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Experimental methods for measuring the optimum amount of dispersant for seven Sumitomo alumina powders

M. BURKE, R. GREENWOOD*, K. KENDALL
Birchall Centre for Inorganic Chemistry and Material Science, Department of Chemistry, Keele University, Keele, Staffordshire, UK ST5 5BG
E-mail: cha27@keele.ac.uk

Seven Sumitomo alumina powders of different surface areas and particle size distributions were studied with a view to determining the optimum amount of dispersant (Darvan 821A) required to stabilise aqueous suspensions prepared from the powders. Three different techniques were used; sedimentation, particle sizing and acoustophoresis. Acoustophoresis proved to be the most accurate and quickest way of establishing the optimum amount. It was also shown that the optimum amount of dispersant (0.59 mg/m^2) required to stabilise the different sized alumina powders was independent of the powder surface area/size. Sedimentation results demonstrated that the larger particles acted like hard spheres with thin double layers and gave a smaller relative sediment height than the small particles under the same conditions, i.e. volume fraction and electrolyte strength. This was because the small particles acted as soft spheres with thick double layers that resulted in the particles keeping far apart from one another and hence giving a larger sediment volume. © *1998 Kluwer Academic Publishers*

1. Introduction

In colloidal processing it is important to know exactly how much dispersant is required to stabilise the powder against aggregation. Aggregation of powder particles in aqueous suspension occurs due to the van der Waals attractive force. However, this attractive force can be overcome by either the adsorption of a polymer layer onto the particle surface, such that the particles never physically come close enough for the attractive force to dominate- termed steric stabilisation. Or the particles can be stabilised electrostatically; by varying the pH the surface charge density can be adjusted such that large repulsive forces are generated.

In the ceramic industry polyelectrolytes are traditionally used to impart stability to ceramic suspensions. A polyelectrolyte is essentially a polymer chain that contains dissociable groups such as carboxylic acid groups. As the pH of the suspension is increased the polyelectrolyte becomes more dissociated such that stabilisation of the powder particles is obtained by a combination of steric and electrostatic effects. For the groups to be fully dissociated it is necessary to work in relatively basic conditions.

For economic and stability reasons it is essential that the optimum amount of dispersant is added to a suspension. Too little and stabilisation is incomplete such that aggregates may exist producing flaws in the final product and reducing the products mechanical properties. Adding too much dispersant is an unnecessary extravagance and can also lead to reduced stability as an unadsorbed polyelectrolyte molecule will have the same effect as increasing the salt concentration, i.e. reducing colloidal stability and causing flocculation. Hence the remit of this paper is to investigate the methods for determining this optimum amount and deciding which method reveals quick, reliable results.

Ceramic particle surfaces in suspension are either positively or negatively charged depending on the pH conditions. It is important to have an idea of the amount of this surface charge, which is normally measured via the surface charge density. However, this is very difficult to measure so zeta potentials are measured instead as a reasonably accurate estimate. The zeta potential is defined as the potential at the plane of shear, which is approximately one hydrated ion away from the particle surface [1–4].

The magnitude of the zeta potential is directly related to the magnitude of the repulsive force. For small zeta potentials the repulsive force is small, such that overall the van der Waals attractive force dominates so aggregates form. However, with larger zeta potentials the repulsive force between particles is larger than the van der Waals attractive force, hence preventing the particles from aggregating.

Electrophoresis and acoustophoresis are both methods for measuring the zeta potential of a suspension.

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* Author to whom all correspondence should be addressed.

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The former is an established technique for dilute suspensions. The suspension is subjected to an alternating electric field (strength E) which causes the charged particles to move. The velocity (v) of the particles is then related to the zeta potential via the mobility which is defined as v/E. Acoustophoresis is a relatively new technique and has the advantage of working at much higher volume fractions than electrophoresis [5, 6]. In this technique an alternating electric field of a known frequency is applied to the suspension which causes the particles to oscillate at the same frequency. The liquid within the shear plane around the particle also moves with the particle, but due to difference in permitivity and density (thus inertia) the movements are out of synch. This results in a cyclic longitudinal pressure variation in the suspending liquid, i.e. a sound wave.

This acoustic wave is then detected by the transducers. The amplitude of this acoustic signal and its phase difference is then recorded in the dynamic mobility spectrum (frequency range 300 kHz to 11.5 MHz). From this the zeta potential and the particle size can be calculated. This technique has been used by numerous researchers to study concentrated ceramic suspensions and the adsorption of polyelectrolytes [7–14].

