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Effects of Poly(acrylic acid) and Poly(ethylene oxide) Adsorption on the Stability of Alumina Suspension

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Abstract−The effect of adsorbed polymer on the stability of alumina suspension was investigated. Poly(ethylene oxide) (PEO), poly(acrylic acid) (PAA) and similar kinds of polymer salts were used as a dispersant. The amount of polymer adsorbed on alumina surface and the suspension stability was measured. The pH, molecular weight, and concentration were considered as experimental parameters. PEO shows low affinity on the alumina surface while PAA has high affinity. In the case of PAA adsorption, the surface charge change by polymer adsorption influences suspension stability strongly, but not in the case of PEO adsorption. In simultaneous adsorption of PEO and PAA, the PAA concentration was fixed and PEO concentration was varied. The stability of suspension increased with increasing PEO concentration, and this is partly due to the steric stabilization by adsorption of PAA-PEO complex or adsorption of PEO through pre-adsorbed PAA and the depletion effect of non-adsorbed polymer. Suspension adsorbing sodium salts of PAA and poly(methacrylic acid) (PMA) each showed similar stability. But, when the PEO and these kinds of salts were added together to the suspension, the one with PAA sodium salt could keep a higher stability even with lower molecular weights of PEO compared with suspension with PMA sodium salt.

Key words: Alumina, Suspension, Stability, Adsorption, PEO, PAA

INTRODUCTION

Fine powders of ceramic materials are used in many applications and fields. Usually these have high purity and submicron size and these properties depend greatly on microstructures. Colloidal processing, which is composed of dispersion of starting powders in liquid media and following consolidation, is superior to general dry pressing in control of densities and microstructures of green and sintered compacts [Hirata et al., 1992] .

However, a major problem in colloidal powder processing is related to the aggregation of particles, which is the cause of wide pore size distribution and microstructural inhomogeneities. The dispersion properties in aqueous solution are influenced by the interaction energy based on Van der Waals attraction force and electrostatic repulsive force between particles [Hirata et al., 1992; Chi-Jen et al., 1998]. Because a decreasing of particle size reduces these interaction energies, the submicron size particles rarely form highly concentrated suspension.

The addition of polymer can increase the stability of suspension [Fendler, 2001]. Thus, studies on adsorption of water-soluble polymers, such as nonionic polymer as well as polyelectrolyte on the colloidal particles in aqueous phases, are important to an understanding of the stability and flocculation of colloidal dispersion by polymers that are attached by physical adsorption to the surface of the particles [Kawaguchi et al., 1987].

Several researchers have studied polymer adsorption on alumina particles and its effects on suspension stability. When poly(acrylic acid) (PAA) is adsorbed on alumina particles, the adsorbed amount of PAA decreases with pH because of the surface characteristics of alumina and dissociation degree of PAA with pH [Hirata et al., 1992]. In the case of poly(vinylpyrollidone) (PVP) adsorption, the adsorbed amount of PVP is very small and nearly independent of pH, but the adsorption can be enhanced by simultaneously adding PAA. At low pH, stability of alumina suspension by PVP adsorption alone decreases with pH, while the contrary tendency appears by PAA adsorption alone. The stability of alumina suspension with simultaneously adsorbed polymers is dependent on both steric hindrance by polymer adsorption and the change in electrostatic repulsion force with pH [Ishiduki et al., 1997]. Also, the adsorption of PAA and poly (vinyl alcohol) (PVA) onto alumina has been reported. The adsorption density of PAA decreases with an increase of pH while that of PVA shows the opposite trend. In simultaneous adsorption of PAA and PVA, PVA does not affect the adsorption of PAA on alumina, but the presence of PAA prevents the adsorption of PVA [Santhiya et al., 1999]. Adsorption of poly(ethylene oxide) (PEO) on alumina was investigated by several researchers. According to them, adsorption of PEO on alumina is almost negligible even with PEO of large molecular weight. PEO is adsorbed via an acid-base reaction between oxygen of PEO and surface hydroxyl group [Mathur et al., 1997].

