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The role of ammonium polyacrylate in dispersing concentrated alumina suspensions

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Abstract

The role of low molecular weight ammonium polyacrylate (NHPA) has been characterised as a dispersant for the colloidal powder processing of high solids content alumina suspensions. It has been found to be a very effective dispersant under the correct conditions, yielding fluid, highly homogeneous aqueous suspensions. Minimum suspension viscosities, one measure of the degree of suspension dispersion, were observed at two different NHPA concentrations for each solids loading examined. The first viscosity minimum was independent of the solids loading; however it produced bodies of relatively low green density. The second viscosity minimum increased with increasing solids loading and yielded components of the highest green density. Adsorption data revealed that maximum adsorption of NHPA onto the alumina surface occurred at this secondary minimum concentration. From the evidence presented it is concluded that the first minimum is rather unstable, decaying as the sample is dried. The second minimum is the more stable, yielding the most favourable properties expected for a dispersed suspension. Predictions of the adsorbed polymer configuration are offered as an explanation for the presence of the two minima. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Ammonium polyacrylate; Dispersion; Suspensions; Viscosity

1. Introduction

Colloidal powder processing is now a widely used method of producing high integrity ceramic components; there is an abundance of literature outlining the principles involved.[1–4] Typically, when ceramic powders are added to a suspending medium such as water the presence of attractive van der Waals forces result in the powders aggregating to form clusters of particles called 'soft' agglomerates. These so-called flocculated suspensions create a relatively high suspension viscosity that can make processing rather difficult and, more importantly, they become potential sites for areas of high stress that can lead to a reduction in the final properties of the component. It is therefore essential that these agglomerates are either prevented from forming or eliminated from the suspension prior to fabrication of the green body. Such agglomerate-free systems are termed dispersed and tend to be relatively fluid and homogeneous. When dried they yield high density compacts. Dispersed systems can be achieved by controlling the surface charge of the powders in solution. There are three main routes: electrostatic, steric and electrosteric dispersion, the latter being effectively a combination of the other two methods. It involves the adsorption of either uncharged polymers onto an electrostatically charged surface or by the adsorption of charged polymers referred to as polyelectrolytes. Typical interparticle potentials versus interparticle separation distance for each of the three dispersion routes are given in Fig. 1. Since ammonium polyacrylate is classed as a 'weak' polyelectrolyte, electrosteric dispersion is the focus of this paper.

Polyelectrolytes are polymers that possess a charge that is present along the length of the polymer chain, as opposed to other polymers that have a charged species at one end of the molecule only. The description here is restricted to 'weak' polyelectrolytes that are derived from weak acid groups such as carboxylic acids and are consequently affected by the pH of the suspension. In contrast 'strong' polyelectrolytes tend to be relatively unaffected by pH changes.

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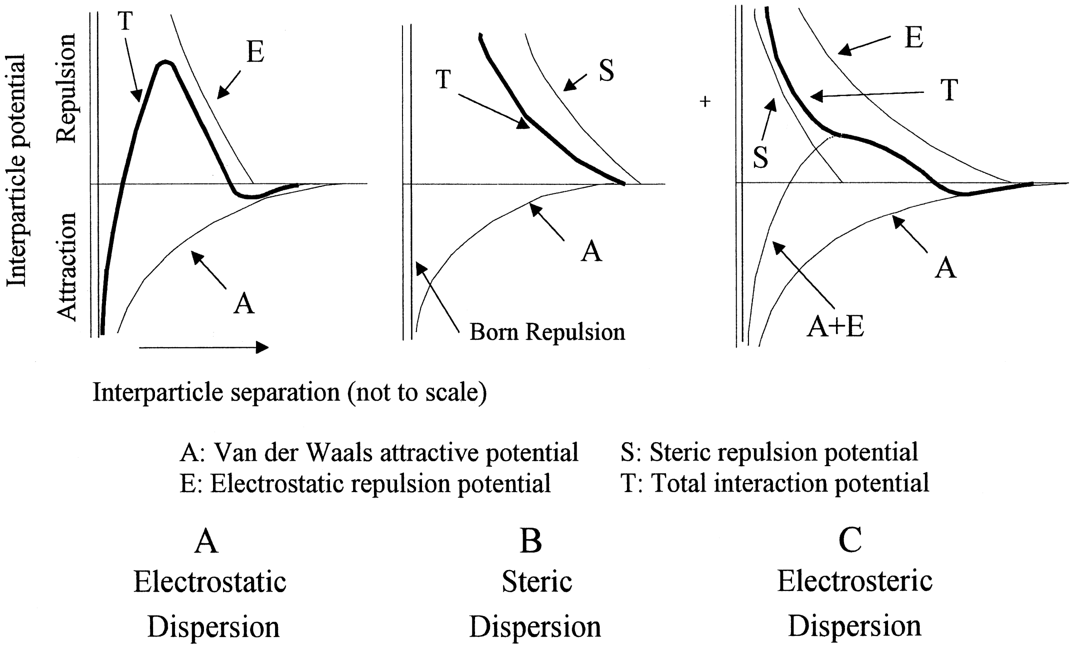
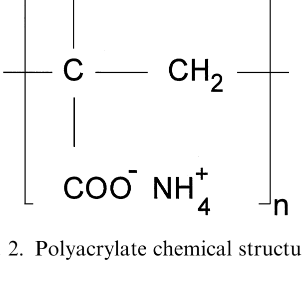


Fig.1. Interparticle potential as a function of interparticle separation for three dispersion mechanisms.

The total interaction potential versus interparticle distance plot of Fig. 1c is effectively the superposition of both electrostatic and steric repulsions. For weak polyelectrolytes such as polyacrylate, Fig. 2, under certain conditions one mechanism will dominate. In solutions of low electrolyte concentration and at a pH above the dissociation point for the acid group, the charged polyelectrolyte will be stretched as a consequence of electrostatic repulsions along the polymer length.[5,6] It will therefore adsorb onto the powder surface in a thin, flat train configuration, with the formation of loops suppressed (Fig. 3). In this scenario the steric barrier is not of sufficient thickness to contribute to the overall dispersion of the system, hence it is primarily achieved by electrostatic repulsion. When the polyelectrolyte is associated or the electrostatic repulsions are suppressed by the presence of high concentrations of electrolyte, dispersion can only be achieved sterically. Under these conditions the polymer is coiled in solution and the adsorption characteristics resemble those of uncharged homopolymers. Dispersion will result only if the adsorbed layer is sufficiently thick so that loops and tails extend beyond the reach of van der Waals forces.[7]



$$\left[-\underset{COO^{-}\,NH_4^{+}}{\overset{H}{C}}-CH_2-\right]_n$$

Fig. 2. Polyacrylate chemical structure.

The above treatment of polymer configuration assumes a constant charge on the substrate onto to which the polymer adsorbs. Adsorption onto a ceramic oxide powder however, is made more complicated by the pH dependent behaviour of the surface layers. Cesarano et al.[8,9] comprehensively studied the dispersion of highly concentrated alumina suspensions using sodium polymethacrylate over a wide range of pH. At low pH alumina is positively charged and at high pH negatively charged with a point of zero charge (PZC) in between. It was reported that the quantity of polymethacrylate required for monolayer polymer coverage of the particles and hence complete electrosteric dispersion decreased with increasing pH. This was attributed to the dominance of a loop and tail configuration at low pH, whilst at higher pH values up to the ceramic's PZC, the presence of a train configuration of stretched negatively charged polymer adsorbed onto positively charged surface sites was considered to exist. At pH values above the PZC, electrostatic repulsions between the negative powder and negative polymer caused the linear polyelectrolyte to dangle into the solution, adsorbing to the surface only at the few minor regions of positive surface charge. This model has been supported by Tjipangandjara et al.[10] who studied the configuration of adsorbed polyacrylic acid (20 ppm, molecular weight 88,000) on alumina from solutions of fixed and varying pH using fluorescence spectroscopy techniques.

