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Extensions of polyacrylic acid ammonium salts in the adsorption layer to fluidize alumina slurries

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An average shell volume occupied in the adsorption layer on alumina by a polyacrylic acid ammonium salts molecule (PAA) defined as the average area occupied by an adsorbed PAA on alumina multiplied by the average thickness of the water layer at the limit of thickening, has been calculated from the adsorbed amount of PAA and from the flow points of alumina in the presence of PAA of different molecular weights. A steric effect of the PAA dispersant on the dispersion of alumina resulted in a flow with no yield stress. This was due to the change of the extension of PAA in the adsorption shell from a sphere to an ellipsoid with a long axis which exceeded the effective distance that the van der Waals attraction force reaches at a molecular weight for the PAA of between 10 000–20 000.

1. Introduction

Based on the experience that a material which can fluidize a slurry is a good dispersant, the lowering of the viscosity of a slurry has been used as a measure for the evaluation of the effectiveness of a dispersant [1]. A material which has a dispersing effect is not, however, necessarily a good fluidizer for a slurry. Polyelectrolyte dispersants have a dispersing effect together with a fluidizing effect. [2–5] Shear rate $\dot{\gamma}$ versus shear stress σ curves of alumina or zirconia slurries retaining PAA of various molecular weights had a yield stress for molecular weights less than 10 000 but had no yield stress for molecular weights greater than 20 000. The change occured in the molecular weight range between 10 000–20 000 [6, 7]. The wet point and the flow point are defined as the least amount of water for a unit amount of powder to make a lump or to flow, respectively [8]. The flow point of alumina has a minimum at an optimum amount of PAA. The slurry at the minimum amount retains the smallest amount of water to enable flow and this minimum can be defined as the limit of thickening. This minimum could be lowered by reducing the molecular weight of the PAA from 45 000 to 2500. In addition the optimum concentration of the PAA for the minimum could also be reduced by reducing the molecular weight of the PAA [5, 6]. The dispersion accompanied by fluidization and the limit of thickening should be related to the structure of the length extension of PAA in the adsorption layer on the alumina and also to the interaction among such solid particles in the concentrated slurry. There is a reason why a polyelectrolyte with an optimum length works as a dispersant accompanying the fluidizing effect [9, 10]. In the electrostatic model for dispersion a dispersant is adsorbed on to the solid particles and produces electrostatic repulsions that exceed the van der Waals attraction in order to disperse the solid particles. The dispersant however has an additional steric effect since the PAA expands in the adsorption layer thereby exceeding the effective distance that the van der Waals attraction force operates over. There is no reported measurement for the polymer length that results from the steric effect [11–13].

The purpose of this report is to calculate an averaged shell volume in the adsorption layer on the alumina occupied by a PAA, from the adsorbed amount of the PAA and from the flow points of alumina in the presence of PAAs of different molecular weights. We will also compare the shell volume with the extended size of the PAA and discuss the distribution of the PAAs in the adsorption layer shell. A measure for the polymer length to produce dispersion accompanying the fluidizing effect by steric effects will be obtained.

2. Experimental procedures

2.1. Materials

The alumina used in these is α-alumina supplied by Alcoa Co., Alcoa A16-SG, with an average grain size of 0.3 μm. The PAA of molecular weight 2500 was supplied by Scientific Polymer Products, Inc. and was dissolved into an ammonia solution and diluted to the required concentrations. PAAs of molecular weight 5900, 11000, 21000 and 45000 were supplied by the Daiichi Kogyo Seiyaku Co..

2.2. Determination of the flow point and the wet point

Twenty grams of alumina powder was weighed. After adding a certain amount of PAA solution to the

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powder, water was dropped on to the powder from a burret. After kneading of the mixture, the amount of water required for the mixture to make a lump was read from the burret and is taken to be the wet point. The addition of extra water from the burret, meant that we supplied sufficient water for the mixture to start to flow and this amount was read from the burret and is taken to be the flow point. The amount of water added initially to the PAA was calibrated to the flow point value.

2.3. Measurements of the amount of PAA adsorbed on Al_2O_3

The alumina slurries containing PAAs of various molecular weights were centrifugated at 12000 rpm for 60 min after standing for 24 h. The supernatant liquid was separated in order to determine the amount of unadsorbed PAA. The PAA solution has an absorption in the ultraviolet region in the form of an absorption edge. A linear calibration curve was obtained for this absorption at 195 nm for the concentration range of 0.01–0.8 wt% PAA. The calibration curve was used for the determination of the PAA concentration in the supernatant liquid. Hence the amount of PAA absorbed by the alumina could be calculated by a simple subtraction of this figure from the initial PAA concentration added to the system.