Another aim of this paper to investigate the effect of particle size and particle surface area on the optimum adsorbed amount of dispersant. The effect of molecular weight of the dispersant on the adsorbed layer thickness on spherical particles has been widely studied [15] and experiments agree with theory. Several investigators have also investigated the effect of particle size on the adsorbed layer thickness [16–18].

2. Experimental

Seven alumina powders were received from the Sumitomo Chemical Co. Ltd., Tokyo, Japan. The only difference between the samples being the particle size distribution, the surface areas and the impurity levels. The seven powders were coded AA5, AA2, AA1, AA07, AA05, AA04 and AA03 where the number refers to the approximate d_{50} value of the particle size distribution in microns.

The surface area of the powders was measured using BET single point nitrogen adsorption and compared to the manufacturer's values. Particle sizing experiments were carried out using the Malvern Mastersizer E particle sizer (Malvern Instruments Ltd, Malvern, Worcs, UK) and a sonic probe to disperse the particles (Jencons Scientific Ltd, Leighton Buzzard, Beds, UK). This involved mixing 10 g of powder with 20 ml of double distilled water in a plastic beaker, to produce suspensions with volume fractions (ϕ) of 0.11. The volume fraction of the suspension is defined as the volume of the powder/total volume of the suspension. The suspension was then de aggregated using ultra sound (60% amplitude in pulse mode, 1 s on, 1 s off, for a total sonication time of 1 minute). Darvan 821 A (R. T. Vanderbilt, Norwalk, CT, USA) was selected as the dispersant and the particle size distribution noted as a function of the amount of dispersant added for each of the seven powders. As a very small amount of dispersant has a large effect on the particle size distribution, the dispersant was diluted down to allow accurate concentrations to be prepared. Hence, all the suspensions were prepared from a stock solution of 2.6 g of Darvan 821A in 180 ml of double distilled water. Darvan 821A was supplied as a solution containing 40% active material (ammonium polyacrylate). From previous acoustophoresis experiments on alumina powders Darvan 821A has proved to be a good dispersant [19].

After the particle sizing measurements the suspensions were decanted into 25 ml glass measuring cylinders for sedimentation tests and the top sealed with parafilm to prevent evaporation. In sedimentation studies two interfaces can be followed; the upper interface of the supernatant and the suspension and the lower interface of the sediment and the suspension. Here the initial height of the suspension was noted and the two interfaces followed with time. The volume fraction of all suspensions was taken to be 0.11.

Another widely used method for determining the optimum dispersant concentration is by measurement of zeta potentials. As Darvan 821A is a polyelectrolyte it is possible to measure the change in zeta potential of a suspension as the dispersant adsorbs onto the particle surface. In this study an Acoustosizer (Colloidal Dynamics, USA) was used to study the adsorption of a solution of Darvan 821A (typically 3 g in 60 ml water). 400 ml of alumina suspension was used at a volume fraction 0.08 for the sub micron powders. Higher volume fractions of 0.16 were used for the AA1, 2 and 5 powders, so that there was a sufficiently high surface area for adsorption to occur over. Again all water was double distilled. Suspensions were prepared by vibro milling the powder with approximately 200 g of 2.5 cm alumina grinding media for 30 minutes. This was sufficient to disperse the powders without increasing the surface area.

The Acoustosizer was calibrated in air and with the standard solution at 25 °C on a daily basis. Graphs of zeta potential against the amount of added dispersant were then calculated. This was based on the amount of active dispersant adsorbed per unit surface area of powder, to allow comparison between the powders.

3. Results

3.1. Powder characteristics

In Table I the specific surface areas of the powders were compared to those reported by the manufacturer. There was excellent agreement between the two sets of results and both revealed that the surface area per gram

TABLE I Comparison of measured to reported surface areas of the seven alumina powders

Powder	Measured surface area (m^2/g)	Reported surface area (m^2/g)
AA03	4.2	4.6
AA04	4.3	4.3
AA05	3.1	3.2
AA07	2.1	2.0
AA1	1.5	1.4
AA2	0.96	0.90
AA5	0.45	0.50

TABLE II Particle size distribution of the alumina powders, taken from manufacturers sedigraph experiments

Powder	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
AA03	0.22	0.45	1.30
AA04	0.32	0.50	0.80
AA05	0.34	0.51	0.86
AA07	0.68	0.90	1.40
AA1	0.90	1.20	1.70
AA2	1.50	2.00	2.80
AA5	3.70	4.60	6.20

TABLE III Reported impurities (manufacturers values) of the seven alumina powders