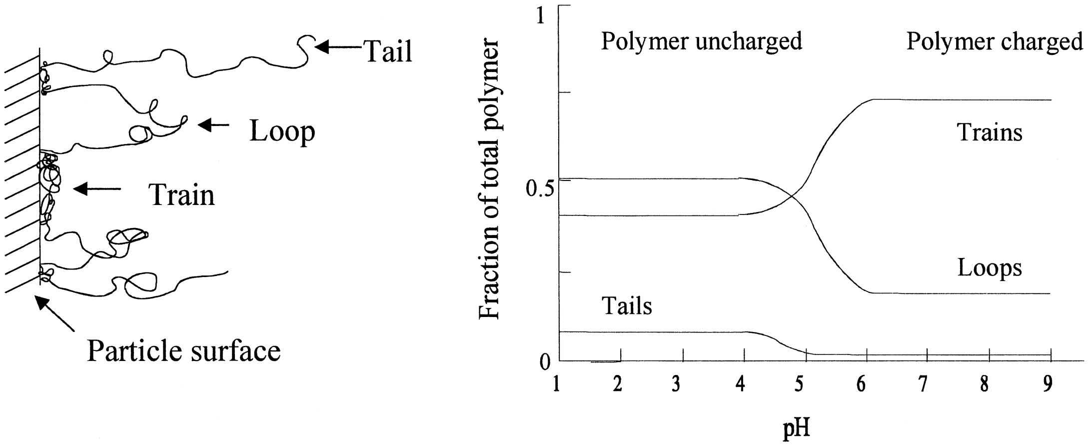


Fig. 3. Train, loop and tail configurations for polyelectrolyte attached to ceramic powder surfaces in suspensions.

2. Experimental

The main purpose of the research was to determine the role of ammonium polyacrylate, NHPA, as a dispersant for 70–81 wt% solids content alumina suspensions at high pH. Specifically, the experiments aimed to:

- Characterise the dispersive ability of NHPA for colloidal processing as a function of pH and solids content via viscometry, sedimentation, densimetry and adsorption techniques.
- Gain insight into the adsorbed polymer configurations and hence evidence regarding the theories described above by monitoring the effect of the particle surface charge on dispersion.

2.1. Sample preparation

The ammonium polyacrylate (NHPA) used was a commercially available product, Dispex A40 (Allied Colloids, Bradford, UK). It is a 37.6% concentrated solution of average molecular weight 3500 g mol^{-1}. The quantities of active dispersant used are quoted in mg of NHPA used (not Dispex) per g of alumina powder (mg g^{-1}).

Appropriate quantities of distilled water, weighed to ± 0.02 g, and NHPA solution, weighed to ± 0.003 g, were mixed until the dispersant was uniformly distributed. The water associated with the dispersant solution was accounted for in the calculation. A16SG alumina powder [Alcoa Manufacturing (GB) Ltd, Worcester, UK], weighed to ± 0.02 g, was added to the mixture and the blends stirred until a homogeneous suspension formed, all samples being based on a total weight of 50 g. Any acidic pH adjustments required were made using concentrated HCl or 0.1 M HCl whilst alkaline adjustments were made using concentrated NH_4OH or 0.1 M NaOH, the concentrations used depending on the desired pH change. The slurries were then subjected to ultrasonic agitation produced by a Kerry ultrasound unit (Kerry Ultrasonics Ltd, Hitchin, UK) using 150 W at 20 kHz, after which the beakers were sealed to prevent water evaporation and left for 1 h to cool and attain equilibrium. The optimum duration of the ultrasonic dispersion was experimentally predetermined by monitoring the time required to produce the minimum viscosity, and hence maximum dispersion, in two suspensions prepared with 1.40 mg g^{-1} NHPA at 70 and 81 wt% alumina. Fig. 4 shows that minimum viscosity was achieved at 60 s for 70 wt% suspensions and at 45 s for 81 wt% suspensions. The rise in viscosity above 45 s for samples containing higher solids is attributed to water evaporation from the sample due to the high temperatures reached. It was arbitrarily decided to use an ultrasonic time of 60 s for 70–80 wt% suspensions and a time of 45 s for samples above 80 wt%. Finally, after being subjected to ultrasound the samples were held at a reduced pressure of 60 mm mercury for 1 h to remove as many air bubbles as possible prior to rheological testing.

2.2. Rheological measurements

Suspension flow behaviour was monitored using a Bohlin Visco 88 viscometer (Bohlin Instruments UK, Cirencester, UK), a controlled speed device that measures shear stress and viscosity as a function of shear rate. A concentric cylinder (C30) measuring system was used. After samples were placed in the viscometer they were left for 5 min to re-equilibrate and hence minimise the effects of previous shear history. Measurements were recorded in a sweep cycle of continuous increasing and then decreasing shear rate ranging from 18 s^{-1} to 1200 s^{-1}. The sample was then left for 5 min to equilibrate again after which time the viscosity was recorded at a constant shear rate of 109 s^{-1} for 3 min or until the viscosity became independent of time.

Initially, the viscosity of alumina slurries with no NHPA added was measured as a function of pH to

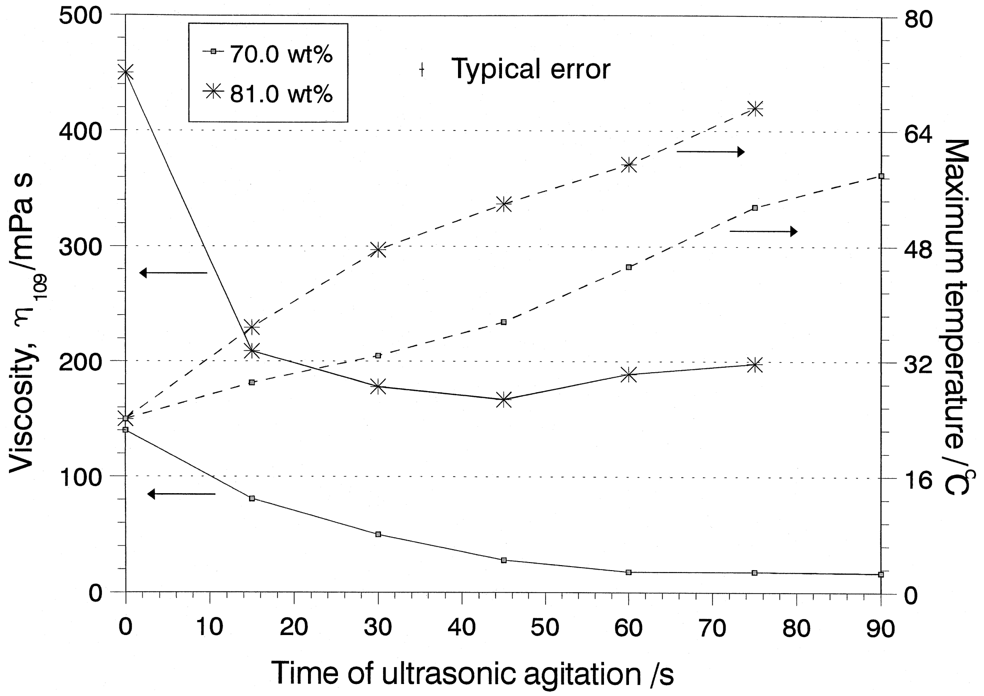


Fig. 4. Effect of ultrasonic agitation time on viscosity for dispersions containing 1.40 mg g^{-1} NHPA.

determine the PZC of the alumina. Subsequently, the effect of the powder surface charge on the concentration of NHPA required for optimum dispersion was monitored by measuring the viscosity of samples prepared at pH 8.0 ± 0.2, which, within error, was the PZC of the powder. The pH was maintained at 8.0 throughout sample preparation by continually monitoring and modifying as appropriate the suspension pH as the powder was added.

2.3. *Adsorption experiments*

Experiments were carried out to determine the amount of NHPA adsorbed from solution onto the alumina powder. This was achieved by measuring the quantity of NHPA remaining in solution. The analytical technique used was first derivative titrational analysis, making use of the acidic nature of the polyacrylate. A typical titrational plot is given in Fig. 5a. The volume of acid coinciding with the first peak is subtracted from the volume associated with the second peak. The resultant volume is directly proportional to the mass of NHPA remaining in solution. A calibration plot of the amount of acid needed to neutralise a known quantity of NHPA in solution was established. This is shown in Fig. 5b.

Dispersed 70 wt% alumina samples with varying NHPA concentration were prepared and centrifuged at 2800 rpm for 1 h. The cloudy supernatant was removed and centrifuged again under the same conditions in an attempt to remove the remaining particles. A known portion of supernatant was extracted, diluted to approximately 40 ml and its pH adjusted to 9.1 before being analysed by first derivative titration. The amount of NHPA in the portion of supernatant was calculated using the calibration plot and extrapolated to determine the total quantity of non-adsorbed NHPA in solution. This was subsequently subtracted from the original amount of NHPA added to the dispersion to determine the amount adsorbed.