In the present work, the adsorption behavior of PAA and poly(ethylene oxide) (PEO) was investigated and the simultaneous adsorption of these two polymers was also carried out. The stability of alumina suspension was also studied with varying pH, polymer concentration and molecular weight, in the case of PEO. In addition, the stability of suspension was compared as PAA salt and poly(methacrylic acid) (PMA) salt was added to it. Also, the effect on disper-

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‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

sion stability by simultaneous adsorption of PAA (or PMA) salt and PEO was measured.

EXPERIMENTAL

1. Materials

Alumina powder (Type DX) was purchased from EMS company. The mean particle size of this commercial alumina powder was 0.3 μm according to manufacturer, but the real diameter, which was measured by using DLS (Dynamic Light Scattering) after shattering, was 500 nm. BET surface area of alumina particle was 28.11 m^2/g and the measured point of zero charge (PZC) was about 7.9. PAA (M.W.=250,000), PEO (M.W.=10,000, 200,000, 4,000,000), PVP (M.W.=29,000) were obtained from Aldrich Co Ltd. They were used without further purification.

2. Procedures

Alumina powder was dispersed into distilled water. The suspension was made to be 2 weight percent solution. Prepared HCl solution was added to control the pH of alumina suspension. pH was adjusted in the range of 3-4. This pH adjustment made the suspension keep more uniform size distribution and smaller particle size. After these procedures, the suspension was shattered by using a lab-scale mechanical blender with high speeds. The shattering procedure was kept for about 5 hours. Then, the alumina dispersion solution was sonicated with an ultra-sonicator for about 30-60 min.

The aqueous polymer solution of various polymers such as PAA, PMA, PEO, PVP and PVA was prepared. The polymer solution was injected into the alumina suspension. The pH of this adsorption solution was adjusted by using HCl solution or NH_4OH solution. The adsorption solution was agitated for about 24 hour at 28.5 ±0.5 °C.

The adsorption solution was centrifuged by a high speed refrigerated centrifuge, and the sediment was oven-dried for about 2-3 days. These dried sediments were powdered by using Mortar Porcelain, and these powders was analyzed by Elemental Analysis (EA) instrument (EA1110-FISONS). The EA measures the carbon content of sediment. In the individual adsorption experiment, the adsorbed polymer amount can be obtained from this carbon amount.

The stability of alumina suspension was measured from UV absorbance analysis. In this analysis, a higher absorbance value means that the suspension is more stable. The more particles suspend, the higher the suspension turbidity becomes. Because UV light hardly goes through well the suspension under this condition, high absorbance value is observed. HP 8452 was used as a UV spectrometer. The alumina suspension with adsorbed polymer was left for a few hours to several days in a settling cell (a 10 ml mess cylinder was used as the settling cell). The mess cylinder was capped with a sealing film to prevent the water from vaporizing. And when a clear region appeared in the upper region, the top portion of the settling cell was picked by using micro-pipette and its UV absorbance was measured at fixed wavelength (usually 600 nm).

RESULTS AND DISCUSSION

1. Particle Characterization

The particle size distribution of alumina in aqueous solution was estimated by Dynamic Light Scattering (DLS) instrument. Fig. 1 represents the particle size distribution; the average particle size was 500 nm. The surface charge of alumina particle changes with solution pH. The zeta potential variation with pH was measured with a Zeta Potential Analyzer to determine the isoelectric point (IEP). The approximate IEP value of alumina was about 7.9.

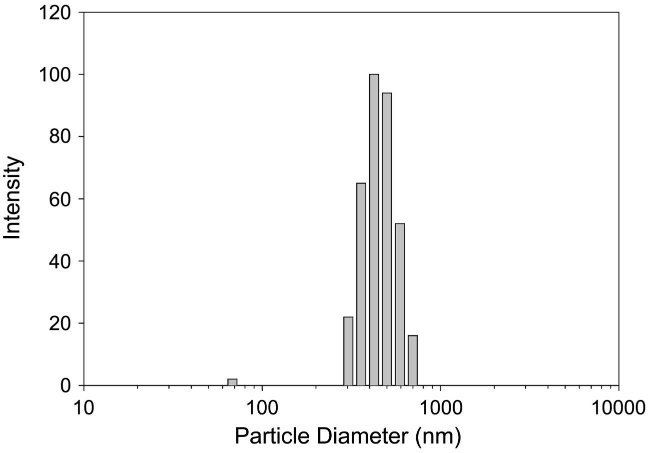

Fig. 1. The particle size distribution of alumina suspension after 5 hour shattering.