Powder	Si (ppm)	Fe (ppm)	Na (ppm)
AA03	8	5	<5
AA04	3	3	<5
AA05	5	5	<5
AA07	<2	5	<5
AA1	3	<2	<5
AA2	10	<2	<5
AA5	50	10	8

of powder decreased with increasing particle size, as would be expected. Table II summarises the manufacturers reported values for the particle size distribution of the various powders. The d_{50} values were taken directly from the data sheets, however, the d_{10} and d_{90} values were estimated from the supplied sedigraph data. The AA03 powder which was nominally the powder with the smallest d_{50} value in fact had a wide particle size distribution. The powders AA04 and AA05 had a narrower size distribution such that more than 95% of the particles were less than one micron in size. The other powders had a large proportion of their particle size distribution in the non colloidal size range (i.e. greater than one micron).

Table III lists the reported impurities in the seven powders. The first five powders had the same low level of impurities, however, the AA2 and AA5 powders had very high silicon contents and high sodium and iron levels. These results, however, do not reveal where about these impurities are located. As it is the surface chemistry of the powders that control the interparticle forces this could be an important consideration.

3.2. Particle sizing data

A typical plot of the effect of the Darvan 821A dispersant on the particle size distribution (d_{10}, d_{50} and d_{90} values) of the seven powders was plotted in Fig. 1, (Darvan 821A adsorbed onto the AA04 powder). The dispersant concentration was plotted as the amount of active component (i.e. 40% of actual weight), per unit surface area of powder. Powders AA 1, 2 and 5 gave suspensions with bimodal size distributions with a small amount of fine particles, but with the bulk of the distribution occuring at the expected size range for that powder. The other powders gave suspensions with a wide particle size distribution, as would be expected from the manufacturers data.

With no dispersant present the particles are aggregated and there was a wide particle size distribution. On addition of the dispersant the particles become de aggregated and the individual particles are stabilised so the particle size distribution becomes narrower. At the optimum dispersant concentration the particle size distribution was minimised. This effect was more apparent with the sub micron sized powders where the colloidal