It should be noted, however, that even after two centrifuge cycles a small quantity of alumina powder remained in the supernatant of all samples. This will have affected the titration readings, particularly at low NHPA concentrations. Therefore, it was necessary to compensate for the effects of the powder in the supernatant. This was achieved by examining supernatants from suspensions prepared with between 0.31 and 0.76 mg g^{-1} NHPA where it could be reasonably assumed that complete adsorption of NHPA occurred and no polymer remained in solution. The amount of NHPA calculated to be in solution at these concentrations was subtracted from all other samples of higher NHPA levels. The use of this correction factor was supported by the following experiment. When sufficient HCl was added such that the supernatant pH was lowered to < 3, the powder precipitated out in samples dispersed with > 2.4 mg g^{-1} NHPA. The precipitate was removed and the supernatant re-analysed under increasing pH conditions using 0.1 M NaOH. The calculated amounts of NHPA adsorbed (Table 1) were identical to those

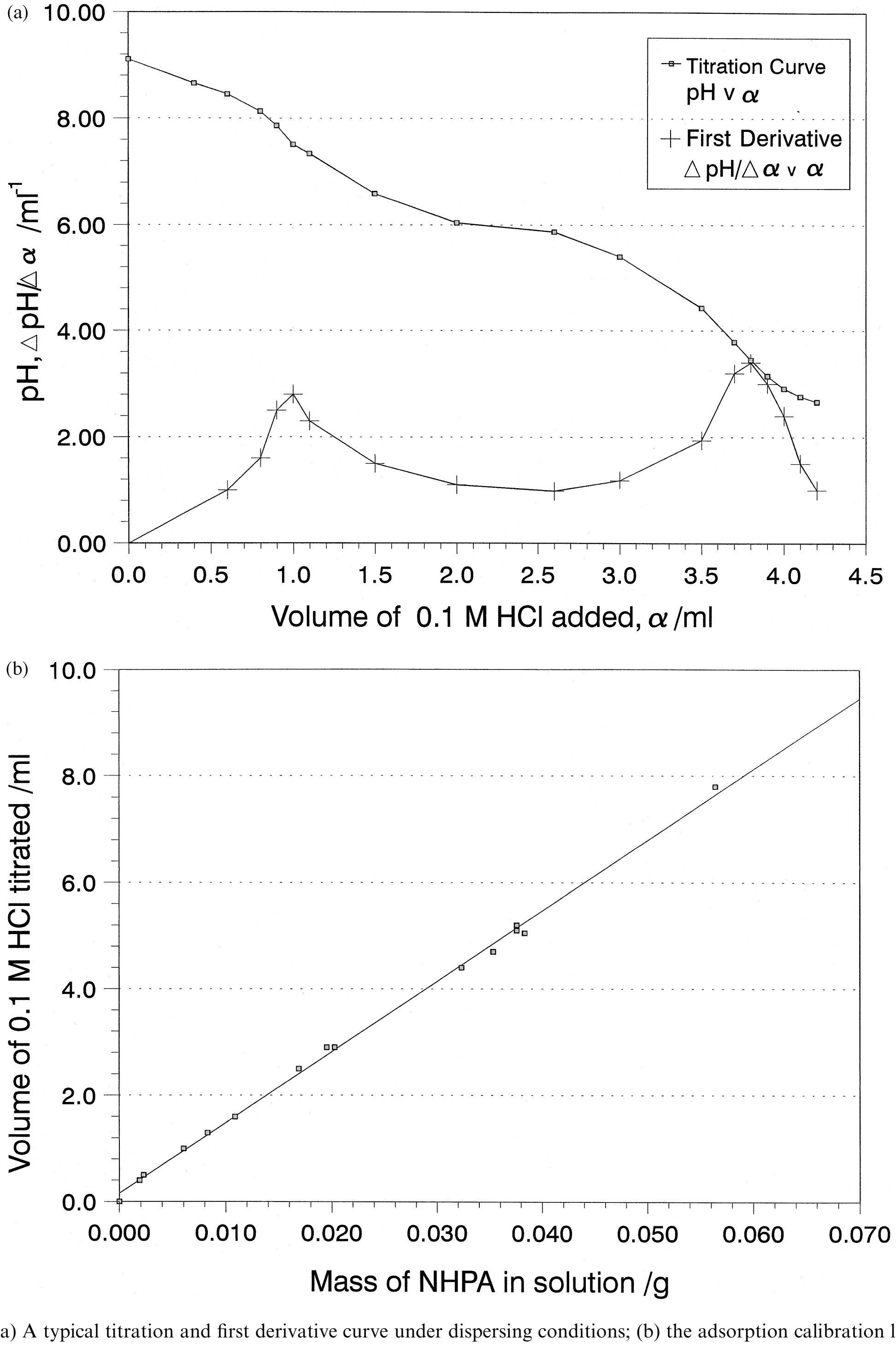


Fig. 5. (a) A typical titration and first derivative curve under dispersing conditions; (b) the adsorption calibration line used.

obtained for the corrected titre approach thereby justifying its use. Dispersions containing <2.4 mg g^{-1} NHPA did not undergo precipitation.

2.4. Sedimentation behaviour

A series of samples with varying solids contents and NHPA additions were left to settle in a vibration-free environment. The height of the sediment formed and the transparency of the supernatant formed were noted over a 3 month period.

2.5. Maximum packing volume fraction

A modified version of Eilers[11] equation, [Eq. (1)], was used in its linear form, Eq. (2) to calculate the maximum packing volume fraction, $\phi_{\max,}$ of the suspensions. That is, the volume fraction, ϕ, at which the suspensions are

Table 1
Adsorption of 5.71 mg g^{-1} NHPA onto alumina as a function of time under dispersing conditions

Amount of NHPA added to suspensions		Volume of supernatant	Volume of 0.1 M HCl titrated	Mass of NHPA in supernatant	Amount of NHPA adsorbed	
(g) ± 0.001	(mg g^{-1}) ± 0.03	V$_s$ (ml) ± 0.05	α (ml) ± 0.2	M^s_{NHPA} (g) ± 0.002	(g) ± 0.008	(mg g^{-1}) ± 0.2
0.098	2.80	5.40	0.5	0.003	0.095	2.7
0.173	4.94	5.00	3.6	0.026	0.096	2.7
0.199	5.69	3.00	2.8	0.020	0.100	2.9

concentrated to such an extent that they no longer act as a fluid but rather as a solid.

$$\frac{\eta_{109}}{\eta^o_{109}} = \eta^r_{109} = \left[1 + \left(\frac{C_E\phi\phi_{\max}}{\phi_{\max} - \phi}\right)\right]^2 \qquad (1)$$

$$\left[\frac{1}{\left(\eta^r_{109}\right)^{1/2} - 1}\right] = \frac{1}{C_E}\left[\frac{1}{\phi}\right] - \frac{1}{C_E\phi_{\max}} \qquad (2)$$

where C_E is a disposable constant.

The viscosity of the liquid phase was taken to be that of water at ambient temperature (1.0 mPa s). Therefore the relative viscosity, η^r_{109}, was equal to the measured viscosity of the suspension, η_{109} in mPa s. The left-hand term of Eq. (2) was plotted against $1/\phi$ to produce a linear plot from which the intercept and hence $\phi_{\max}$ could be calculated.

2.6. Green density

The densities of green compacts were measured using the mercury immersion method after they had been dried at 85°C to constant mass. Each value quoted is the average of at least three samples.