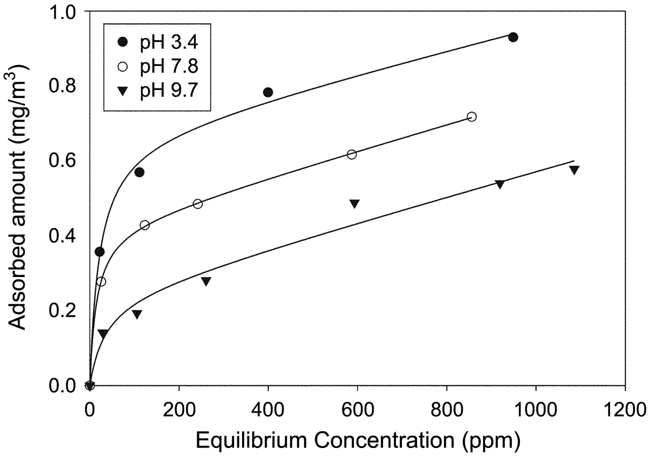

Fig. 2. Adsorption behavior of poly(acrylic acid) on alumina with pH and concentration.

2. Polymer Adsorption Behaviors

Fig. 2 shows the adsorption isotherm of PAA on alumina, and that the adsorbed amount of PAA increases with decreasing pH. The interaction between PAA and the alumina surface can be described into two ways. One is the electrostatic force between the positively charged alumina surface and dissociated PAA, and the other is the hydrogen bonding between the undissociated PAA molecules and hydroxyl groups on alumina surface [Ishiduki et al., 1997; Santhiya et al., 1999]. The fact that conformation of adsorbed polymer is affected by the change of solution pH has been reported. Polymer chains have coiled conformation at pH 4 but stretched conformation above the point of zero charge (PZC) due to the intrapolymer electrostatic repulsion [Esumi et al., 1996]. This difference in conformation affects the steric stabilization.

Fig. 3 shows the adsorption behavior of PEO with concentration and pH. On the whole, the adsorbed amount of PEO was small. This result is in a good agreement with other research [Mathur et al., 1997]. In this case, hydrogen bonding is the predominant mechanism of adsorption. As can be seen from Fig. 3, the adsorbed amount of PEO is very small and nearly independent of pH and concentration.

3. The Effect of Polymer Adsorption on Suspension Stability

After PAA (M.W.=250,000) molecule was adsorbed on alumina particle surface, the stability of the suspension was investigated by measuring the UV absorbance at 600 nm. Fig. 4 shows how the stability of alumina suspension varies with pH, time, and concentration.

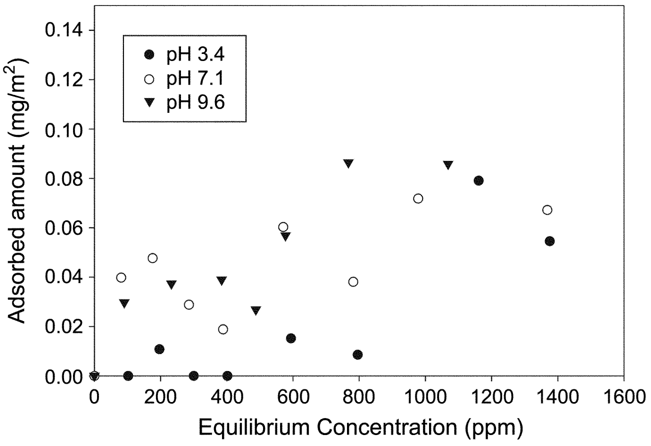

Fig. 3. Adsorption behavior of poly(ethylene oxide) on alumina with pH and concentration.

