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# Stability of dispersions of colloidal alumina particles in aqueous suspensions

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## Abstract

The colloidal stability of suspensions of alumina particles has been investigated by measuring particle size distribution, sedimentation, viscosity, and zeta potential. Alumina particles were found to be optimally dispersed at pH around 3 to 7.8 without dispersant and at pH 8.5 and beyond with dispersant. The above results corroborate zeta potential and viscosity measurement data well. The surface charge of alumina powder changed significantly with anionic polyelectrolyte (ammonium polycarboxylate, APC) and the iep shifted toward more acidic range under different dispersant conditions. It was found that the essential role played by pH and dispersant (APC) on the charge generation and shift in the isoelectric point of alumina manifests two features: (i) the stability decreases on approaching the isoelectric point from either side of pH, and (ii) the maximum instability was found at pH 9.1 for alumina only and at pH 6.8 for alumina/APC, which is close to the isoelectric points for both the system, respectively. Using the model based on the electrical double-layer theory of surfactant adsorption through shift in isoelectric points, the authors could estimate the specific free energy of interaction (7.501 kcal/mol) between particles and dispersant. The interaction energy, zeta potential, sedimentation, and viscosity results, were used to explain the colloidal stability of the suspension.

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*Keywords:* Alumina; Zeta potential; Isoelectric point; Dispersion volume; Specific interaction energy

## 1. Introduction

Dispersion of particulate matter in both aqueous and non-aqueous media plays an important role in industries such as cosmetics, chemicals, pharmaceutical, microelectronics, paints and pigments, mineral processing, and ceramics, to name just a few [1,2]. Many of the industrial applications involve particles in the submicrometer or nanometer size range. In such ranges, the surface chemistry/surface property controls the processing behavior of the particles in the suspensions [3]. It is important to understand and manipulate the surface phenomena in order to control the processing conditions to achieve better desirable products [3]. The dis-

persion of powders depends upon many factors, including the following: the solvent must wet the particles, the particles must become separated from one another and mixed with the solvent system, and they must remain segregated/separated and not reagglomerate [4]. All these mainly depend upon interparticle forces, a distinguishing feature of all colloidal system. The contact area between particles and the dispersing medium in a colloidal system is very large (surface area 10–300 m$^2$/g); as a result, interparticle forces strongly influence suspension behavior [5]. There are number of interparticle forces that play an important role in dispersing the ceramic suspension. Among those, the dominating force is the van der Waals force (1 kcal/mol), which is attractive in nature between like particles and exhibits power law distance dependence [6]. The strength of this force depends on the dielectric properties of ceramic particles and intervening medium. To mitigate this attractive

force to achieve the desired degree of suspension stability, one approach is to generate like charges of sufficient magnitude on the surface of the suspended particles. This causes strong electrostatic repulsion between the suspended particles and thereby dispersion of the suspension. Hence, the determination and control of surface charge/zeta potential can be used to control the property of the suspension.

Proper dispersion of colloidal system in aqueous/nonaqueous media is often achieve through control of the charge/zeta potential on the particles in different ways, such as (i) variation of pH, (ii) using polyelectrolyte, or (iii) addition of potential-determining ions (pdi). Therefore, measurement and control of the surface charge/zeta potential of the particles may be used to control the properties of the suspension. The stability of an aqueous colloidal system can be tailored by generating like charges of sufficient magnitude on the surface of the ceramic particles. The properties that are most important in determining the nature of dispersions include the charge density of the suspended particles and the ionic strength of the medium [7]. The relative magnitude of these two parameters determines the nature of particle interaction in the suspension. When the magnitude of surface charge density relative to ionic strength is high, than the net particle interaction is repulsive and a low-viscosity stable suspension is achieved. In contrast, an agglomerated suspension is achieved when the magnitude of surface charge density relative to ionic strength is low [7,8]. When the particle has the same charge, dispersion occurs, due to electrostatic repulsion between them. However, this manipulation of charge by controlling pH only may not be sufficient to obtain a homogeneous well-dispersed and stabilized dispersion, which is required in many ceramic forming processes [9]. Generally, the most practical way of maintaining a stable dispersion is through the use of a chemical stabilizer called a dispersant. Commonly, these dispersants are polyelectrolyte surfactants, which adsorb on the surface of the particles and modify the surface charges and thus the electrostatic forces. The primary property of the dispersant is their ability to disperse fine particles and to stabilize the dispersion.