2.4. Measurement of the flow curves

A cone and plate viscometer (Tokyo Keiki, model Visconic EMD) was used for the viscosity measurements. Shear rate–shear stress curves were obtained for 75 wt% alumina slurries containing various amounts of PAA at 30 °C.

3. Results and discussions

3.1. Averaged spatial volume occupied by a PAA molecule in the adsorption layer shell on alumina in the slurry at a concentration limit

The flow points and wet points of alumina in the presence of PAAs of different molecular weight are shown in Fig. 1. The flow point minimum of the alumina slurries at a suitable concentration for fluidization in the presence of various PAAs of different molecular weight are listed in Table 1. An averaged thickness of the water layer to the total alumina surface, $\langle H \rangle$, was calculated at each minimum and is also tabulated in Table 1 with the length of the PAA at different molecular weights. A PAA of molecular weight greater than 20 000 has a length longer than the averaged thickness of the water layer and has to be folded in the adsorption layer at the thickening limit.

The adsorbed amounts of the PAAs with different molecular weights were determined at various amounts of addition as is shown in Fig. 2. The averaged area that a PAA molecule occupies on the adsorbed surface of alumina, $\langle S^2 \rangle$, was calculated by dividing the surface area of the alumina by the adsorbed amount of PAA at the minimum flow point and is shown in Fig. 3. The shell volume with a basal area, $\langle S^2 \rangle$, and a height, $\langle H \rangle$, defines an averaged spatial volume occupied by a PAA molecule in the adsorption layer shell.

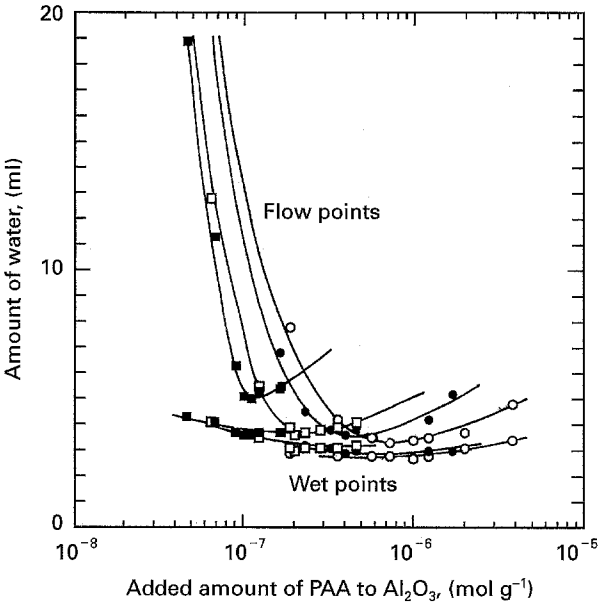

Figure 1 Flow point and wet point of alumina retaining PAA of various molecular weight for various added amounts
Curves are for ○: PAA 2500, ●: PAA 5900, □: PAA 21000, ■: PAA 45000.

TABLE I The flow point minimum of alumina slurries at the suitable concentration for fluidization in the presence of various PAAs of different molecular weights

Molecular weight of PAAs	2500	5900	21000	45000
Length of PAA $\langle L \rangle$ ($\times 10^{-1}$ nm)	70	200	730	1560
Concn. of PAA at the flow point min. (wt% PAA/Al_2O_3)	0.20	0.25	0.44	0.50
Flow pt. at the min. (ml per 20 g Al_2O_3)	3.50	3.70	3.85	5.20
$\langle H \rangle$($\times 10^{-1}$ nm)	290	300	320	400
$\langle S^2 \rangle$($\times 10^{-2}$ nm^2)	1089	2025	4096	7726
$\langle S^2 \rangle^{1/2}$($\times 10^{-1}$ nm)	33	45	64	88
$\langle h^2 \rangle$($\times 10^{-2}$ nm^2)	1089	2500	9025	19044
$\langle h^2 \rangle^{1/2}$($\times 10^{-1}$ nm)	33	50	95	138

