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Electroacoustic and Rheological Properties of Aqueous Ce-ZrO$_2$ (Ce-TZP) Suspensions

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Abstract

Ce-ZrO$_2$ (13 mol% CeO$_2$) powder was found to be slightly soluble under acidic conditions and the isoelectric point was determined to be pH_{iep} = 7·9 using electroacoustics in concentrated suspensions. The adsorption isotherms of two well-characterized polyelectrolyte dispersants, Dispex A40 and Duramax D3007, were related to the molecular structure. The fully ionized polyacrylic acid (Dispex A40) adsorbed in a flat conformation on the Ce-ZrO$_2$ powder, while the Duramax D3007 displayed higher adsorbed amounts which was attributed to possible multilayer adsorption caused by the zwitterionic nature and the existence of hydrophobic parts of the Duramax D3007. It was found that the viscosity is at a minimum at monolayer coverage of the dispersant when the polyelectrolyte-covered particles are highly negatively charged. The study illustrates how rheology and electroacoustics can be utilized in the investigation and optimization of the properties of concentrated ceramic suspensions. © 1997 Elsevier Science Limited. All rights reserved.

1 Introduction

Transformation-toughened ceramics are a class of ceramics with excellent mechanical and thermal properties. Amongst these toughened materials, tetragonal zirconia polycrystal materials (TZP) are probably the most extensively investigated since these materials, e.g. ceria-stabilized TZP, can combine a high fracture toughness (comparable to that of cast iron) with a high strength.[1,2] Some of these materials also display excellent wear properties and a good thermal shock resistance. The excellent mechanical properties are due to the stress-induced transformation of the metastable tetragonal phase to the stable monoclinic phase which occurs at the crack tip.[3] The thermodynamic stability of the tetragonal phase of pure zirconia is unfavourable, but with the use of stabilizing oxides it can be retained at room temperature. Normally, in pure zirconia, the transformation occurs over the range 600– 1200°C. Most commercially available partially stabilized TZP powders utilize ceria- and yttria-stabilized zirconia systems by careful composition and microstructural control.[2,4,5] Typically, Ce-stabilized TZP (Ce-TZP) systems contain tetragonal grains with 9–20 mol% ceria present.

Unfortunately, the mechanical properties of yttria-stabilized TZP (Y-TZP) are reduced due to low temperature ageing in moist air.[6,7] This is associated with microcracking due to the surface transformation, which progresses into the specimen interior. The change in surface monoclinic content correlates with the change in strength. In contrast, at an optimum amount of 12 mol% ceria, Ce-TZP ceramics are resistant to low-temperature water degradation.[7,8] They are also cheaper than yttria-stabilized powders, but have a lower hardness, which is a definite disadvantage in wear applications. Partly as a result of this, recent studies on Ce-TZP have concentrated more on composites with alumina.[9–12]

Hot-pressing and hot-isostatic pressing,[9,10] which are often used to densify poorly sinterable materials, are unsuitable for Y- and Ce-TZP due to oxide reduction. Also, the high cost of these forming methods is a definite disadvantage. Hence, other, cheaper and more reliable methods of forming green bodies are of great interest. The concept of colloidal processing has been successfully applied to the field of structural ceramics and several studies have shown that the inhomogeneities can be minimized, and reliable ceramics have been produced, by controlling and manipulating the interparticle forces in the suspension during processing and forming.[13–16] One relatively simple, colloidal processing method of preparing green bodies of a complex shape is slip casting.[17]

