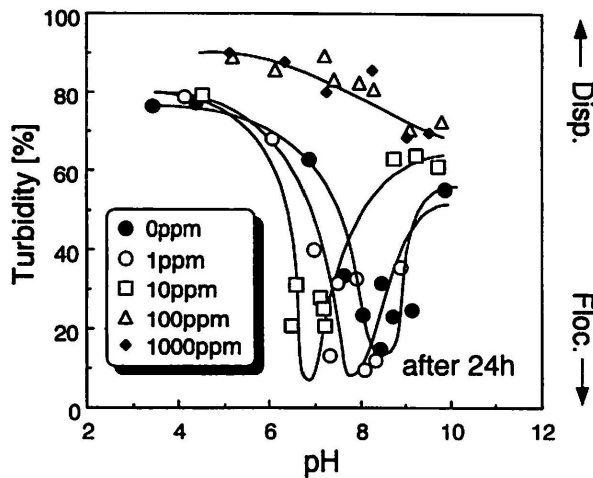


Fig. 8 Turbidity of  $\text{Al}_2\text{O}_3$  slurry at different PAA2000 concentrations as a function of pH  
(Solid content: 1 wt%)

sedimentation rate of  $\text{Al}_2\text{O}_3$  is very fast due to flocculation. The turbidity of  $\text{Al}_2\text{O}_3$  suspension is higher, more than 60%, and a good dispersion is observed at a wide pH range in the presence of PAA2000 at 1000 ppm, where the adsorption conformation of PAA2000 is estimated, as shown in Fig. 7. The data are in good

agreement with those in Fig. 2. As is obvious from Fig. 8, the increase in pH of the suspension causes a slight decrease in the turbidity of the  $\text{Al}_2\text{O}_3$  suspension. The results indicate that the stability of the system in the higher pH regions, for example around pH 8, decreases and displays a stronger tendency to flocculate than in the acidic pH region, for example around pH 4. Taking account of the adsorption conformation of PAA on  $\text{Al}_2\text{O}_3$  estimated in Fig. 7 and the zeta potential of  $\text{Al}_2\text{O}_3$  shown in Fig. 3, the steric hindrance effect must play a big role as a new parameter of dispersion force in the lower pH range, where the adsorption layer is in the form of loops and tails. Electrical repulsion must also greatly influence the zeta potential of  $-20$ – $-30$  mV. Although electrical repulsion is very large in the higher pH where  $\text{Al}_2\text{O}_3$  particles have a greater negative charge,  $-40$  mV, the steric hindrance effect is negligible because of the flat conformation of the adsorption layer. It is concluded that the steric hindrance effect with polymeric adsorption layer greatly influences the stability of  $\text{Al}_2\text{O}_3$  suspension because the dispersion of  $\text{Al}_2\text{O}_3$  particles in the lower pH region (pH 4) is better than the dispersion in the higher pH region (pH 8).

The effect of the thickness of the PAA adsorbed layer on the stability of  $\text{Al}_2\text{O}_3$  was investigated. Figure 9 shows the relationship between the molecular weights of PAA and the sedimentation volume of the  $\text{Al}_2\text{O}_3$  slurry in the PAA concentration range of 15000 ppm (corresponding to 1000 ppm in Fig. 2), where