Electrostatic repulsive forces are the main source of stabilization of the suspension, due to common surface charge on the particles. Two other forces, such as the steric hindrance and a combination of electrosteric repulsions, may also be responsible for the stabilization. However, the colloidal stability, which is governed by the total interparticle energy $V_{total}$, can be mathematically expressed as follows [10],

$$V_{total} = V_{vdw} + V_{elect} + V_{steric} + V_{structural}, \tag{1}$$

where $V_{vdw}$ is the attractive potential energy due to long van der Waals interactions between the particles, $V_{elect}$ the repulsive potential energy resulting from electrostatic interactions between like charged particles surfaces, $V_{steric}$ the repulsion between particles surface coated with the adsorbed polymeric species, and $V_{structural}$ the potential energy resulting from the presence of nonadsorbed species in solutions, which may either increase or decrease the suspension stability.

In the present study, various slip/slurry characterization techniques such as particle size distribution, sedimentation, zeta potential, and viscosity measurements have been used for optimizing the aqueous alumina suspension as a function of pH and results are correlated with each other.

## 2. Experimental

### 2.1. Powders and chemicals

The high purity $\alpha$-alumina (AL160 SG4) used in this investigation was kindly supplied by M/s, Showa-denko, Tokyo, Japan. The average particle size was 0.6 μm with a specific surface area (BET) of 7.9 m$^2$/g. The detail physical and chemical properties are summarized in Table 1. A scanning electron micrograph (Model, JSM-6100F, JEOL Tokyo, Japan) of alumina powder is shown in Fig. 1.

A commercial ammonium salt of polycarboxylate, APC, D-305 (M/s, Chukyo, Yushi, Nagoya, Japan), was used as dispersant. The material has an average molecular weight of 8000–10,000 g/mol. It consist of 40% aqueous solution. Physical properties of the dispersant used is listed in Table 2. In all the experiment doubly distilled water has been used for the preparation of suspension. Analytical grade NaOH and

Table 1
Some properties of alumina powder

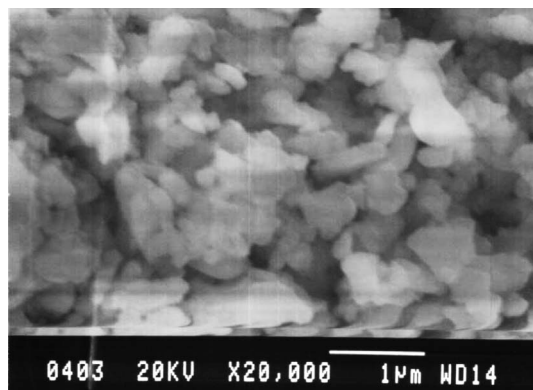| Powder characteristics | Typical values |
|---|---|
| Type | Calcined alumina |
| Crystallinity, $\alpha$ (%) | 99.89 |
| Designated lot/symbols | AL160 SG4 |
| Typical compositions | $\alpha$-Al$_2$O$_3$ |
| Average particle sizes, $D_{50}$ (μm) | 0.6 |
| Specific surface areas (m$^2$/g) | 7.9 |
| Density (g/cm$^3$) | 3.9 |
| Isoelectric point (pH) | 9.1 |



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Fig. 1. SEM micrograph of alumina sample.

Table 2
Physical and chemical properties of dispersant

| Characteristic properties | Typical values |
|---|---|
| Supplier | Chukyo Yushi, Nagoya, Japan |
| Trade name | D-305 |
| Chemical name | Ammonium polycarboxylate |
| Chemical formula | $(C_5H_{13}O_2N)_n$ |
| Molecular weight (g/mol) | 8000–10,000 |
| Density (g/cm$^3$)$^*$ | 1.22 |
| Active matter (wt%) | 40 |
| pH | 6.37 |
| State | Liquid, aqueous solution |
| Ionicity | Anionic |

$^*$ Measured in the laboratory.

HCl were used to modify pH of the system. Unless otherwise stated, 5% weight by volume alumina has been used for all the experiment.