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Many studies have shown that the state of the dispersion (colloidally stable* or flocculated) and the consolidation method employed have a significant influence on the casting behaviour and the resulting green-body properties. Generally, colloidally stable suspensions are preferred since they usually produce higher average packing densities and a more narrow pore size distribution compared with strongly flocculated suspensions.[13,18] As an alternative to colloidally stable suspensions, recent studies have shown that weakly flocculated suspensions can also result in excellent green-body characteristics and provide some additional beneficial features.[19–21] For example, Chang *et al.* showed that mass segregation of a mixed powder system during centrifugal casting could be avoided if a weakly flocculated suspension was used.[19] In addition, weakly flocculated concentrated suspensions display a plastic-like rheological behaviour which can be utilized during reshaping or simply in decreasing the amount of binder added.[20,21] Although weakly flocculated slips may result in the optimum microstructural features using the colloidal processing concepts, it is often difficult in practice to tune the suspension properties to yield the right degree of flocculation and to maintain the weakly flocculated state for an extended period of time. Quite often, the weakly flocculated suspensions show a tendency for clogging and increase in the degree of flocculation with time, i.e. ageing effects. For robust processing and reliable products, it is necessary to develop ceramic powder suspensions which have a long-term stability. Colloidally stable, well dispersed suspensions possessing a low relative viscosity generally fulfil these requirements.

Colloidally stable, aqueous suspensions of TZP powders have been obtained by creating a high charge on the particle surface which results in a strong double-layer repulsion. Such high surface charge densities can be created by working far away from the point of zero charge (pzc) of the powder. Since Y-TZP has a pH_{pzc} = 6–8,[22,23] several studies have been made at high or low pH. However, in these extremes of pH, other undesirable effects such as dissolution may also occur. Partial dissolution of the yttria occurs mainly in the acid region, whereas no dissolution occurred in basic conditions.[24,25] The dissolved polyvalent Y^{3+} ion acts as a counter ion in the solution which decreases the range of the double-layer repulsion, thus causing the suspension to flocculate.

In order to avoid the problems with working at very high or very low pH values, repulsive particle interactions are commonly produced by the additions of suitable dispersants (sometimes called deflocculants).[26] These additives will adsorb at the particle surface and generate a repulsive interaction caused by electrostatic or steric effects. One commonly used type of dispersant is polyelectrolytes, often based on polyacrylic acid. There have been numerous studies on the effect of polyelectrolytes on aqueous dispersions of alumina using rheology and microelectrophoresis, and recently using electroacoustics.[27–29] The most widely used commercial dispersants appear to be polyacrylic acid based, either in the acid form or neutralized with sodium or ammonia. Generally, the lower molecular weights ($M_w < 10\,000$) are more effective. There are also several reports on the effect of polyacrylate dispersants on the stability and rheology of zirconia dispersions. The effect of molecular weight[30,31] has been studied on the yield stress–pH behaviour. Contrary to prevailing practice it may not be necessary to have full coverage to achieve better flow properties, hence excessive use of additives can be avoided and a combination of dispersant and pH control may be a more effective method. Several studies on slips consisting of Y-TZP powders have compared the rheological properties[22,32–34] with the green-body density, in order to define appropriate conditions for slip preparation and optimum processing conditions. It was found that high zeta potentials (a high charge on the particle surfaces) correlated with low viscosity and good colloidal stability (from sedimentation tests) over a wide pH range.

In summary, previous studies have shown that colloidal processing can successfully be used on TZP materials. However, most of the reported studies have been performed on the yttria-stabilized zirconia system. In this study, we have performed a thorough characterization of the electroacoustic and rheological properties of a Ce-TZP powder in aqueous media. The surface composition, solubility and electrokinetic properties of the powder have been determined and related to the suspension properties. The core of the study has focused on the effect of two different dispersants on the rheological properties and the electroacoustic behaviour at high solids concentrations. The commercial dispersants were characterized extensively to allow some insight regarding the adsorption mechanism and the conformation of the adsorbed polyelectrolytes. An analysis of the adsorption

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*The word 'stabilization' has two meanings in this report. Firstly, there is the classical colloidal chemistry use of the word in which particles are prevented from flocculating via an electrostatic or steric repulsion. Secondly, there is the ceramic processing definition in which additional oxides are added to a powder to allow thermodynamic stabilization of a certain required phase, at room temperature. We hope that the situations in which this word occurs are well defined.

isotherms and the effectiveness of the dispersants in imparting colloidal stability and low viscosity to Ce-TZP suspensions showed that the main stabilizing mechanism was electrostatic.