3.2. Extension of PAA molecules in aqueous solution

PAA has a certain extension in length due to bending and rotational motions of the segments in aqueous solution as is shown in Fig. 4. The ends of the linear PAA chain have an averaged distance, $\langle h^2 \rangle^{1/2}$, due to the motions that can be calculated by the following equation;

$$\langle h^2 \rangle^{1/2} = [2nl^2\sigma]^{1/2}$$

where n = the number of segments in one PAA molecule, l = the length of one segment, and σ, the constant for a constraint of the motion of the segment. The value, $\langle h^2 \rangle^{1/2}$, can be interpreted as an unidimensionally averaged theoretical size for the extension of PAA in the solution. The size of the extension of PAA

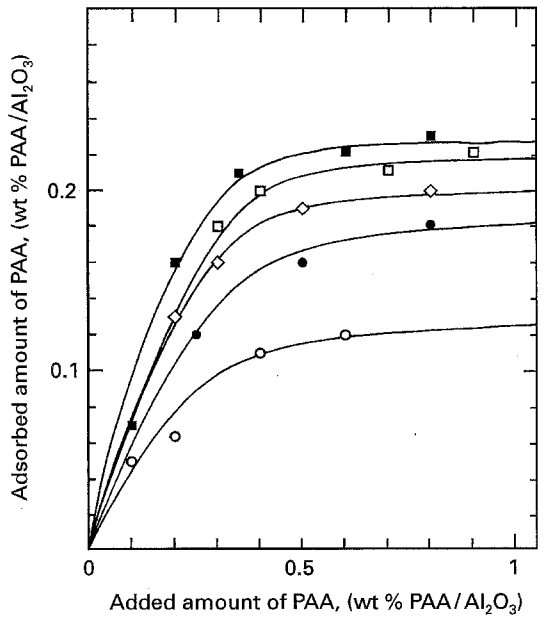

Figure 2 Adsorbed amount of PAA of various molecular weights to the added amount of PAA to alumina
Curves are for ○: PAA 2500, ●: PAA 5900, ◇: PAA 11000, □: PAA 21000, and ■: PAA 45000.

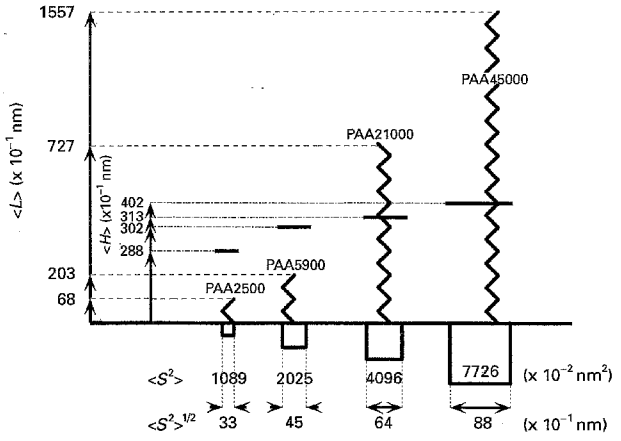

Figure 3 Comparison of the length of PAA of various molecular weights, $\langle L \rangle$, the averaged area that a PAA molecule occupies on the adsorbed surface of alumina $\langle S^2 \rangle$ and the averaged thickness of water layer to the total alumina surface, $\langle H \rangle$.

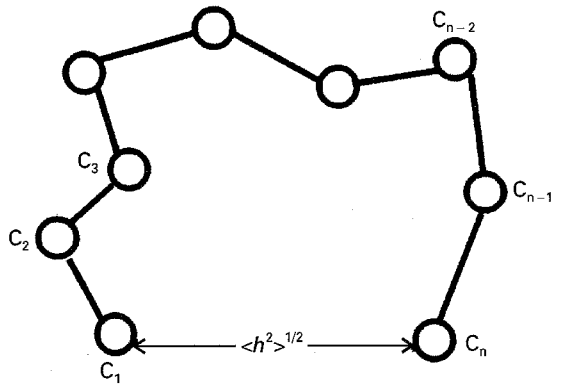

Figure 4 Extension of PAA in solution.

is illustrated in Fig. 5 as a square with a side length, $\langle h^2 \rangle^{1/2}$, for one dimensional size, with an area, $\langle h^2 \rangle$, for two dimensional size, and with a sphere with diameter, $\langle h^2 \rangle$, for a three dimensional size.