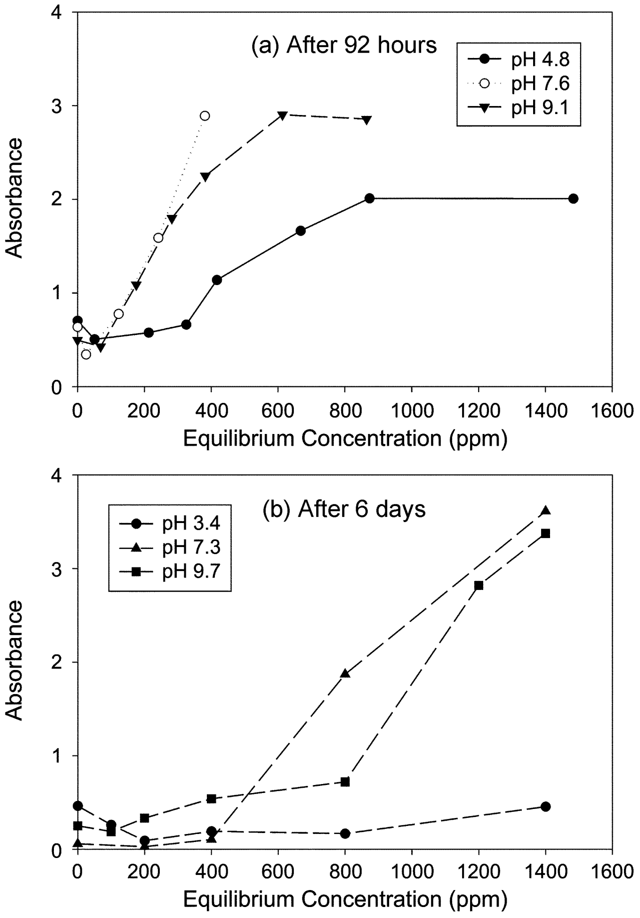

Fig. 4. The stability of alumina suspension with adsorbed PAA. The measurement was carried out after (a) 92 hours and (b) 6 days from beginning settlement.

On the whole, the stability of suspension seemed to be contrary to the trend of the adsorbed amount of PAA. The stability of this suspension was dependent on the electrostatic repulsion force rather than steric stabilization. The stability in low pH of Fig. 4(a) is still quite high, and there is an absorbance plateau above about 900 ppm. But after 6 days, the stability in low pH was independent of the equilibrium concentration and had quite low absorbance value compared with the case of high pH. This trend can be explained by the zeta potential change with PAA adsorption. Although the adsorbed amount was large in low pH, the zeta potential of the alumina particle became almost zero.

Though the absolute value of the zeta potential of alumina increased with pH, the experiment at near pH 7 showed better stability than the case of experiment near pH 9. One of the reasons why this phenomenon occurred may be that there was an optimum condition of pH and concentration for stability. In the case of low pH, the adsorbed amount was large, but electrostatically unstable. The values of zeta potential at pH near 7 and 9 were not so different. And this means that the electrostatic stabilization effect is almost the same. In this situation, the major contribution to particle stability is the steric effect by adsorbed polymer. As the adsorbed amount decreased with pH, steric effect at pH 7 was a little larger. It gave the result that the stability near pH 7 was a little superior to that near pH 9. Therefore, the dispersion stability of suspension seemed not to increase monotonically and to have an optimum condition with increasing pH.

The zeta potential change with PAA adsorption is shown in Fig. 5. Fig. 5 shows that the zeta potential of particles decreased as the concentration of polymer increased. And because the IEP of suspension also decreased in pH 1-3 range as the polymer was introduced, the alumina suspension became unstable state in the low pH region. That is, there was little electrostatic repulsion interaction between particles in low pH and the aggregation could occur more easily than in high pH.