3. Results

3.1. Rheological behaviour

A typical rheological flow curve for a suspension dispersed with NHPA is given in Fig. 6. As would be expected all samples possessed pseudoplasticity and thixotropy. However, dilatancy effects were also noticed at solids contents above 81 wt% in suspensions containing up to 2.15 mg g^{-1} NHPA (Fig. 7), the critical shear rate for the onset of dilatancy decreasing with increasing solids loading (Fig. 8). Above 2.15 mg g^{-1}

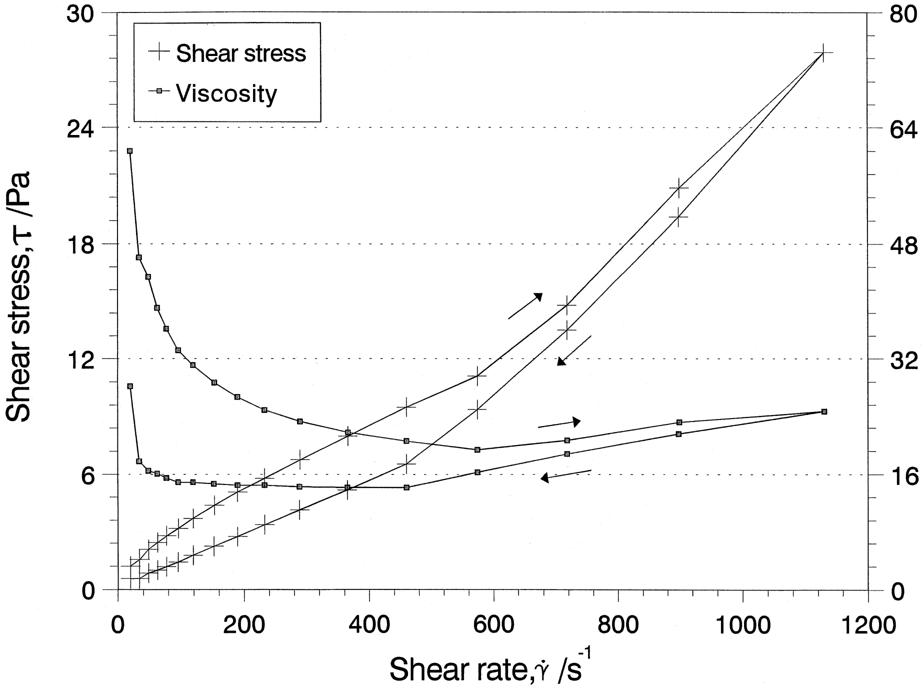


Fig. 6. Typical rheological flow behaviour of samples dispersed with NHPA. This example was prepared with 1.40 mg g^{-1} NHPA at 70 wt% alumina.

NHPA no dilatancy effects were noted over the solids content range tested.

The measured viscosities of suspensions prepared with 70 wt% alumina are plotted as a function of NHPA concentration in Fig. 9. In these experiments the suspension pH was ~9.5, the inherent pH of the suspension. Two viscosity minima can be seen, separated by a maximum. A primary minimum occurred at 1.4 ± 0.1 mg g^{-1} whilst a secondary began at 2.7 ± 0.2 mg g^{-1}. Given the shape of the curves, a minimum is defined as being the concentration at which minimum viscosity is first reached. The corresponding maximum was situated at

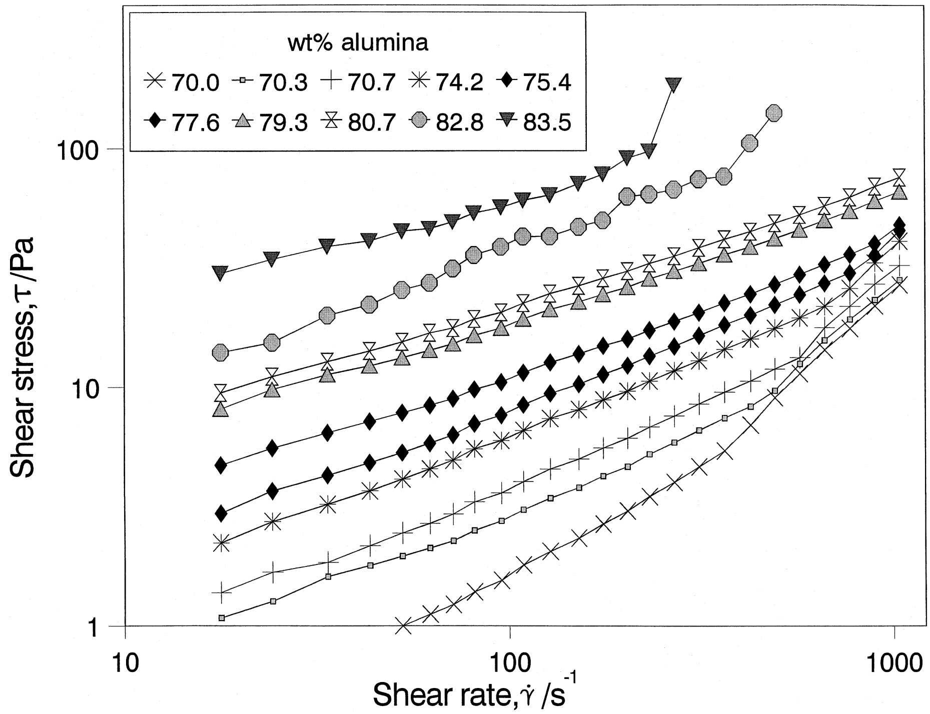


Fig. 7. Flow behaviour of a dispersion containing 1.40 mg g^{-1} NHPA at pH 9.5 during evaporation from 70 wt% alumina, showing dilatancy at high shear rates.

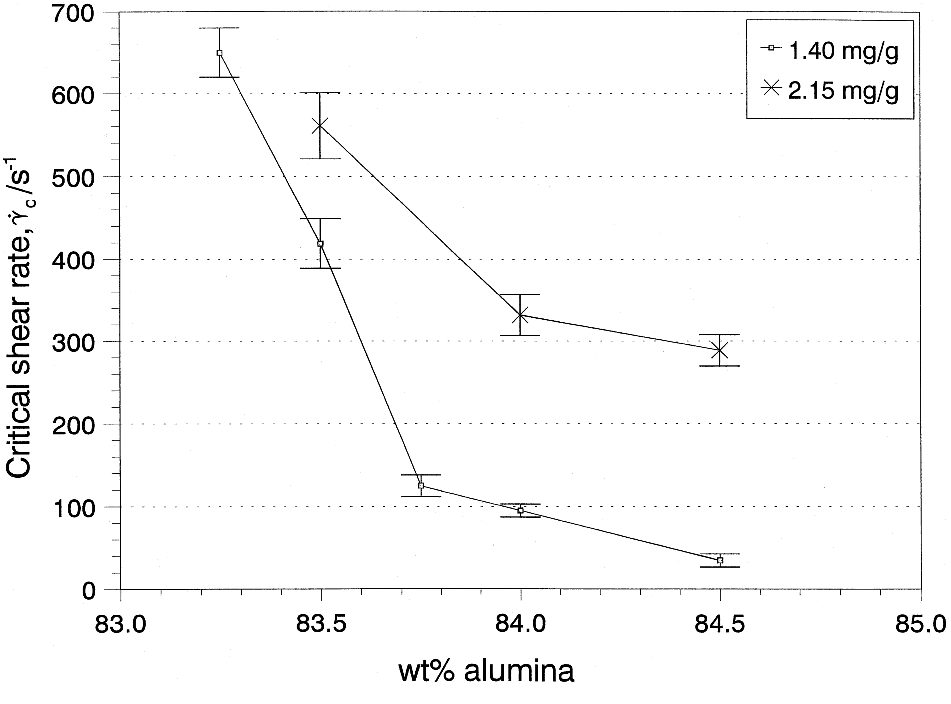


Fig. 8. Critical shear rate for dilatancy onset versus suspension solids loading at pH 9.5.

2.1 ± 0.2 mg g^{-1}, although the viscosity value is significantly lower than that found at polymer concentrations < 1.0 mg g^{-1}.

The measured viscosity of suspensions prepared at increasing alumina contents is plotted as a function of NHPA content in Fig. 10. The primary minimum again occurred at 1.4 ± 0.1 mg g^{-1}, regardless of the solids loading. The maximum followed a similar trend, tending to first reach its peak at 2.1 ± 0.2 mg g^{-1} throughout the solids loading range examined. The secondary minimum, however, increased with solids loading. The concentrations of NHPA required to reach the second minimum are plotted in Fig. 11.

A plot of viscosity versus NHPA concentration at pH 8.0 is given in Fig. 12. Only one minimum was observed, occurring at a NHPA concentration of 3.85 mg g^{-1}.