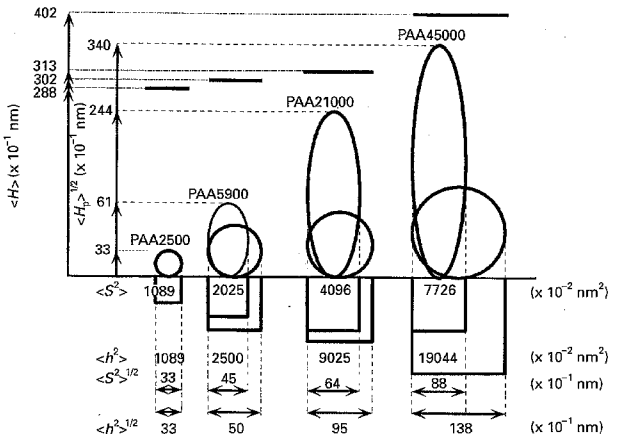

Figure 5 Comparison of the averaged shell volume for PAA molecules, $\langle S^2 \rangle \langle H \rangle$ and the deformed extension of PAA in the adsorption shell.

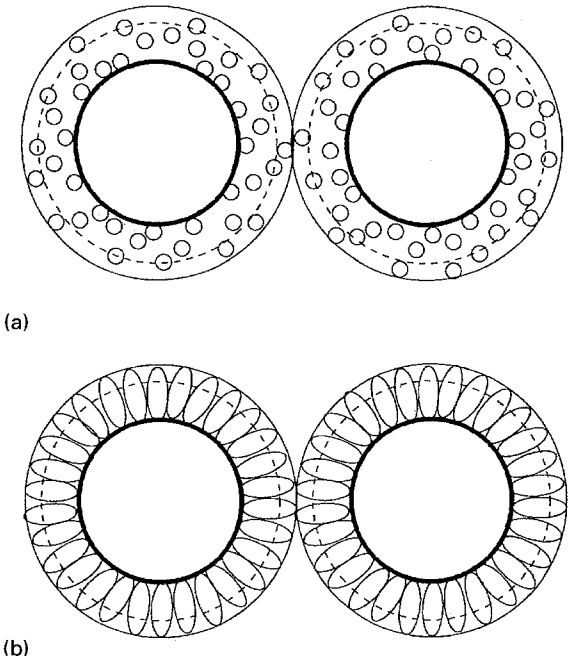

Figure 6 Proposed structure models of adsorption layer on alumina based on the averaged shell volume of a PAA for PAAs of different molecular weight
(a) Adsorption layer for PAAs of molecular weight less than 10 000
(b) Adsorption layer for PAAs of molecular weight more than 20 000.

3.3. Comparison of the size of extension of PAA in solution with the shell volume, $\langle S^2 \rangle \langle H \rangle$

For PAA of molecular weight less than 10 000, the theoretical two dimensional extension of PAA in solution, $\langle h^2 \rangle$, agreed with the averaged area, $\langle S^2 \rangle$, that is the area a PAA molecule occupies on the adsorbed surface of alumina. The size, $\langle h^2 \rangle^{1/2}$, is sufficiently smaller than the average thickness of the water layer at the limit of thickening, $\langle H \rangle$. Therefore the PAA molecule could be retained in the shell being distributed in the adsorption layer of thickness, $\langle H \rangle$, keeping its natural extension size as is shown in Fig. 6(a).

On the other hand, for molecules of PAA with molecular weight more than 20 000 the two dimensional extension, $\langle h^2 \rangle$, is larger than the surface area