## 2.2. Zeta potential measurement

The zeta potential (electrophoretic mobility) of very dilute aqueous alumina suspension (0.01 wt%) solid was measured by microelectrophoresis with a zeta sizer (Model 3000 HAS, Malvern Instruments, UK). The zeta potential was determined as a function of either pH or dispersant amount.

## 2.3. Sedimentation test

Measurement of dispersion characteristics of the alumina suspension was carried out using the conventional sedimentation technique in a graduated cylinder. All experiments were carried at 5 wt% solid slip. The suspensions were first stirred thoroughly for 5 min in a beaker and then transferred to the measuring cylinder (50 ml capacity), where it was allowed to stand undistured for 48 h. The dispersion volumes were then read directly from the graduated cylinder. The higher the dispersion volume, the more stable is the suspension. The sedimentation behavior of the suspension was studied as a function of time at different pH. The total height of the suspension in the measuring cylinder was taken as dispersion volume at the time $t = 0$ and subsequently the maximum level of turbidity (the solid sedimented plus the solid particles under dispersion) below the clear liquid as the dispersion volume at the different time intervals [4,11,12].

## 2.4. Rheological behavior

Rheological studies were carried out on concentrated (12.8 vol%) suspension using rotational viscometer (Model: RheoStress 600, M/s Haake, Karlsruhe, Germany). The rheological behavior of the alumina suspensions has been studied by measuring their viscosity and shear stress as a function of shear and pH of the slurry.

## 3. Results and discussion

### 3.1. Particle size distribution

When particles are dispersed in an aqueous medium, the surface charges on the particles are bound to influence the state of dispersion or aggregation. With changes in pH condition, the particles undergo either dispersion or aggregation depending on the polarity and the extent of surface charge developed by the particles. Fig. 2 shows the pH dependence of the diameter of the particles in a 5 wt% suspension in the absence of dispersant APC. As the pH is increased, the apparent size increases until a maximum is reached around pH 9.5, which is very close to the iep. This apparent increase in particle size reflects agglomeration as the zeta potential decreases and no longer provides enough electrostatic repulsion between the particles. This increase in particle size is reflected in both the dispersion volume (Fig. 3) and viscosity (Fig. 4). If we compare dispersion results in Fig. 3, it is well corroborated with the particle size data. The results show that the pH of the suspension greatly influences the dispersibility of alumina particles and simple techniques such
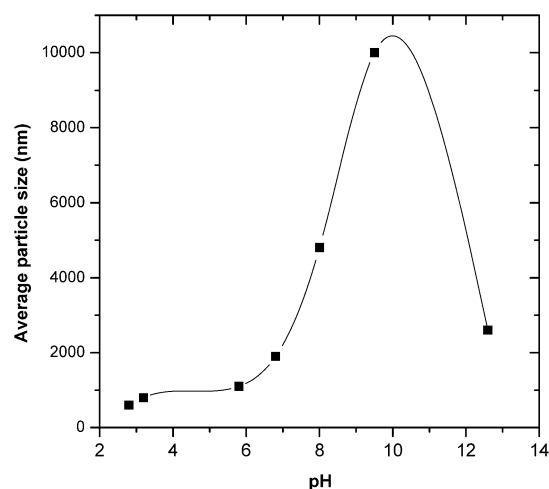


Fig. 2. Effect of pH on particle size distribution of alumina in the absence of APC.
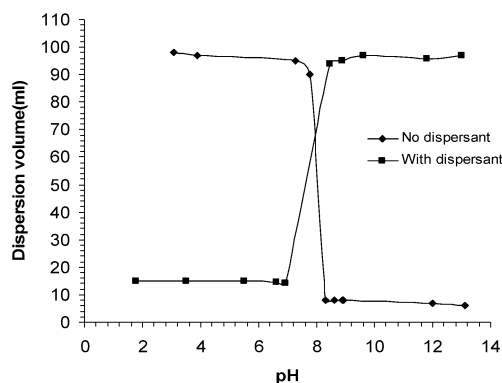