As the polymer concentration of PAA increased, the absolute value of the zeta potential increased in the case of PAA adsorption above

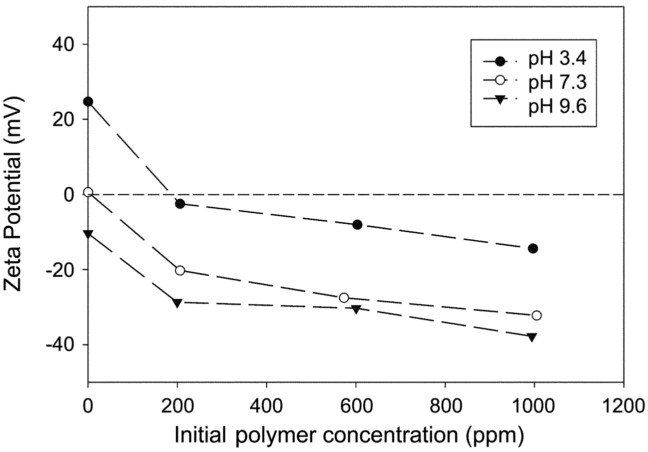

Fig. 5. Zeta potential change of alumina suspension adsorbing PAA with pH and concentration.

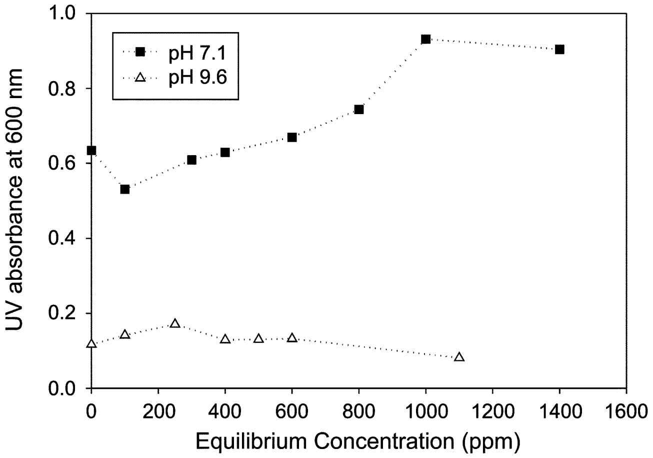

Fig. 6. Stability of alumina suspension with pH and PEO concentration.

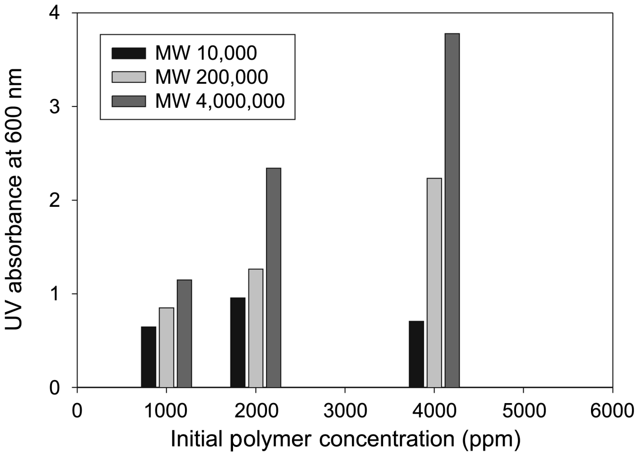

Fig. 8. Stability with molecular weight and concentration of PEO.

pH 3. Therefore, the particle stability also could be enhanced by increasing concentration of PAA.

In the low concentration range below 100 ppm, some unstable state appeared. This is due to the bridging flocculation in low polymer concentrations. That is, the tail extending towards the solvent of adsorbed polymer can be attached to the partially covered surface of another particle in low polymer amounts and thus flocculation occurs. These phenomena could be observed visually during settling procedure.

In Fig. 6, the stability with pH and PEO concentration is shown. Alumina suspension showed better stability in lower pH. In this figure, the suspension at pH 7.1 showed the higher stability than the one at pH 9.6. Originally, the absolute value of zeta potential was higher in the case of pH 9.6. But, the PEO adsorption made the iso-electric point of suspension increase a little more than the bare alumina state. So at pH 9.6, the suspension was more unstable than at pH 7.1. However, it was observed that stability was nearly independent of the polymer amount at pH 9.6. In Fig. 7, the absorbance change with time at pH 9.6 is shown for various initial PEO concentrations. There was little absorbance difference between the samples that had various initial concentrations and the result showed this suspension is very unstable.

In the case of pH 7.1, the stability increased little by little as the concentration of polymer increased. Because the zeta potential of suspension rarely changed with concentration of PEO adsorbed, increasing zeta potential was not responsible for the stability increasing with concentration at pH 7.1.