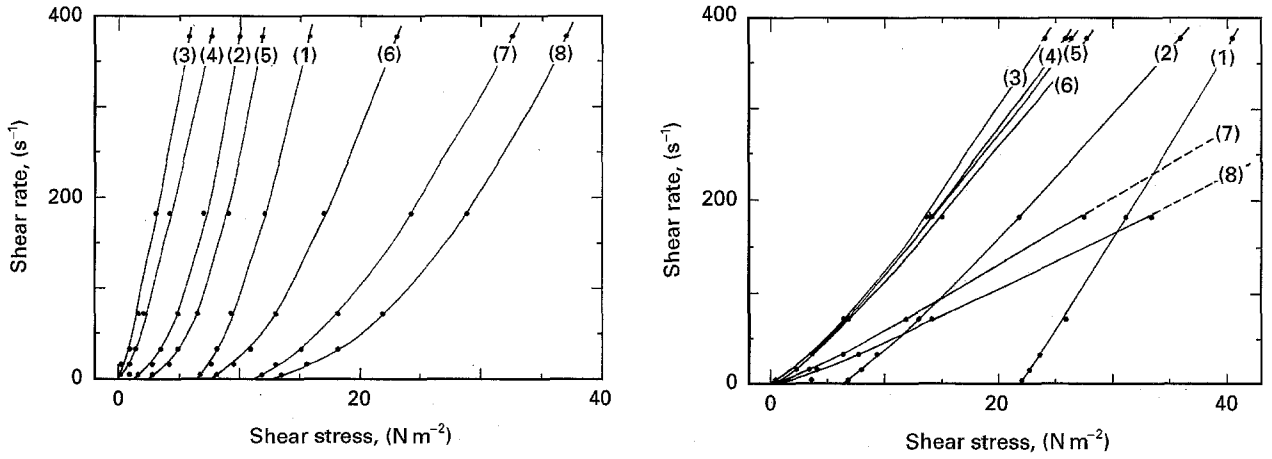

Figure 7 Typical two types of shear rate to shear stress curves of alumina slurries retaining various amounts of PAAs of various molecular weights.
(a) For the slurries retaining PAAs of molecular weight 2500 as a representative example for the molecular weight less than 10 000 for the amounts (1) 0.05, (2) 0.12, (3) 0.18, (4) 0.23, (5) 0.70, (6) 1.2, (7) 1.7 and (8) 2.1 wt% (dwb of alumina) at 75 wt% alumina
(b) For the slurries retaining PAAs of molecular weight 45 000 as a representative example for the molecular weight more than 20 000 for the amount (1) 0.2, (2) 0.4, (3) 0.6, (4) 0.7, (5) 0.9, (6) 1.1, (7) 1.8, and (8) 2.7 wt% (dwb of alumina) at 70 wt% alumina

occupied by a molecule, $\langle S^2 \rangle$, and also the extension, $\langle h^2 \rangle^{1/2}$, for one dimension is smaller than the averaged water layer thickness, $\langle H \rangle$, at thickening limit. When the PAAs illustrated in Fig. 5 as spheres with a diameter, $\langle h^2 \rangle^{1/2}$, can deform in the adsorption layer by shrinking the occupied surface area from $\langle h^2 \rangle$ to $\langle S^2 \rangle$ and elongating the length in the direction of the bulk from $\langle h^2 \rangle^{1/2}$ to $\langle H_P \rangle$ thereby creating ellipsoids without a change in the volume. The size of the ellipsoids after deformation can be expressed with a short axis, $\langle S^2 \rangle^{1/2}$, and a long axis, $\langle H_P \rangle$. The ellipsoids for each PAA with a different molecular weight are shown in Fig. 5. For a PAA of molecular weight greater than 20 000, the $\langle H_P \rangle$ values are close to the water layer thickness, $\langle H \rangle$, at the thickening limit. The deformed extension of PAAs with molecular weight greater than 20 000 can, therefore, limit the water layer thickness for the thickening due to their bulkiness.

3.4. Relation between the fluidity of the concentrated slurries in the presence of PAA and the structure of configuration of PAA in the adsorption layer

Alumina slurries with retained PAA of molecular weight less than 10 000 have varied yield stresses in each shear rate–shear stress curve and for molecular weights greater than 20 000 have no yield stress for variation in the amount of PAA as is shown in Fig. 7(a, b). The change in the fluidity occured in the molecular weight range between 10 000–20 000 and can be related to the change in the configuration of the PAA in the adsorbed layer. For a PAA with a molecular weight less than 10 000, PAA molecules in the adsorption layer have to take the configuration shown in Fig. 6a in which the molecules can distribute in a considerably thick water layer to be more than their extension size. The PAAs with molecular weights greater than 20 000 are sufficiently bulky compared to the thickness of the water layer even in the assumed folded form shown in Fig. 6b. The disappearance of the yield stress for molecular weights greater than 20 000 must be due to this bulkiness in accordance with the electrosteric model for a polymer dispersant. On the other hand for molecular weights less than 10 000 the slurry would behave as predicted by an electrostatic model for the dispersion, due to the disappearance of the steric effect with decreasing molecular weight of the PAA.

Therefore a criterion to select a polymer dispersant with a fluidizing effect in flow types is to choose a molecular weight of PAA between 10 000–20 000 depending on whether a steric effect is expected or not.

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