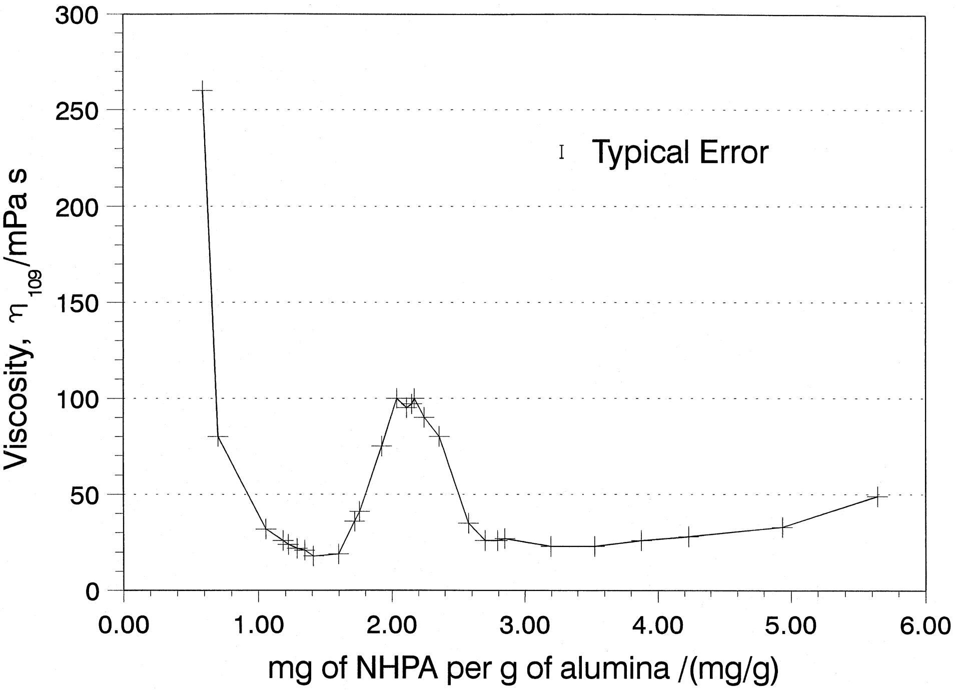


Fig. 9. Viscosity versus NHPA concentration at 70 wt% alumina and a suspension pH of 9.5.

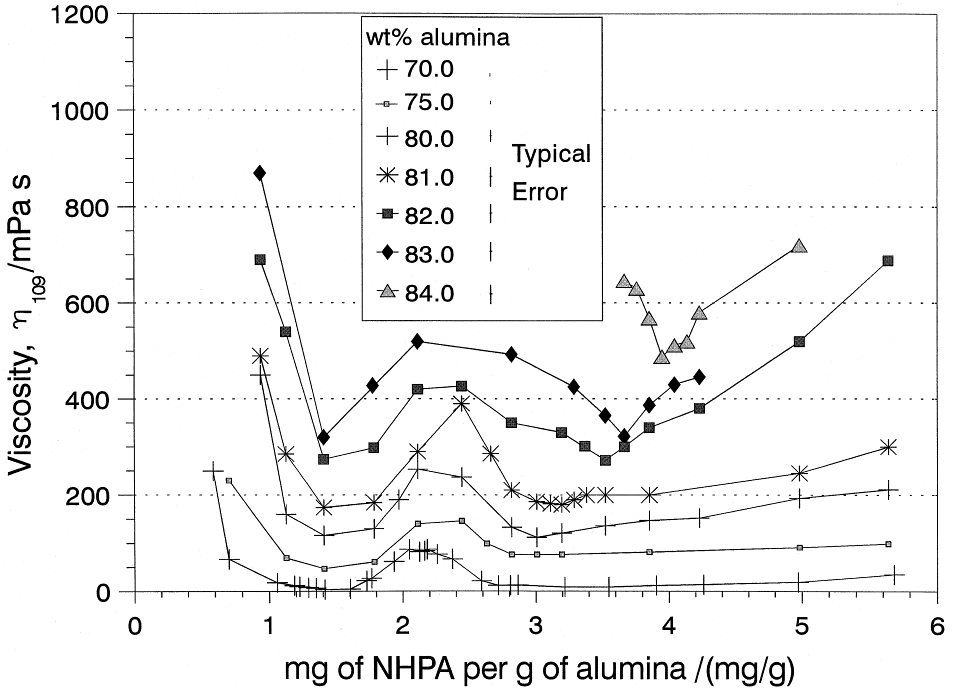


Fig. 10. Viscosity as a function of both NHPA concentration and wt% alumina at pH 9.5.

3.2. Adsorption data

Titrational analysis results of samples dispersed with 0 to 5.71 mg g^{-1} NHPA are summarised in Fig. 13. The concentration of NHPA adsorbed from solution increased with the amount of NHPA in solution up to a plateau level of average value 2.7±0.2 mg g^{-1} NHPA. The effect of time allowed for adsorption is summarised in Table 2. It can be seen that 1 h was sufficient for complete adsorption.

3.3. Sedimentation behaviour

The sedimentation behaviour of dispersed suspensions is given in Table 3. All samples showed very little

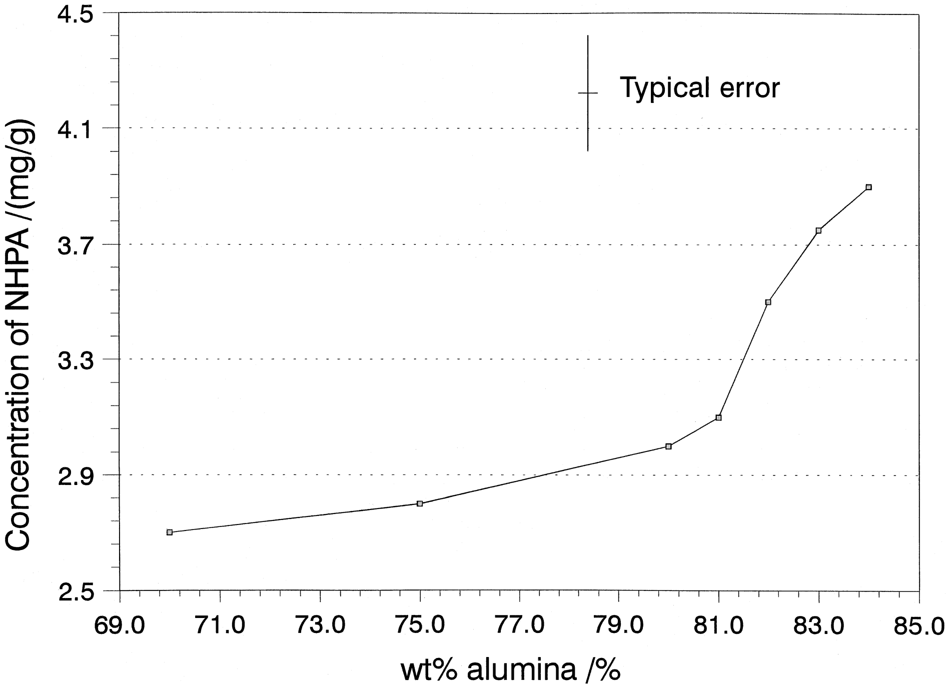


Fig. 11. Concentration of NHPA required to reach the second minimum as a function of solids loading.

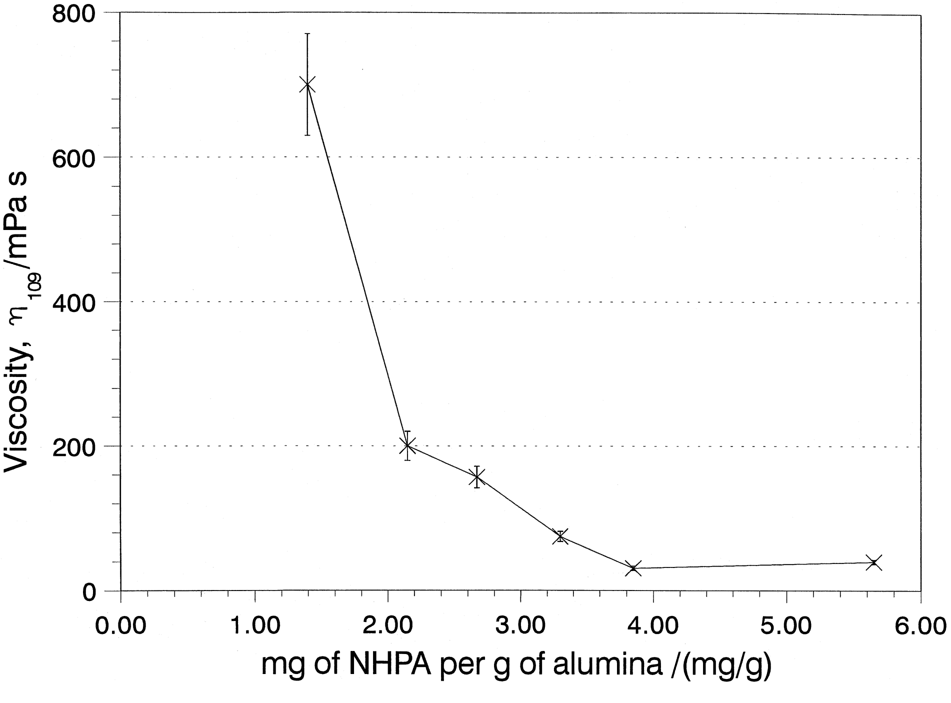


Fig. 12. Suspension viscosity as a function of NHPA concentration at pH 8.0.