Fig. 3. Effect of slurry pH on dispersion characteristics of 5 wt% alumina particles.
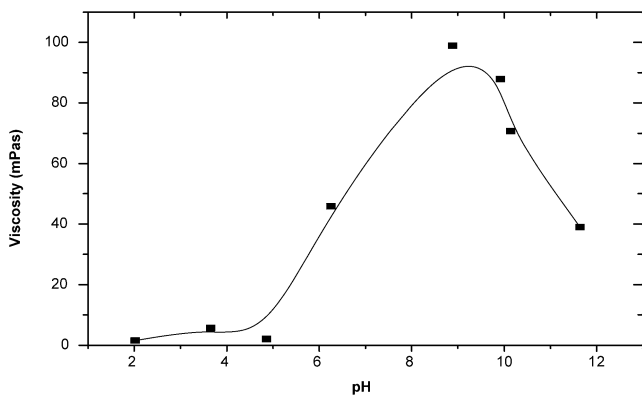
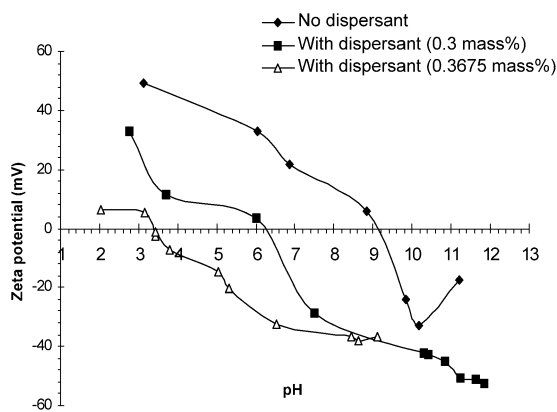Fig. 4. Variation of viscosity with pH.



Fig. 5. Zeta potential dependence on pH and added dispersant concentration.

as particle size analysis probes are very informative about the dispersion state of the powder. The increase in the apparent particle size correlates well with other properties of the suspension.

### 3.2. Zeta potential and interaction of Al₂O₃ particles with APC

The quantum of surface charge/zeta potential on the particle surface is an important particle characteristics, as it determines many properties of the suspension. A well-dispersed suspension can be obtained with high surface charge density to generate strong repulsive forces. The stability of alumina particles in aqueous suspension is closely related to its electrophoretic properties. The surface chemical properties of the powder are determined by the $H^+$ ion and $OH^-$ ions adsorb on the particle surface [4]. In the present case, alumina particle at natural pH ($= 8.4$) is slightly positively charged, as shown in Fig. 5. Fig. 5 further shows the effect of pH on the zeta potential of $Al_2O_3$ with and without dispersant. The isoelectric point (iep) of untreated alumina powder is found to be at pH 9.1, which is in close agreement with the reported value [10]. The isoelectric point (iep) is the pH value where surface concentration of $H^+$ and $OH^-$ are equal. The surface charge is negative at pH greater than at $pH_{iep}$ and positive at

Table 3
Computed value of specific free energy of interaction for alumina and APC

| System | Concentration (ppm) | $pH_{iep}$ | $\Delta pH_{iep}$ | $-\Delta G^0_{SP}$ ($RT$ units) |
|---|---|---|---|---|
| No dispersant | – | 9.1 | – | – |
| Alumina/APC | 3000 | 6.3 | 2.8 | 7.502 |

pH less than $pH_{iep}$. It is further seen that the iep has been shifted to the more acidic side (pH 6.3) with the addition of dispersant APC. The shift in iep on addition of APC is due to the following reason: the negatively charged carboxylic group dissociated from dispersant is adsorbed on the positively charged alumina surface and consequently, the surface is negatively charge. When APC is adsorbed onto the surface of the alumina particle, the hydroxyl groups associated with alumina particles reacts with the carboxylic groups of APC and hence will result in a shift of iep to a lower value [4].

### 3.3. Calculated interaction energy

The specific energy of interaction between the alumina powder surface and the dispersant APC was calculated using the following equation [13],

$$\Delta pH_{iep} = 1.0396 C_0 \exp\left(\frac{-\Delta G^0_{SP}}{RT}\right), \qquad (2)$$