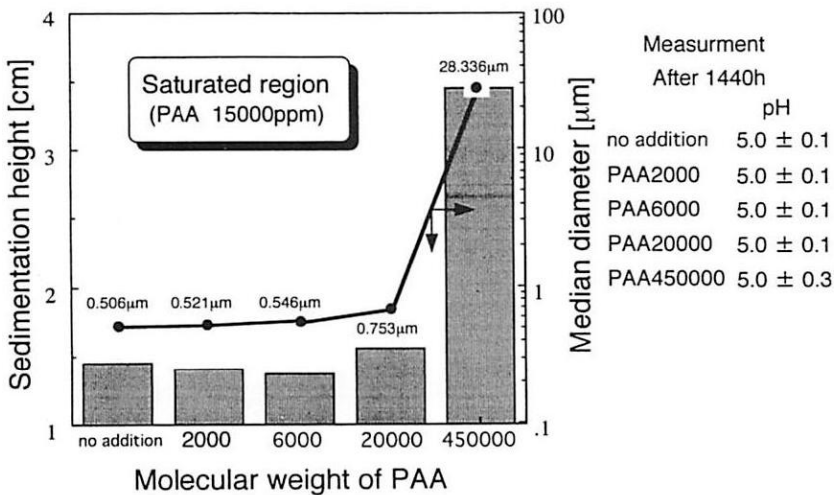


Fig. 9 Relationship median diameter and sedimentation height of  $\text{Al}_2\text{O}_3$  at various molecular weights of PAA



the adsorption of PAA on the  $\text{Al}_2\text{O}_3$  reaches saturation. In considering Fig. 6, the thickness of adsorbed layer of PAA is seen to increase with an increase in the molecular weight of PAA. The stability of dispersion of  $\text{Al}_2\text{O}_3$  in the presence of PAA with different molecular weight is determined from sedimentation volume. The sedimentation volume in a well-dispersed case should show small volume, because of close packing. The sedimentation volume of  $\text{Al}_2\text{O}_3$  in the presence of PAA6000 shows the lowest value. So, PAA6000 would seem to be the best dispersant amongst the different PAA used in our experiments. The sedimentation volume of the slurry containing PAA450000 is higher than the others, and PAA450000 works as a flocculant. The reason is thought to be that PAA molecules involve some  $\text{Al}_2\text{O}_3$  particles, since PAA20000 and 450000 are polymers with such long chains that the chain length is longer than that of  $\text{Al}_2\text{O}_3$  particles. Figure 10 shows the sedimentation volume of  $\text{Al}_2\text{O}_3$  in the presence of the PAA with different molecular weight at a PAA concentration of 150 ppm (corresponding to 1000 ppm in Fig. 2), where the adsorption of PAA is unsaturated. In Fig. 10 the pH of the slurry is adjusted to the pH of P.Z.C.. Although there exists an optimum molecular weight for the minimum sedimentation volume in the saturated adsorption range shown in Fig. 9, the sedimentation volume of  $\text{Al}_2\text{O}_3$  increases with an increase in the molecular weight of PAA in the unsaturated adsorption range shown in Fig. 10. Whether

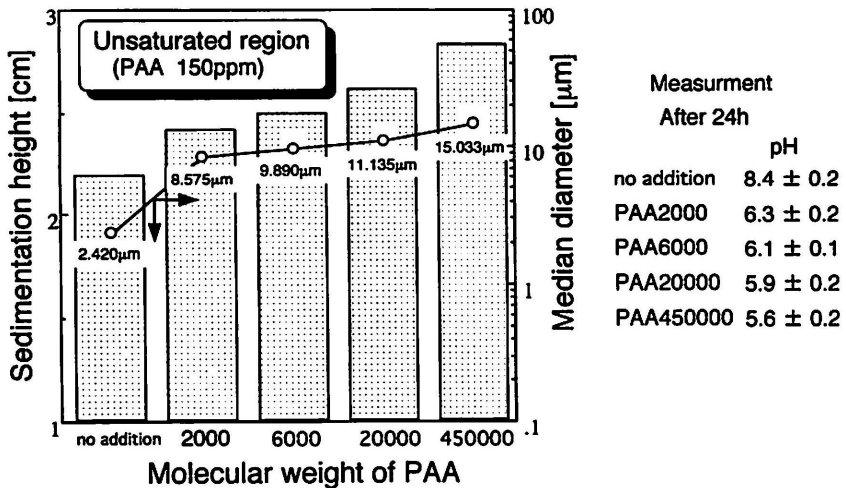


Fig. 10 Relationship median diameter and sedimentation height of  $\text{Al}_2\text{O}_3$  at various molecular weights of PAA

the adsorption of PAA reaches saturation or not, and how big the PAA molecules are compared with the size of suspended particles, are both important factors in determining the effect of the molecular weight of PAA on the stability of Al<sub>2</sub>O<sub>3</sub>.