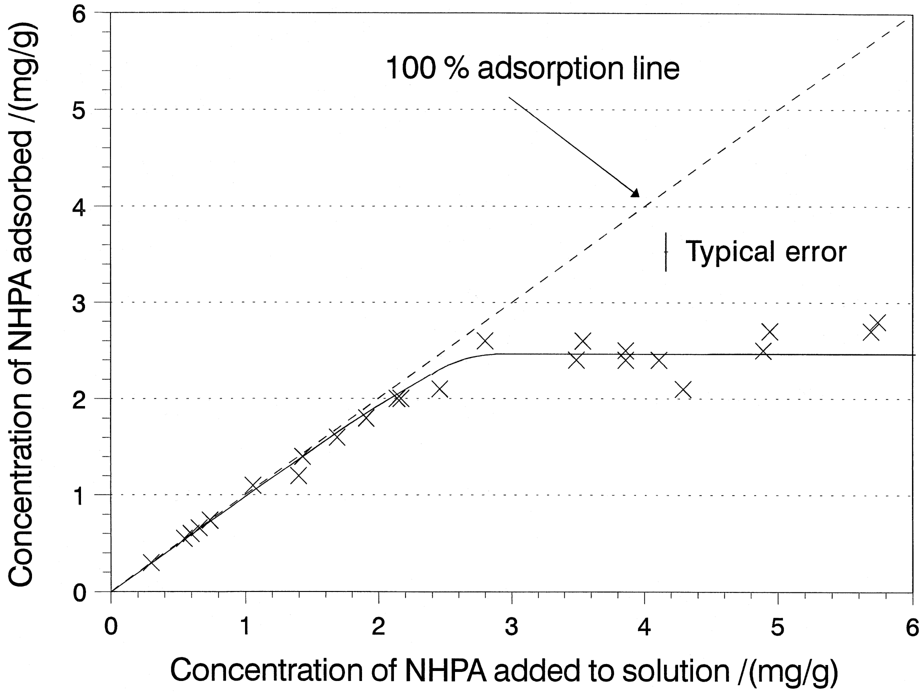


Fig. 13. Concentrations of NHPA adsorbed from solution onto powder under dispersed conditions, showing complete polymer coverage at 2.7 ± 0.2 mg g^{-1} NHPA.

Table 2
Adsorption of NHPA onto alumina under dispersing conditions, analysed under increasing pH conditions

Time after preparation (h)	Volume of supernatant V_s (ml) ± 0.05	Volume of 0.1 M HCl titrated α (ml) ± 0.2	Corrected volume of HCl titrated α-C_fV_s (ml) ± 0.2	Mass of NHPA in supernatant M^s_{NHPA} (g) ± 0.002	Amount of NHPA adsorbed	
					(g) ± 0.008	(mg g^{-1}) ± 0.2
1	4.00	5.0	3.9	0.028	0.095	2.7
6	4.80	6.0	4.7	0.034	0.094	2.7
12	5.20	6.5	5.0	0.037	0.094	2.7
24	5.00	6.0	4.6	0.034	0.098	2.8

Table 3
Final sediment volumes for dispersed samples after 3 months

Concentration of NHPA (mg/g)	Final sediment volume (initial volume 10 ml)(ml) ± 0.2
1.40	9.7
2.15	9.8
2.70	9.7
3.85	9.7

tendency to sediment, maintaining a large volume of 9.7 ± 0.2 ml and a cloudy supernatant over the 3 month period of testing.

3.4. Maximum packing volume fraction

The calculated values for the maximum packing volume fraction, ϕ_{max}, obtained using the modified Eilers equation, [Eq. (2)], are presented in Table 4. The linear plots on which the calculations were based are given in Fig. 14. The trend was modelled using linear regression, from which C_E was calculated from the gradient and, in turn, ϕ_{max}, from the intercept.

3.5. Green density

Fig. 15 shows the green density of samples plotted as a function of the concentration of NHPA present in suspensions. The green density increased with NHPA concentration and reached a maximum plateau value at 2.80 mg g^{-1} NHPA, comparable to the second viscosity minimum.

4. Discussion

4.1. Characterisation of suspensions

Fig. 16 reveals that the zero point of charge (ZPC) for the alumina was at pH 7.5–8. This is similar to that

Table 4
Calculated values for the maximum packing volume fraction, $\phi_{\max}$, using Eilers equation

Concentration of NHPA (mg g^{-1})	$\phi_{\max}$	Equivalent wt% alumina
1.40	0.61 ± 0.02	86 ± 1
3.85	0.64 ± 0.04	87 ± 2

reported by Salamone et al.[12] for the same grade of alumina powder, although it is much lower than that reported by other authors such as Aksay et al.[13] and Persson[14] who, using zeta potential measurements, found it to be of the order of 9.5. The samples prepared with NHPA in this research produced an intrinsic suspension pH of 9.5 indicating that dispersion was achieved by adsorption of negatively charged NHPA onto slightly negatively charged alumina powder, a situation which would perhaps not appear electrostatically favourable. Despite this however, the results offered here have shown that NHPA is a very effective dispersant for alumina at the intrinsic suspension pH, the vast majority of samples being pseudoplastic and thixotropic (Fig. 6). Complete suspension fluidisation was achieved with as little as 1.4 mg g^{-1}, this holding true over the measured solids loading range of 70 to 83 wt%. Above this solids loading dilatancy, a common rheological feature with highly concentrated particulate suspensions, became dominant preventing measurement.

Of key interest is the polymer concentration at which complete dispersion is achieved. Achievement of minimum viscosity is generally associated with maximum dispersion. However, in this research two minima separated by a maximum were observed at differing concentrations of NHPA (Figs. 9 and 10). The first minimum and the onset of the maximum remained at a fixed level of NHPA, although the latter tended to get broader, whilst the secondary minimum occurred at steadily increasing levels of NHPA. The presence of two minima has also been noted by Hirata et al.[15] whilst monitoring the viscosity of alumina suspensions dispersed with a higher molecular weight ammonium polyacrylate. The question remains as to which minimum corresponds to the most stable state of dispersion.

The data from the sedimentation tests (Table 3) indicate that there was no sign of sedimentation over the three month period of testing at either viscosity minimum. Similarly, the maximum degree of packing, $\phi_{\max}$, modelled from the viscosity data using the modified Eilers equation (Table 4) indicate that there is a comparable degree of maximum packing at the first viscosity minimum (1.4 mg g^{-1} NHPA) and at concentrations above the second minimum (3.85 mg g^{-1}). Both these results suggest that the first minimum corresponds to complete sample dispersion, in agreement with the work of Hirata et al.[15]

However, adsorption data given in Fig. 13 suggests that adsorption of NHPA onto the alumina surface is not complete until an NHPA concentration of 2.7 mg g^{-1} is reached. This coincides with the second viscosity minimum. Complete adsorption is generally considered to be the condition for maximum dispersion, corresponding to full monolayer coverage of the particle surface by