2 Experimental Procedure

2.1 Powders and chemicals

A polycrystalline, partially stabilized tetragonal zirconia powder, Ce-ZrO_2, containing 13 mol% ceria (CEZ-10, lot no. K0530, Zirconia Sales Inc., GA, USA) was used in all the studies. The powder was characterized by several different techniques. X-ray diffraction (XRD; Philips) was used to determine the phases present, scanning electron microscopy (SEM; Jeol JSM - 5300) showed the particle size distribution and morphology, and multipoint BET adsorption isotherms (Micromeritics Flow Sorb II 2300) were used to determine the specific surface area. X-ray sedimentation (Micromeritics Sedigraph 5000ET) was performed on 1 vol% suspensions and yielded the particle size distribution. Finally, electron spectroscopy for chemical analysis (ESCA; AXIS-HS, Kratos, UK) was used to determine the chemical composition of the surface film of the powder.

Two commercially available dispersants were chosen: Dispex A40 (Allied Colloids, UK) and Duramax D3007 (Rohm and Haas, USA). Dispex A40 is a low-molecular-weight polyacrylic acid neutralized with ammonia, whereas Duramax D3007 is described by the manufacturer as the sodium salt of an acrylic copolymer. The two dispersants were characterized by the following techniques: gel permeation chromatography (GPC), ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy and finally elemental analysis.

All the water used was double distilled. The chemicals used to adjust the pH (1 M HCl and 0·5 M KOH) were supplied by Merck, whilst the electrolyte concentration was controlled with NaCl (Fluka).

2.2 Solubility

Suspensions at different pHs were centrifuged down and the resulting supernatant analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian Liberty 200). The pH was adjusted in 15 ml suspensions with a volume fraction of solid material, Φ, 0·03 using either 1 M HCl or 0·5 M KOH to pH values from 3 to 9. Each sample was sealed and kept under continuous stirring using a magnetic stirrer plate. The pH was measured as regularly as possible and, if it varied by more than 0·1 pH units, it was adjusted back to its initial pH. At specific time intervals, the suspensions were centrifuged at 3500 rev min^{-1} for 30 min (MSE Mistral 2000). The clear supernatants were placed in sealed plastic bottles and analysed for Ce and Zr content, and the remaining powders were dried. Plastic storage bottles were always used so as to avoid the problem of silica leaching from glass bottles.

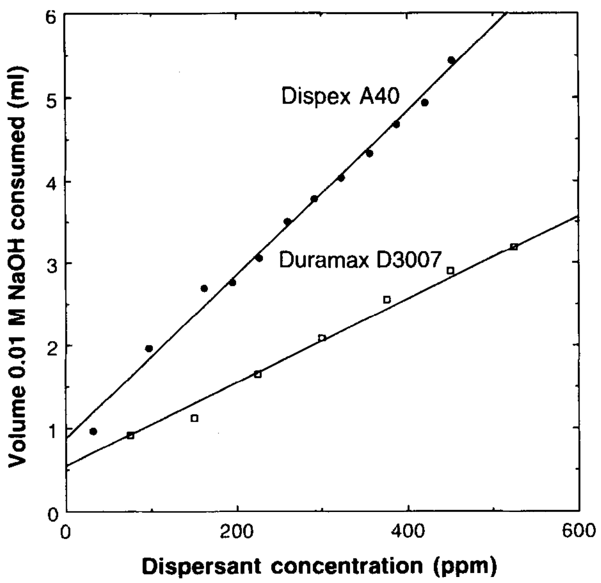


Fig. 1. Calibration curves of amount of 0·01 M NaOH needed to titrate the polyelectrolytes: ●, Dispex A40; □, Duramax D3007.