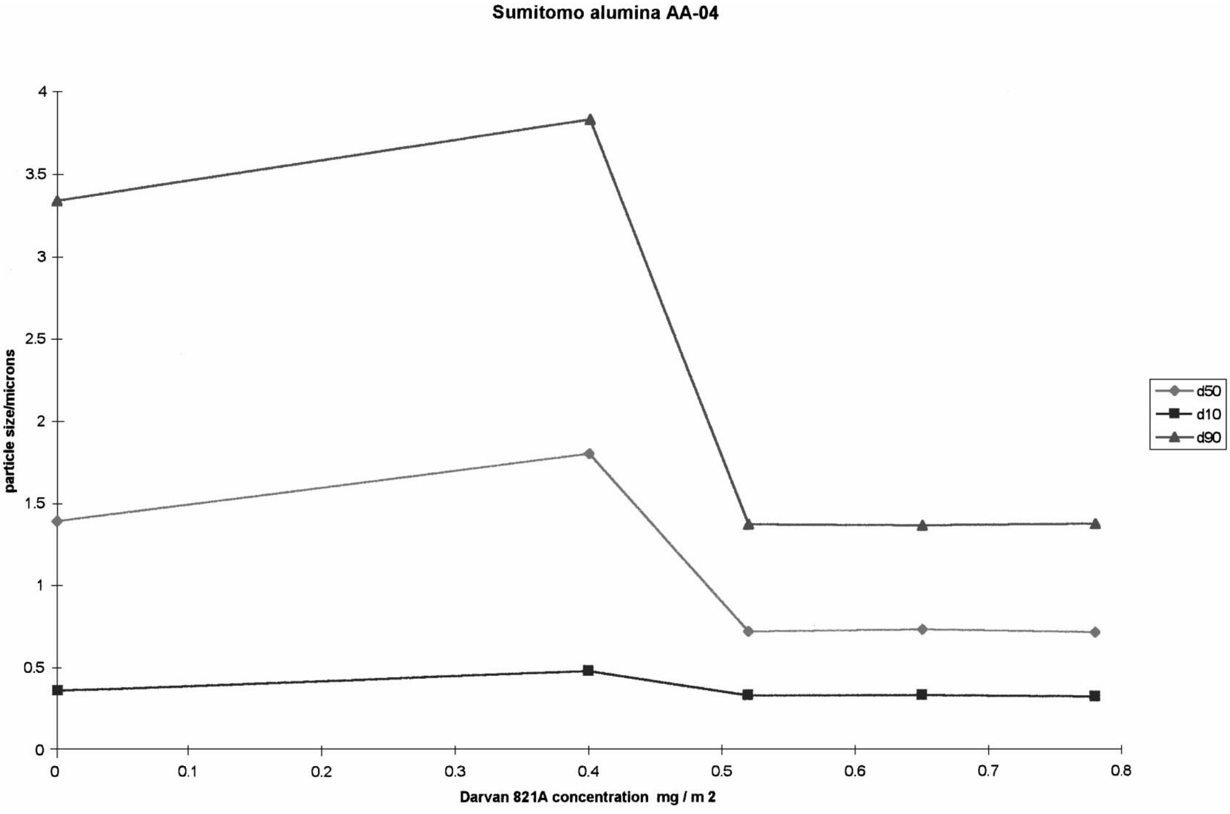

Figure 1 Particle size of a suspension prepared from the AA04 powder as a function of the amount of Darvan 821A dispersant added.

TABLE IV Optimum dispersant concentration of Darvan 821A per powder, as estimated from the three different methods

	Optimum dispersant concentration (mg/m^2)		
Powder	Sizing	Sedimentation	Acoustophoresis
AA04	0.40–0.52	0.52–0.65	0.57 ± 0.03
AA03	0.00–0.69	0.00–0.69	0.59 ± 0.03
AA05	0.56–0.75	0.75–0.90	0.69 ± 0.04
AA07	0.55–0.83	0.55–0.83	0.53 ± 0.04
AA1	0.77–1.16	0.77–1.16	0.58 ± 0.03
AA2	0.00–1.20	1.20–1.80	0.49 ± 0.04
AA5	0.00–0.44	0.00–1.28	/

forces were dominant and aggregates were more likely to form, than in the larger sized powders.

From these initial experiments it is only possible to estimate a range wherein the optimum concentration may be found. The best estimate for the optimum amount of dispersant for the AA04 powder in Fig. 1 is 0.52–0.65 mg/m^2. More accurate estimates for the optimum amount could be obtained by preparing several more samples within that range. The optimum dispersant ranges for Darvan 821A adsorbed onto the seven powders are summarised in Table IV.

As the same diluted dispersant solution was used for all seven powders the size of the optimum dispersant range increased with increasing particle size/surface area, i.e. the experiments were less sensitive as the surface areas of the powders become smaller. So powder AA5 was used again with a different concentration of dispersant solution and the optimum range identified as 0.00–0.44 mg/m^2. This is indicative of how difficult it is to design an accurate experiment to locate the optimum amount.

The actual particle size distribution as measured on the Malvern Mastersizer was greater than that reported by the manufacturer. This may be due to different sizing techniques that have been employed, i.e. the Sedigraph. However, the same general trend of increasing coarseness as the surface area decreased was noted and an indication of the likely optimum concentration can be obtained. Particle sizing using the Malvern is probably best limited to the sub micron powders, where sedimentation is less of a problem.

3.3. Sedimentation results

It proved impossible to measure the upper and lower sedimentation interfaces as most samples sedimented quickly (2–3 days). The larger particle sized suspensions sedimented extremely quickly which was as expected, see Table V. It was fairly difficult to measure the position of the sediment with great accuracy and all the measuring cylinders may not be manufactured to exactly the same dimensions introducing some errors into the results. However, despite this some interesting results were obtained. All the suspensions had a clear supernatant above the sediment, except when no dispersant was present in which case there was a slight turbidity due to fine particles still in suspension. Additionally some of the suspensions, prepared from the finer particles and containing less than the optimum amount of dispersant, were slightly cloudy again due to very fine particles in suspension.

TABLE V Effect of particle size on the sedimentation rate of a suspension

Particle radius (μm)	Sedimentation rate ($m\ s^{-1}$)	Approx. time for a 10 cm sediment
0.1	7.3×10^{-8}	16 days
1	7.3×10^{-6}	4 hours
10	7.3×10^{-4}	2 minutes

The rate of sedimentation for dilute suspensions of rigid, non interacting, spheres can be calculated by equating the buoyancy and drag force to the gravitational force [20].

$$v_0 = \frac{2a^2 \Delta\rho g}{9\eta} \tag{1}$$

where $\Delta\rho$ density difference between particles and the medium
η = viscosity of the medium
a = particle radius
g = acceleration due to gravity

For alumina particles in water at 25 °C, the density of water is 997.3 kg/m^3, the density of alumina is 3990 kg/m^3 and the viscosity of water is 8.9×10^{-4} Pa s. The sedimentation rates for three different particle sizes of alumina are given in Table V. The time taken to generate a 10 cm sediment is also noted. The smaller the particle size the greater the effect of Brownian motion on the particles and the greater the retarding drag force. This is also reflected in the time taken to produce a fixed amount of sediment. This explains why the larger particles sedimented quickly and why there was insufficient time to collect data on the rate of sedimentation. Instead of following the two interfaces with time, the height of the final sediment after six weeks was recorded and normalised with respect to the initial height of the suspension.