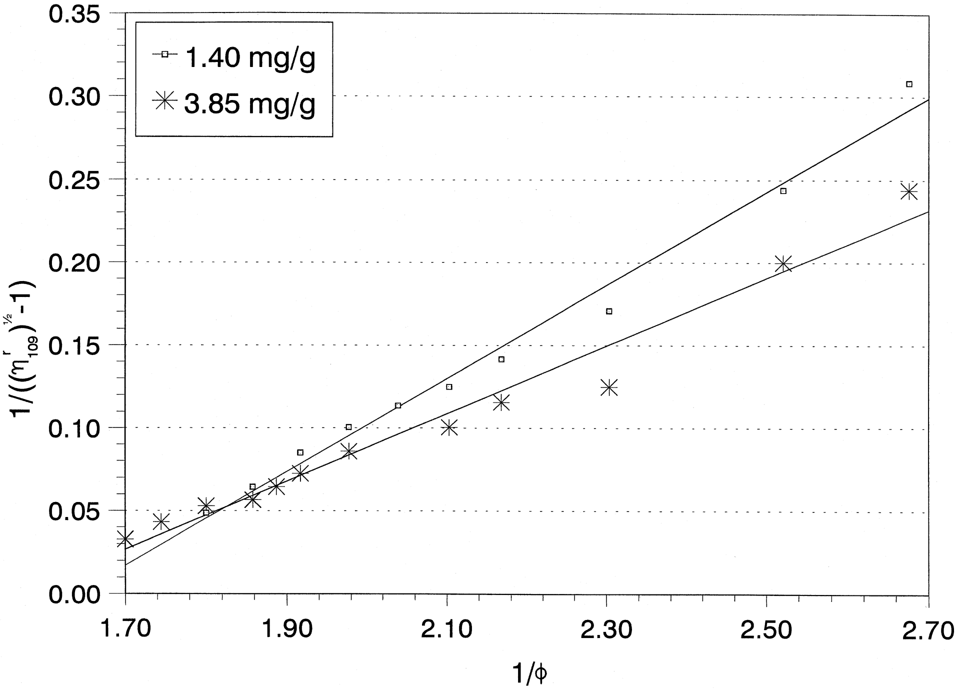


Fig. 14. Fit of Eiler's equation to samples dispersed with 1.40 and 3.85 mg g^{-1} NHPA at pH 9.5.

NHPA. In this context, therefore, it is possible that the first minimum does not correspond to full dispersion.

The results of the green density measurements also support the argument that complete dispersion is not achieved until the second minimum. The green density of a dried suspension is an indirect measure of the degree of dispersion. Other factors being equal, due to its higher degree of homogeneity a highly dispersed suspension will tend to pack to a higher green density when dried than one of a lower degree of dispersion. The green density data (Fig. 15) indicate that maximum density is not achieved until an NHPA concentration of 2.8 mg g^{-1}. This approximately coincides with the second viscosity minimum.

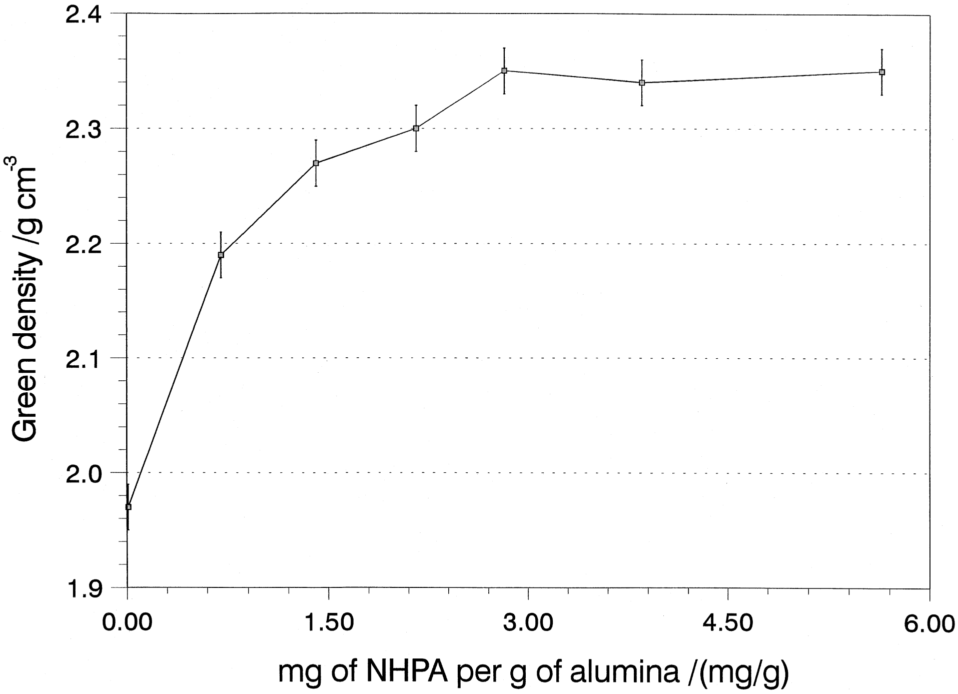


Fig. 15. Green density of samples dispersed at 70 wt% alumina at pH 9.5 as a function of NHPA concentration.

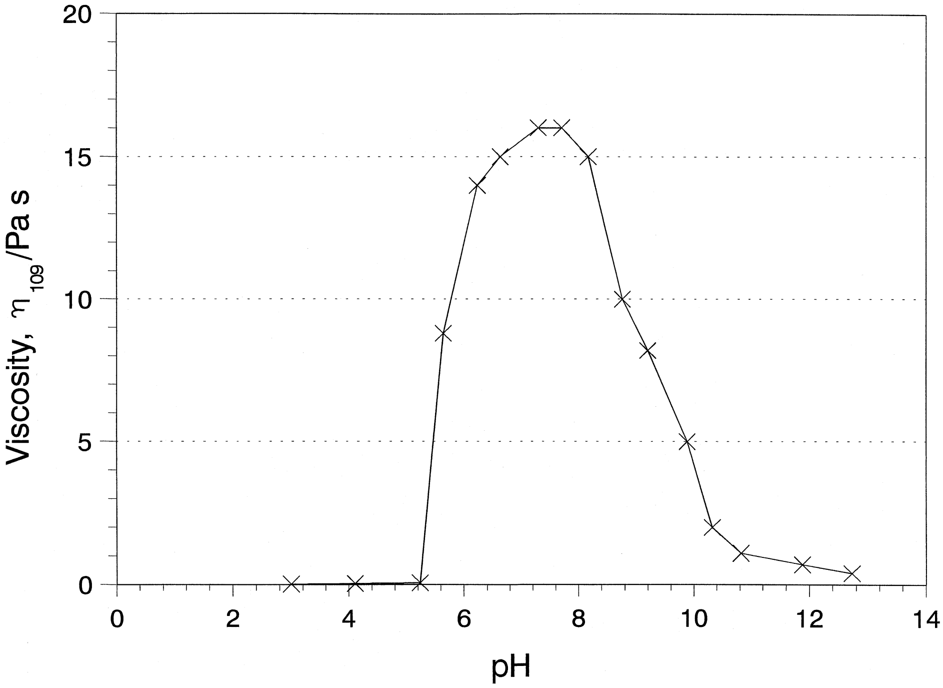


Fig. 16. Effect of pH on the viscosity of an A16SG alumina/water slurry at 70 wt% alumina showing a maximum between pH 7 and 8.

This technique assumes however, that the degree of dispersion remains constant during the evaporation of water during drying. For NHPA levels corresponding to the first minimum it is possible that as the effective solids content in the sample increases during drying the configuration of the NHPA adsorbed onto the alumina changes, resulting in a loss of dispersion.

The effect of water evaporation on suspensions can be simulated to a degree by preparing samples at varying water/solids contents (Fig. 12). As already mentioned, suspensions prepared with 1.4 mg g^{-1} NHPA at alumina loadings of greater than 83 wt% could not be measured due to dilatancy effects. The critical shear rate for onset of dilatancy seen in Fig. 8 would be expected as the solids content is increased.[13] However, the sharp change in gradient observed above 83.5 wt% could, feasibly, be influenced by a reduction in the degree of dispersion,[14] or an effective increase in particle size,[13] in this case due to flocculation. It is therefore plausible that the onset of dilatancy occurs as a result of the loss of the first viscosity minimum at very high solids loadings. This could, in turn, explain why the green density values are rather lower than predicted from the viscosity and sedimentation measurements on suspensions.

Further evidence to support the view of a reduction in the degree of dispersion during drying can be seen by the increase in NHPA levels needed to reach the second viscosity minimum as the solids content of alumina is increased (Fig. 11).

There is thus conflicting evidence for whether the first or second minimum represents complete adsorption. Two possible arguments may explain the results:

1. The correction factor used to obtain the level of adsorbed NHPA by accounting for residual alumina particles during the titration experiments was not correct. This would discredit much of the evidence presented and suggest that complete adsorption did indeed occur at the first minimum. However, evidence already presented in this paper suggests strongly that the correction factor was indeed valid.
2. Although complete adsorption occurred before the second minimum, changes in the adsorbed configuration account for the additional adsorption observed at the higher concentrations. A similar argument was used by Hirata et al.[15] to explain the presence of two minima. This is discussed in more detail later.