or

$$\Delta G^0_{SP} = -RT(\ln \Delta pH_{iep} - \ln C_0 - \ln 1.0396),$$

where $\Delta pH_{iep}$ is the shift in the isoelectric point at the additive concentration $C_0$ and $\Delta G^0_{SP}$ represents the corresponding specific free energy on interaction between the surface alumina powder and the dispersant. $R$ and $T$ are the standard gas constant and the temperature in K, respectively. Table 3 shows the computed data of interaction energy ($-\Delta G^0_{SP}$). The specific energy of interactions $\Delta G^0_{SP}$ is around $-7.5 RT$ unit and which clearly indicates that an APC is strongly adsorbed onto alumina surface, which in turn indicative of strong interaction of alumina with APC. The zeta potential versus pH curve for alumina slurry (Fig. 3) indicates that due to strong adsorption of APC, the isoelectric point of $Al_2O_3$ has been brought down to pH 6.3 from 9.1. The difference of $\Delta pH_{iep}$ value is 2.8 (Table 3). It is known that the higher the value of $\Delta G^0_{SP}$ for a given system, more electrical double layer repulsion. The higher value of $\Delta G^0_{SP}$ in the present case shows suitability of APC as dispersant for alumina suspensions.

## 4. Effect of pH on dispersion characteristics

Fig. 3 shows the dispersion volume plotted against the slurry pH with/without dispersant. The dispersion volume of the suspension in the absence of dispersant in the acidic pH range, 3 to 7.78 is very high (95–98 ml), decreases rapidly

between narrow pH range 7.78 to 8.5. The results clearly show that suspension at acidic pH range generates good dispersion, which could be due to the high positive surface charge in an acidic environment (Fig. 5). As alumina is a basic oxide, it consumes $H^+$ ions and increases pH, resulting in positive surface charges at the surface in pure water. The suspension even without dispersant (APC) is dispersed well owing to its positive charge. The results further reveal that between pH 7.78 and 8.5, a more consolidated structure of the particulate is formed, which is very close to the $pH_{iep}$ (9.1). Further increase in pH above 8.5 has no effect on dispersion volume. Low dispersibility of alumina in this higher pH range can be explained in the light of surface/zeta potential (Fig. 5) where it is clear that the zeta potential does not significantly change beyond iep. The iep of $Al_2O_3$ is 9.1, so the charge on the particles near this pH is zero. Therefore, all particles have a natural tendency of agglomeration/aggregation and settle fast. If we compare sedimentation data with zeta potential (Fig. 5), it is in accordance with DLVO theory. When the positive charge on the alumina particle in the acidic pH range is sufficiently high, the suspension is well dispersed. At the pH around the isoelectric point at the zeta potential is minimal, the alumina particles tend to agglomerate and settle. In alkaline pH the alumina particles are negatively charged but comparatively the magnitude of charge in absence of dispersant is small whereas in the presence of dispersant APC, the surface charge is strongly negative beyond the $pH_{iep}$; as a result, dispersion volume is also high and hence stability of the suspension.

## 5. Rheological properties

Fig. 4 shows viscosity data of alumina suspensions (12.85 vol%) as a function of pH at a constant shear rate of 119.6 $s^{-1}$. The curve clearly shows maxima near the iep (pH 8–9). Lower viscosity are observed in the acidic pH range and increases with increasing pH and found maximum around iep. This shows that the powders are fairly well-dispersed in the pH range 2 to 7.8, as can be compared and correlated with dispersion data too (Fig. 3). The higher viscosities at pH range between 8 and 9 are the characteristics of flocculated suspension around the isoelectric point.

## 6. Conclusions

The following conclusions have been drawn based on this investigation:

1. It is revealed by the present studies that the degree of dispersion and hence the stability of alumina suspensions in aqueous media could be controlled by pH variation and optimum dispersant dosage.

2. It has been found that there is definite pH range with (8.5 and beyond) and without dispersant (3–7.8), where one can get optimal dispersion of the suspensions.

3. The iep of alumina powder without dispersant is around pH 9.1. The iep of alumina powder shifted to more acidic pH 6.3 in presence of dispersant APC. The surface is negatively charged at a wide range of pH greater than 6.3, as a result one can have better working pH range. The dispersant also changes the surface charge appreciably.

4. The interaction energy and iep data's are very informative which gives direct ideas about the kind of interaction between ceramic particles and the polymeric dispersant. Whether the interactions are physisorbing or chemisorbing, therefore, one can get vital clues for manipulating dispersion stability, more so if there is more than one dispersant/chemical additive.

5. There appears to be good correlation between particle size distribution, zeta potential, sedimentation and viscosity measurements. The study also shows that the good understanding of surface chemistry required for colloidal processing of suspensions.

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