From the relative sediment heights as a function of dispersant concentration it was possible to identify an optimum dispersant concentration range for each powder. This corresponded to the dispersant concentration which caused the minimum sediment height. These are listed in Table IV. There was good agreement between the sedimentation results and the particle sizing except for the two larger sized powders, where the dispersant concentration range was too large for reasonable measurements.

When there was insufficient dispersant present for stabilisation of the particles then the dispersant adsorbed onto two or more particles causing them to flocculate, leading to a loose open sediment with a large relative sediment height. This is termed bridging flocculation and was particularly evident in powder AA05 at a dispersant concentration of 0.56 mg/m^2. A large excess of added dispersant led to an increase in relative sediment height as the polyelectrolyte acted like an electrolyte in compressing the double layer. Thus

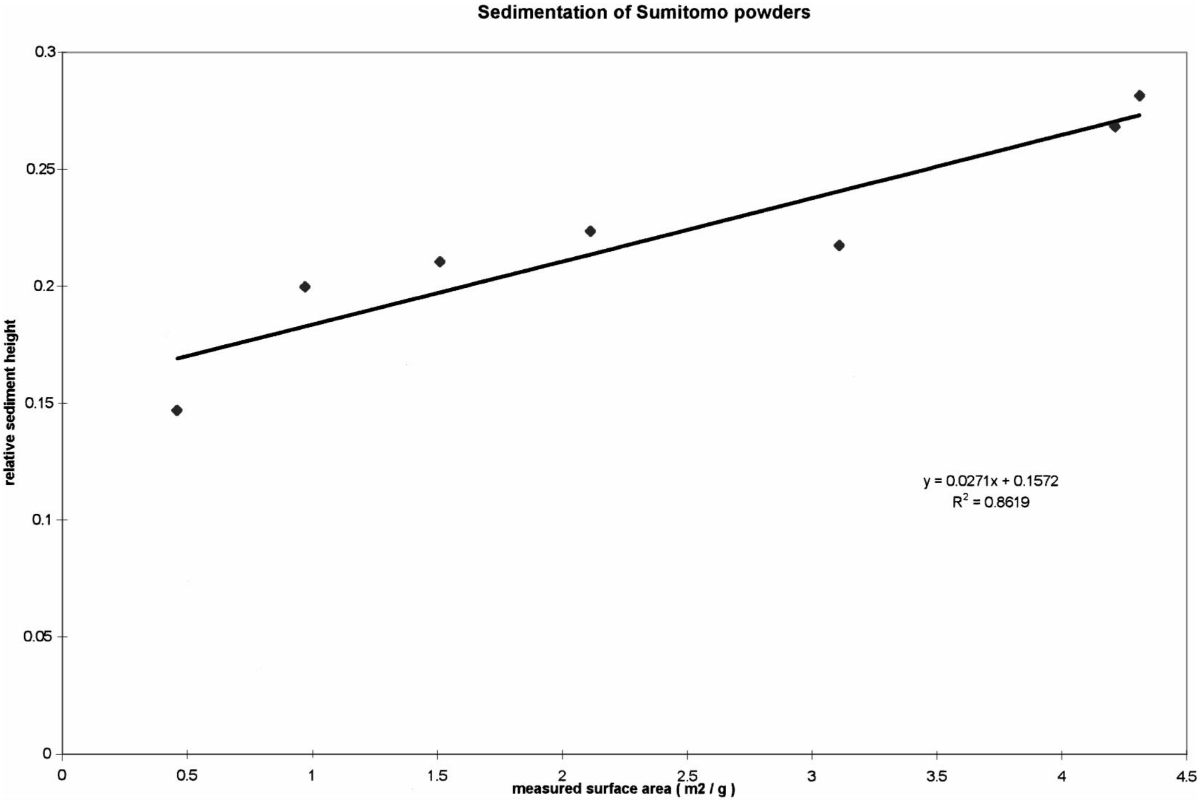

Figure 2 Relative sediment height of the alumina suspensions against the surface area of the powders (volume fraction 0.11, sedimentation time of six weeks, no dispersant present).

causing destabilisation of the system and aggregating the particles to form an open flocculated sediment.