Based on all the results presented above it is suggested that the first viscosity minimum corresponds to an unstable or metastable dispersed state. Whilst it is present in suspensions of up to 83 wt% alumina, it does not correspond to maximum surface coverage of NHPA and appears to be lost on drying, producing green compacts of relatively low density. Further evidence to support this is presented in Fig. 16 that plots the effect of pH on dispersion at 70 wt% solids content. The shift of the viscosity maximum towards lower pH values as the concentration of NHPA increases reflects the increasing adsorption of NHPA and hence negative surface charge. An increasing concentration of NHPA is needed to neutralise the existing positive surface charge and create the PZC. The point of interest is that the height of the viscosity maximum decreases with increasing NHPA levels up to 2.7 mg g^{-1}, the level associated with the second viscosity minimum at 70 wt%. At higher levels of NHPA the viscosity maximum does not change, implying a degree of stability against aggressive hydrogen ions to flocculation. The shift of the viscosity maximum to lower pH levels at higher NHPA concentrations is due to enhanced adsorption from solution in the presence of high concentrations of counter-ions. This is dealt with in another paper by the same authors.[16]

Finally, as discussed earlier, the intrinsic pH of the suspension was 9.5. Since the PZC of the alumina powder was pH 8.0, it is apparent that the fully dissociated and negatively charged NHPA is adsorbed onto an overall negatively charged surface. It was considered possible that the first minimum may be associated with this phenomenon. In order to determine the effect of the powder surface charge on the presence of the first minimum, samples were prepared at pH 8.0, the PZC of the powder. At this pH the NHPA is still fully dissociated as can be seen from the right hand side peak of the titration derivative given in Fig. 5 and therefore expected to remain in a relatively extended configuration. From Fig. 12 it can be seen that the first minimum and associated maximum are absent at this pH. This suggests that the first minimum is associated with the surface charge on the suspension particles or at least on the presence of counter-ions in solution.

4.2. Prediction of the adsorbed polymer configuration

In light of the above observations and those by Hirata et al.,[15] a prediction for the adsorbed polymer configuration at the intrinsic pH (9.5) as a function of NHPA concentration is offered. It should be noted that the proposed configurations are only rationalisations of observations made about the results obtained. Further work is needed to determine the exact adsorbed configurations using techniques such as atomic force microscopy or ellipsometry. The predictions are based on the assumption that the correction factor used in the adsorption test is valid, for which clear evidence has been presented.

Whilst the presence of two minima has been noted by Hirata et al.,[15] it has not been reported by others, notably Cesarano et al.[8,9] In the present work it has been found to exist only under certain conditions.

It is predicted that the configuration of the NHPA up to the first viscosity minimum is associated with a tail type formation, as depicted in Fig. 17a. This prediction arises from the NHPA being fully dissociated and therefore assumes an extended configuration at pH 9.5. The slightly negative overall charge on the alumina (since the PZC occurs at pH 8.0) prevents the NHPA adsorbing as a train type formation; the electrostatic charges present are believed to force the NHPA to adsorb onto the few positive sites available with the tail dangling into solution. By the first minimum there is sufficient NHPA adsorbed to create a Debye length (distance from the particle over which the overall repulsive force between the particles acts) that exceeds the scope of the van der Waals forces thus creating a dispersed suspension. This prediction supports the proposal of Hirata et al.[15]

The fact that the first viscosity minimum was absent at the PZC of the alumina despite the polymer still being fully dissociated suggests that the minimum is related to either the particle surface charge or the concentration of counter-ions in solution or perhaps a combination of both. It is this feature that leads to the proposed prediction of the NHPA configuration at the viscosity maximum being somewhat different to that suggested by Hirata et al.[15] They reported complete adsorption being achieved by the first viscosity minimum whilst the majority of evidence in the current work supports continued adsorption of NHPA up to the second viscosity minimum. In this context it is unlikely that the viscosity maximum is a consequence of excess polymer in solution as suggested by Hirata et al.[15] Instead it is proposed that the maximum is caused by a configurational change in the adsorbed NHPA brought about by counter-ion effects.

At a given solids loading, the quantity of counter-ions in solution will be proportional to the concentration of NHPA added. They are attracted to the negative sites on the powder surface and hence effectively reduce the surface charge. This therefore allows the formation of a linear, train configuration upon adsorption (Fig. 17b). Counter-ion effects may also allow a small degree of polymer looping on the powder surface. Owing to the thin polymer layer the repulsive barrier developed is primarily electrostatic. Under this configuration the Debye length is not sufficient to extend beyond the scope of the van der Waals forces, enforcing a weak secondary type of flocculation or coagulation. Emphasis is placed on a weak secondary flocculation rather than the primary type associated with no addition of dispersant due to the viscosity being much lower and green densities being much higher than those obtained from a fully flocculated suspension. The viscosity increase from the first minimum to the maximum may therefore be accounted for by a contraction of the double layer as a result of a change in the adsorbed configuration.

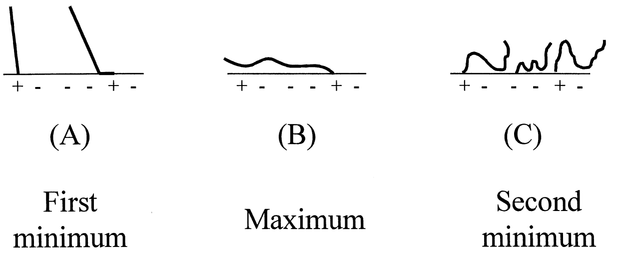


Fig. 17. Schematic representation of the predicted adsorbed configuration associated with different NHPA concentrations at 70 wt% alumina.

At increasing NHPA concentrations above the viscosity maximum the increasing presence of counter-ions in solution facilitate the formation of loops. The degree of loop formation would be expected to be very small compared to that of an uncharged polymer however. Polymer crowding on the powder surface may also promote the extension of polymer chains into solution. The steric barrier provided by the polymer chains, in conjunction with the electrostatic double layer, provides an electrosteric repulsive barrier that exceeds van der Waals attractive forces. Thus the decrease in viscosity observed above the maximum is dictated by the development of the loop and tail configuration at the expense of a more flat train version. The second minimum is therefore predicted to correspond to a completely adsorbed layer of loops and tails (Fig. 17c). The viscosity increase above the second minimum is predicted to be a consequence of non-adsorbed or free polymer in solution.

The independence of the first minimum with respect to solids loading suggests that the tail configuration is resistant to the increasing concentration of counter-ions in solution up to 83 wt% alumina suspensions. At higher solids content dilatancy prevents rheological measurement of the presence of the minimum, but as stated above, it is possible that it is the loss of the first minimum due to counter-ion effects that causes the onset of dilatancy. This would support the view that the predicted tail configuration of the first minimum is unstable.

5. Conclusions

Ammonium polyacrylate (NHPA) of molecular weight 3500 was found to be an effective dispersant for A16SG alumina (PZC of pH 8.0), producing suspensions with an intrinsic pH of 9.5. Minimum suspension viscosity was observed at two different NHPA concentrations for each solids loading examined between 70–84 wt% alumina. They are believed to be a consequence of different adsorbed configurations of NHPA.

The first viscosity minimum occurred at 1.4 ± 0.1 mg g^{-1} NHPA and was independent of solids loading up to 83 wt%. Measured sedimentation data and calculated maximum packing density values supported the view that complete dispersion was achieved at this concentration whilst incomplete adsorption and relatively low green density dried compacts opposed it. Based on the results presented it is suggested that the first viscosity minimum corresponded to an unstable dispersed phase with the NHPA adsorbed in a dangling tail configuration. Whilst the minimum was present in suspensions of up to 83 wt% alumina, it did not correspond to maximum surface coverage by the NHPA and dispersion appeared to be lost on drying.

In contrast, the second viscosity minimum is suggested to correspond to maximum adsorption, occurring at a concentration of 2.7 ± 0.2 mg g^{-1} NHPA at 70 wt% and increasing with increasing solids content up to 4.3 ± 0.2 mg g^{-1} at 84 wt% alumina. It is concluded that this second minimum, comprising NHPA adsorbed in a proposed loose loop and tail configuration, is the most stable dispersed state, yielding the most favourable properties expected for a dispersed suspension.

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