### Conclusion

The dispersion and flocculation behavior of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in aqueous solution was investigated, both in the absence and the presence of polyacrylic acid. The stability of dispersion of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in aqueous solution was examined by changing the amount of polymer added, the molecular weight of polymer and the pH value used as a parameter. The adsorption behavior of polyacrylic acid on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the effect of the polymer adsorption layer were investigated.

The results obtained are summarized as follows.

- 1) The measurements of average particle size of Al<sub>2</sub>O<sub>3</sub>, turbidity of Al<sub>2</sub>O<sub>3</sub> suspension, sedimentation volume and apparent viscosity of Al<sub>2</sub>O<sub>3</sub> slurry are effective methods for evaluation of the dispersion and flocculation characteristics of Al<sub>2</sub>O<sub>3</sub> suspension.
- 2) The adsorption of PAA on Al<sub>2</sub>O<sub>3</sub> causes the zeta potential of Al<sub>2</sub>O<sub>3</sub> to change and shift the P.Z.C. to the acidic pH range.
- 3) The adsorption behavior of PAA on Al<sub>2</sub>O<sub>3</sub> depends on the pH of the suspension. As the pH is decreased, the adsorption of PAA increases and reaches a plateau at higher PAA concentrations.
- 4) When the adsorption of PAA on Al<sub>2</sub>O<sub>3</sub> particles is saturated, the dispersion of Al<sub>2</sub>O<sub>3</sub> in the suspension is enhanced by the steric hindrance effect compared with the suspension stabilized electrostatically without PAA. On the other hand, when the adsorption of PAA on Al<sub>2</sub>O<sub>3</sub> is unsaturated, Al<sub>2</sub>O<sub>3</sub> particles are strongly flocculated by the neutralization of electric charge and the bridging effect.
- 5) The adsorption conformation of PAA can be controlled by the pH of the suspension. The adsorption layer of PAA forms loops and tails at pH 4, while an increase in pH causes the conformation of PAA to change from loops and tails to flat. It is evident that the conformation of PAA is a major controlling factor for the stability of Al<sub>2</sub>O<sub>3</sub> suspension.
- 6) In the saturated adsorption region, PAA6000 is the best dispersant amongst the various PAA with different molecular weights used in our experiments. In the unsaturated adsorption region, on the other hand, PAA acts as a strong flocculant, as molecular weight increases.

## Reference

- 1) F. Kitahara, *Bunsan Gyosyu no Kaimai to Oyogijutsu*, Techno System Co., (1992), (In Japanese)
- 2) I. A. Aksay, F. F. Lange and B. I. Davis, *J. Am. Ceram. Soc.*, **66**[10], 190–192, (1983)
- 3) Aluminum Company of America, *Product Data-Alcoa Reactive Aluminas*, Pittsburgh PA (1972)
- 4) Y. Turitani and M. Koishi, *Kogyo Bunsan Gijutsu*, Nikkan Kogyosinbunsha, (1986), (In Japanese)
- 5) J. Shibata and H. Tamakoshi, *Kagaku Kougaku Ronbunshu*, **20**[5], 701–707, (1994), (In Japanese)
- 6) F. Kitahara and K. Furusawa, *Saishin Koroido Kagaku*, Kondansha, (1990), (In Japanese)
- 7) J. E. Gebhardt and D. W. Fuerstenau, *Colloids and Surfaces*, **7**, 221–231, (1983)
- 8) K. N. Han, T. W. Healy and D. W. Fuerstenau, *J. Colloid and Interface Science*, **44**[3], 175–180(1973)
- 9) T. Sato, *J. Applied Polymer Science*, **7**, 224–231, (1973)
- 10) G. Girod and J. M. Lamarche, A. Foissy, *J. Colloid and Interface Science*, **121**[1], 265–272, (1988)
- 11) J. Cesarano and I. A. Aksay, *J. Am. Ceram. Soc.*, **71**[4], 250–255, (1983)
- 12) K. F. Tjipangandjara and P. Somasundaran, *Adv. Powder Technol.*, **3**[2], 119–127, (1992)
- 13) S. Chiowski, *J. Colloid and Interface Science*, **140**[2], 444–449, (1990)