If the final relative sediment heights for each suspension with *no* dispersant present are plotted against the surface area for all seven powders then an interesting trend occurs, see Fig. 2. (Note that the relative sediment height of powder AA5 was underestimated as some of the fine particles had adsorbed on the glass walls of the measuring cylinder instead of sedimenting out. Powder AA05 was also slightly out of line with the others, but the reason why was not apparent.) The suspensions of the smaller particle sized powders produced a greater sediment volume than the sediments created by suspensions of the larger particle sized powders. This can be explained by the presence of the electrical double layer.

When a charged particle is in suspension, counter-ions in the suspending medium are attracted to the surface, whilst co-ions are repelled. This arrangement of ions has been modeled in numerous ways and is termed the electrical double layer. The thickness of this double layer is represented by the Debye Huckel length, κ^{-1}. The Debye Huckel length is then a measurement of how far the electrical double layer extends out into the suspending medium and gives an indication at what interparticle separation repulsive forces start to act. Addition of an electrolyte to the solution has the effect of reducing κ^{-1} and flocculating the particles.

With no electrolyte present then the double layer thickness (κ^{-1}) is large, probably of the order of 100 nm [21] (corresponding to an electrolyte strength of 10^{-5} M). This increases the effective size of the particles (radius a) and hence leads to a greater effective volume, ϕ_{eff}, given by Equation 2.

$$\phi_{\text{eff}} = \phi\left(1 + \frac{\kappa^{-1}}{a}\right)^3 \tag{2}$$

Obviously this effect will be greatest for the smaller particles. For a fixed volume fraction and electrolyte strength this leads to the smaller particles having a greater sediment volume as they arrange themselves as far apart from each other as possible. Another way of describing this is that the large particles act as hard spheres with *thin* double layers, (relative to the particle size) and so pack closely. Whilst the small particles act as soft spheres with *thick* double layers and pack more openly.

3.4. Acoustophoresis

A typical plot of the amount of Darvan 821A added per unit surface area of the AA04 powder is shown in Fig. 3. Initially the suspensions had large positive zeta potentials of approximately +70 to +80 mV, except the AA2 powder which had much lower zeta potential and the AA5 powder which was negatively charged, see Table VI. This is possibly due to their surface chemistry being different perhaps because of a slightly different manufacturing process, or it could be that the impurities are dissolving out of these powders.

The initial suspensions were also relatively acidic (pH values of 4 to 6) again except for those prepared from the two larger particle sized powders (AA2 and