Fig. 8 represents the effect of PEO concentration and molecular weight on the suspension stability. The stability was higher in higher polymer concentrations and higher molecular weights. In the case of M.W. 10,000, the absorbance value of about 0.6-1 was obtained and it seemed that there was not any particular concentration effect. In the case of M.W.=200,000 and 4,000,000 the stability is better for higher polymer concentrations. For the same concentration, a higher molecular weight of PEO had higher stability. Thus, it seems that the steric effect existed due to the difference in chain lengths of polymers. But, the steric effect due to increasing concentration hardly affected the suspension stability under a constant molecular weight because the adsorbed amount of PEO on alumina was very small and almost constant regardless of polymer concentration. Another stabilization mechanism that can be assumed

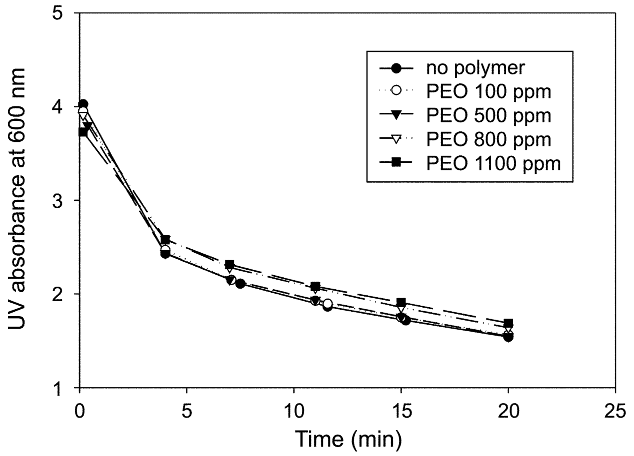

Fig. 7. Absorbance change with time at various PEO concentrations.

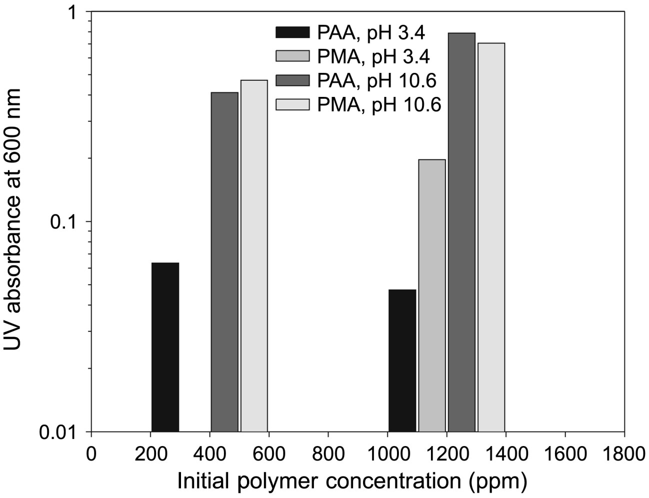

Fig. 9. Stability comparison between PAA and PMA adsorption.

to function is the depletion stabilization due to the molecules remaining in bulk solvent.

4. Stability Comparison between Suspensions with Other Polymers

Fig. 9 shows the stability difference when the PAA sodium salt and PMA sodium salt are adsorbed on alumina at different pH. For both cases, it could be seen that a high pH led to a high stability. At pH 10.6, the UV absorbance had almost the same values, which means that there was no difference in stability between the suspension with PAA salt and PMA salt.

Fig. 10(a) shows the settling experiment after 35 minutes since the experiment began. The 2nd (PAA 400 ppm), 3rd (PAA 1,200 ppm) and 8th (PMA 1,200 ppm) cells in this picture were under pH 3.4 and they showed very unstable status, especially for 2nd and 3rd. And Fig. 10(b) verified this fact. In the case of the 2nd cell, the absorbance of suspension began to decrease immediately as the measurement started, that is, began to settle as soon as the suspension was added into the cell. The suspension of the 3rd kept its stability during about 30 minutes, but after that the stability was reduced abruptly. The suspension of the 8th cell showed the most stable state among the samples in low pH. The stable state was kept for about 100 minutes. From these observations, we can conclude that the suspension stabilized by PMA sodium salt was a little more stable than the one stabilized by PAA sodium salt in low pH range if molecular weight is similar.

5. Simultaneous Adsorption of Two Polymers

Fig. 11 shows the effects of PEO concentration on the stability at pH 3.4 when the fixed amount of PAA is adsorbed simultaneously. From this figure, the stability of the suspension could be enhanced by increasing PEO concentration. Actually, the stability of the alu-

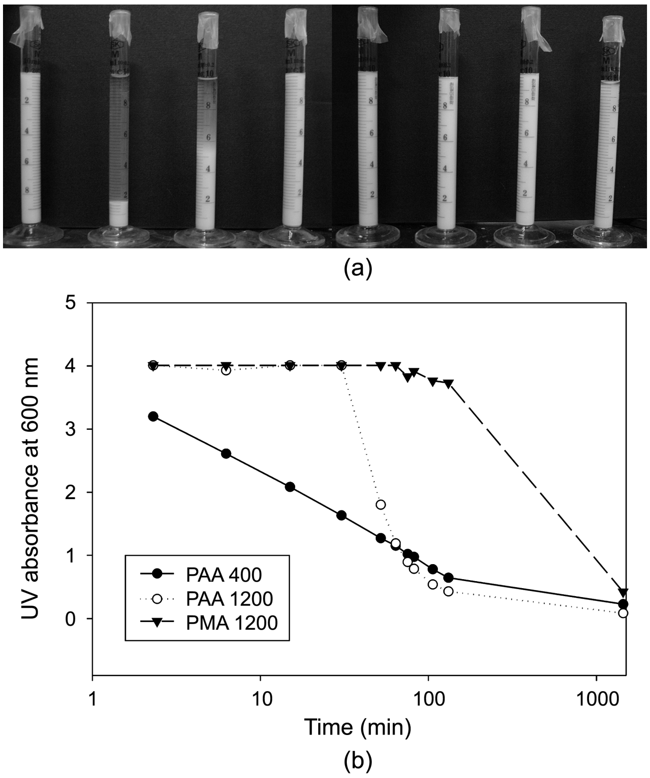

Fig. 10. (a) Picture of suspension settling experiment after 35 minutes since the beginning of settlement. (b) Absorbance change rate of suspension with PAA (PMA), sodium salt at pH 3.4.

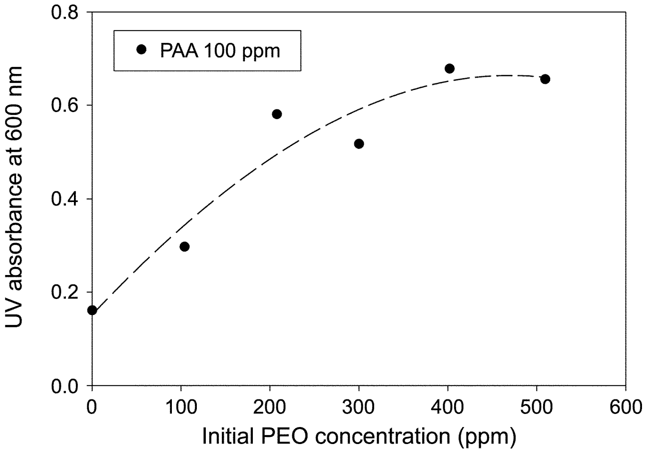

Fig. 11. Effect of PEO concentration on the stability under fixed amount of PAA.