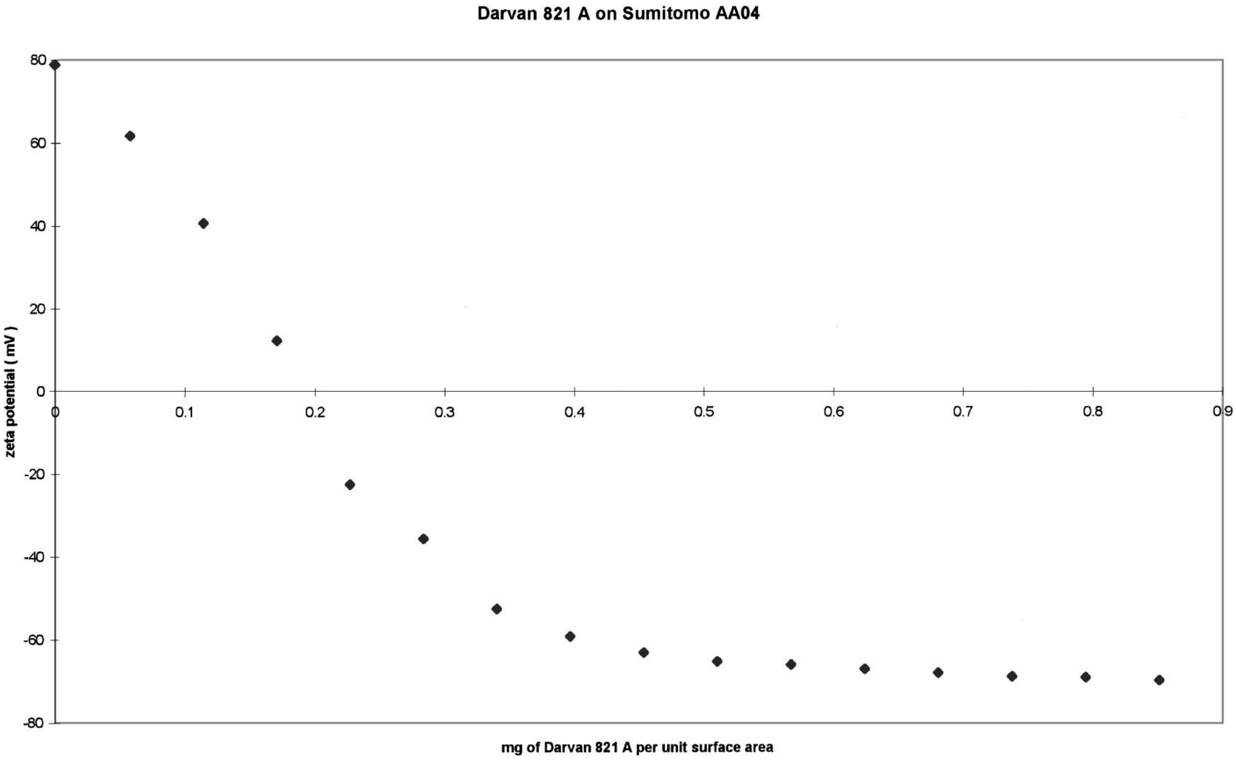

Figure 3 Adsorption of Darvan 821A onto a suspension prepared from the AA04 powder.

TABLE VI Initial and final suspension characteristics

Powder	Initial pH	Initial zeta potential (mV)	Final zeta potential (mV)	Final pH
AA03	4.08	+74.3	−66	7.88
AA04	4.82	+78.9	−69	8.27
AA05	4.48	+77.8	−64	7.84
AA07	5.98	+71.2	−76	8.29
AA1	4.86	+88.2	−76	8.20
AA2	7.01	+13.9	−78	8.18
AA5	6.81	−12.3	—	8.09

AA5) which were near neutral. The pH of the suspensions also increased with the addition of the Darvan 821A. It is the pH of the suspension that controls the degree of dissociation of the polyelectrolyte. As the pH was increased the degree of dissociation becomes greater, i.e. more negative sites develop on the polymer, enhancing its ability to stabilise the suspension. On addition of the dispersant the zeta potential decreased as the dispersant was adsorbed onto the powder surface. As more dispersant was adsorbed the particles became negatively charged to approximately −70 mV.

After a certain dispersant concentration the zeta potential no longer increased and a plateau value was obtained. This was because no more dispersant can adsorb onto the particles. Any more added dispersant remains free in solution. The concentration at which this plateau region starts was taken to be the optimum amount of dispersant required to stabilise the suspension. So in Fig. 3 the optimum concentration was 0.57 mg/m^2. It proved difficult to measure the adsorption of the Darvan 821A onto the AA5 powder, whether this is due to the effects of sedimentation during the measurement or possibly due to the impurity levels causing flocculation it is hard to say.

The optimum concentrations for all the powders are listed in Table IV. Also included are estimates for the errors in reading the position of the plateau. These results were more accurate than those obtained by sedimentation and particle sizing, that are at best in reasonable agreement with the finer sizes and very poor for the large sized powders. The zeta potentials obtained at optimum dispersant concentration are listed in Table VI along with the pH of the suspensions. The dispersant Darvan 821A was based on polyacrylic acid which is completely dissociated at pH $>$ 8.5 [22], so from the final pH values of the suspensions it would be expected that the Darvan is almost fully dissociated in all cases. Also from the magnitude of the zeta potentials at the optimum dispersant concentration it is predicted that concentrated, stable suspensions should be possible with these powders and Darvan 821A.

The optimum amount of dispersant for each powder was then plotted against the measured surface area (see Fig. 4). If the manufacturer's values for the surface areas of the powders were used instead of the measured values, then the optimum amounts varied by only ±0.02–0.03 mg/m^2. It was difficult to say exactly at which point the optimum dispersant concentration was achieved, but it could estimated to be within ±0.02–0.03 mg/m^2, so if the errors are taken to be additive then error bars of ±0.06 mg/m^2 can be added to the graph.

If the data points were then fitted with a straight line with zero gradient, then the intercept was 0.587 mg/m^2. So it can then be stated that the optimum amount of dispersant required to stabilise the alumina powders is independent of their surface area, over the size range

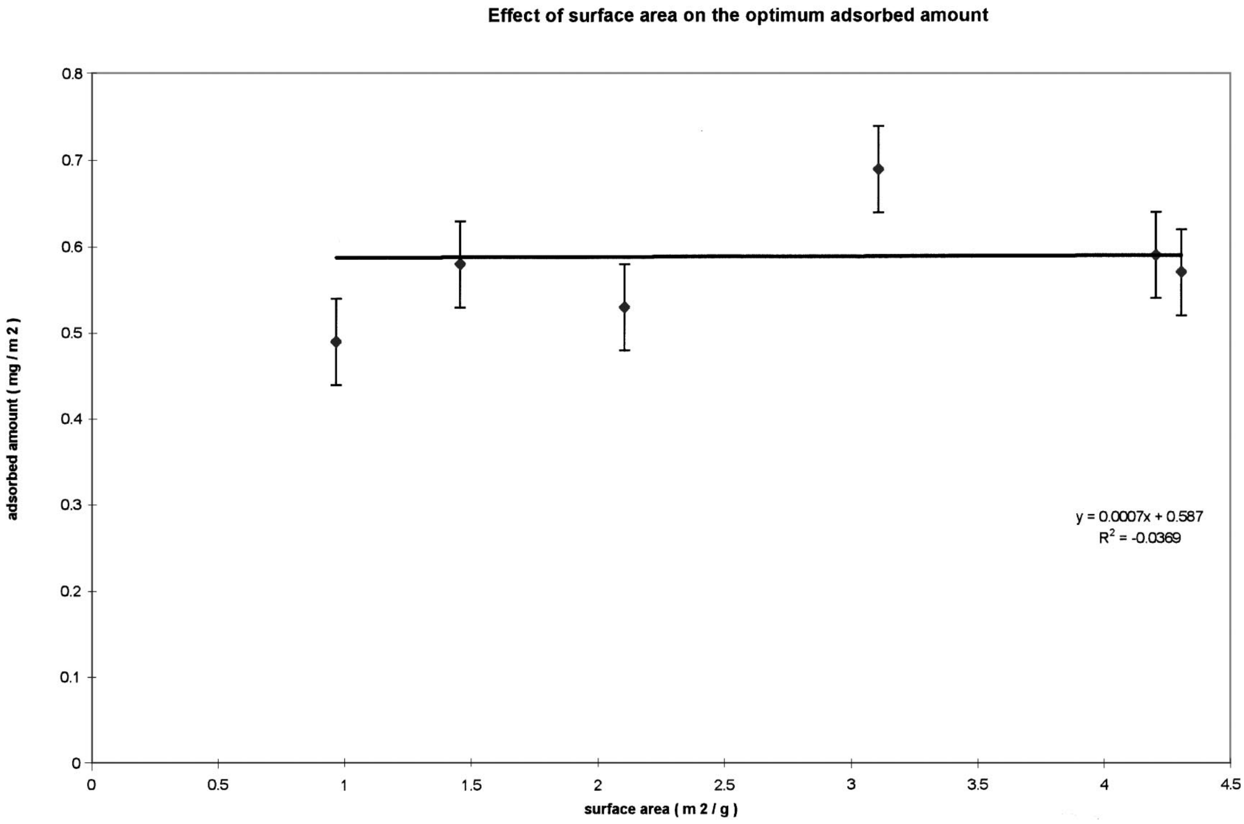

Figure 4 The optimum adsorbed amount of Darvan 821A against the surface area of the powders.

studied. Or the powder particle size did not effect the optimum adsorbed amount, over the volume fraction studied. Again the two powders that were slightly out of line with the other powders were AA05 and AA5.

This then is in agreement with the work of Faers and Luckham [23] who noted the that the optimum amount of ABA block copolymer adsorbed onto polystyrene latices was also independent of the particle size. It would interesting to plot the adsorbed layer thickness against the particle size to confirm other work in the literature, but it is meaningless to measure the adsorbed layer thickness on these alumina particles due to their polydispersity.

initial pH values). This suggests that perhaps they are manufactured slightly differently from the other alumina powders such that they have different surface chemistries.

For the same volume fraction and electrolyte strength, the finer sized powders behaved as soft spheres with thick/diffuse double layers which caused large sediment volumes. Whilst the larger particles behaved as hard spheres with thin double layers which packed to smaller sediment volumes.

Finally, the optimum amount of Darvan 821A dispersant required to stabilise the alumina powders was 0.59 mg/m^2 and was independent of the surface area/particle size.

4. Conclusions

Of the three different techniques used to estimate the optimum amount of dispersant required to stabilise an alumina powder acoustophoresis was the most successful. It was relatively quick and gave a reasonably accurate answer, however, the only minor problem is estimating the position of the plateau value for estimating the optimum amount. Sedimentation experiments take too long and are only as accurate as the concentration range studied. Particle sizing experiments are fairly quick, but appear to be better suited to the sub micron powders. The sizing results are again only accurate if the range of dispersant concentrations is carefully limited, which unfortunately requires prior knowledge of the optimum amount.

Powders AA2 and AA5 were different from the finer powders, with higher impurity levels and different suspension characteristics (i.e. initial zeta potential and

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