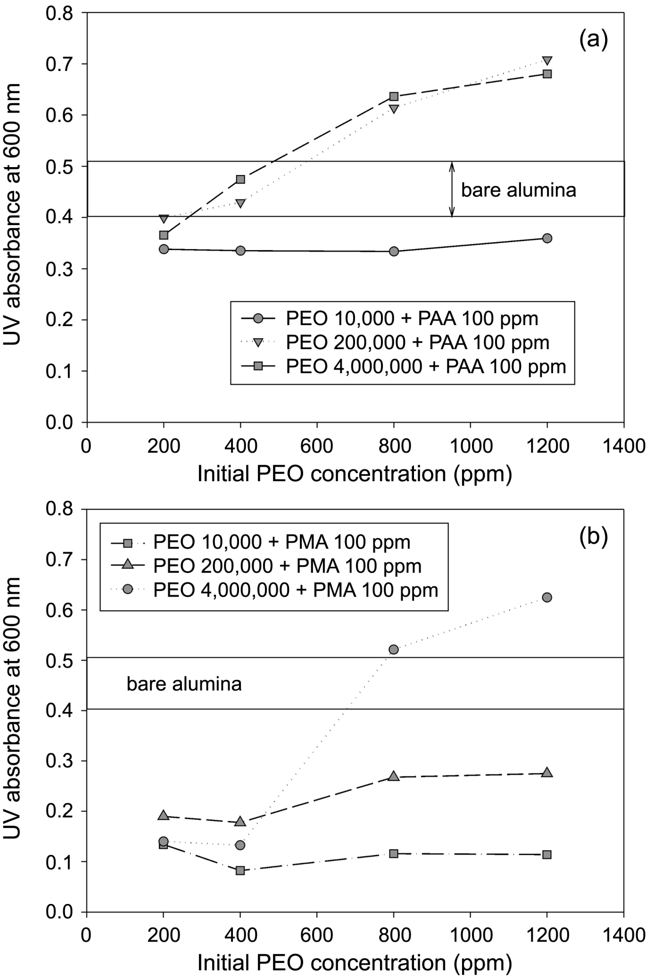

Fig. 12. Effect of simultaneous adsorption of (a) PAA, sodium salt (100 ppm)+PEO and (b) PMA, sodium salt (100 ppm)+PEO on suspension stability (pH=3.4).

mina suspension in which 100 ppm of PAA was added was quite low because of bridging flocculation by polymers. But adding PEO together with PAA improved the stability of suspension up to a certain level. There can be several reasons for this. One is the enhancement of adsorption of PEO by adsorbed PAA molecules through hydrogen bonding between either oxygen of PEO and carboxyl group of PAA. But, as known from the adsorption behavior of PEO, the adsorbed amount of PEO was very small and thus the steric effect of adsorbed PEO was almost the same over the whole experimental range although PEO adsorption occurred. Another reason expected for stabilization is the depletion stabilization by PEO not adsorbed, almost left in solvent. To determine the exact reason, the adsorbed amount of each polymer should be estimated.

In Fig. 12, the effect of simultaneous adsorption of PAA (or PMA) sodium salt and PEO on suspension stability at pH 3.4 is presented. Low molecular weight PEO (M.W. 10,000) seemed to hardly affect the stability of suspension with PAA (or PMA) salt. This indicates that PEO of M.W. 10,000 was not enough to stabilize the suspension that was in unstable state due to electrostatic attraction force. But, PEO with higher molecular weight influenced suspension stability much more. As mentioned already, bridging flocculation also occurred at the low concentration in this case. The reason why the electrostatic effect seldom functions practically is that the alumina particle with PAA (or PMA) sodium salt has almost zero charge value near pH 3. The stability increase in this case is mainly due to depletion stabilization.

However, when PEO of the same concentration and the same molecular weight was used, the PAA salt showed a higher stability. And in the case of the suspension using PAA salt, even PEO (M.W. 200,000) could act as a good stabilizer while it could not in the case of PMA sodium salt.

CONCLUSIONS

The effect of adsorbed PEO and PAA on the alumina suspension stability was investigated. The adsorptioin of PAA proceeded with high affinity. The adsorbed amount of PAA increased with decreasing pH and increasing amount of polymer added. The adsorbed amount of PEO was rather small and nearly independent of pH. The stability increased as the pH increased regardless of the adsorbed amount of PAA in the stability measurements of PAA adsorbed suspension. But there seemed to be an optimum condition of pH and concentration for dispersion stability. In the case of PEO, low molecular weight polymers had little effect on the stability. When PEO with high molecular weights were added, it could be observed that the suspension stability increased as polymer concentration increased at low pH. In simultaneous adsorption of PAA (PMA) sodium salt and PEO, the suspension using PAA sodium salt showed a higher stability. And higher molecular weight PEO made stability increase for both cases.

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