2.3 Adsorption isotherms

The adsorption isotherms of the dispersants at the Ce-ZrO_2/electrolyte interface were determined by mixing the powder and a known amount of dispersant in electrolyte (10^{-2} M NaCl) over 2 days, centrifuging the suspension and determining the amount of dispersant left in solution by titration. The adsorption experiments were carried out in plastic containers at pH = 8·3 and 9·5. The pH of the samples was adjusted continuously over 2 days until stabilization. The samples were shaken on an Ika KS501 Labortechnik vibrating table. All the adsorption isotherms represent 100% active substance of the dispersants.

The amount of dispersant in solution was determined by using a calibration curve. A polyelectrolyte-containing solution of known concentration in 10 mM NaCl electrolyte, was placed into the automatic titrator (Metrohm 670 Titroprocessor) and the pH was decreased to 3·5. The polyelectrolyte was then titrated to pH = 9·5 by adding NaOH. The amount of NaOH consumed as a function of amount of dispersant added is plotted in Fig. 1 and both of the dispersants show a linear dependence. The calibration results were fitted to a straight line using linear regression and these results were used for determining the concentration of the respective dispersants in solution.

2.4 Electrokinetic behaviour

Two different methods were used to determine the electrokinetic properties. The electrophoretic mobility was determined in very dilute suspensions by the microelectrophoresis technique (Malvern Zetasizer 4, Malvern Instruments, UK). In the concentrated suspensions, an electroacoustic method was used which yields both the zeta potential and the particle size distribution of the suspension.

The suspensions for microelectrophoretic measurements were prepared according to a previously developed procedure for Si_3N_4 powders.[35] This procedure gives information regarding the electrokinetic properties of a dilute ($\Phi < 0{\cdot}005$) suspension at a short equilibration time. The powder is added to the electrolyte solution (10^{-2} and 5×10^{-3} M NaCl) at a pre-adjusted pH and stirred for 10 min with a magnetic stirrer. The dispersion was then allowed to sediment for 10 min and the agglomerates removed by decanting. The pH was measured prior to electrophoretic measurement.

The electroacoustic experiments (Acoustosizer, Matec Applied Sciences, USA) were performed on powder suspensions of $\Phi = 0{\cdot}10$, hence substantially higher than the microelectrophoresis measurements. The Acoustosizer utilizes the electroacoustic effect. If an alternating electric field is applied to a colloidal suspension, the particles move back and forth at a velocity that depends on their size and zeta potential and on the frequency of the applied field. As the particles move, they produce an acoustic wave; this effect is known as the electrokinetic sonic amplitude (ESA). From the frequency dependence of the ESA, a dynamic electrophoretic mobility spectrum can be obtained.[36] The particle size distribution and the zeta potential can be calculated from these data if the static dielectric constants of the particles and the medium and the volume fraction of solids are known. The machine operates over frequencies of 250 kHz to 15 MHz. The Acoustosizer was always calibrated in air and then with a standard solution before the electroacoustic properties of the suspension were determined.

2.5 Rheology

All rheological experiments were performed on a constant shear rate rheometer (Bohlin VOR, Bohlin Rheologie, Lund, Sweden) in steady shear rate mode. In steady shear rate mode, the outer cylinder of the rheometer geometry is rotated at known shear rates ($\dot{\gamma}$). The resulting stress (σ) in the sample is transmitted to the inner cylinder, whose movement is then measured by a transducer connected to the inner cylinder by an interchangeable torque bar (covering a wide range of sensitivities). Hence, the viscosity (η) is measured as a function of shear rate.

$$\eta = \frac{\sigma}{\dot{\gamma}} \tag{1}$$

All samples were measured at 25°C in the C25 geometry with a gap between the inner and outer cylinders of 1·25 mm. Pre-shearing was done for 1 min at the highest shear rate obtainable with the torsion bar in question, and then the main experiment started after 30 s, stepping up and then down in shear rate covering the shear rate range 0·1–1000 s^{-1}.

2.6 Preparation and characterization of suspensions

All suspensions were prepared by mixing powder, electrolyte and possibly dispersant in a beaker, followed by pH adjustment and ultrasonication. The high volume fraction suspensions ($\Phi = 0{\cdot}25$) were made by magnetically stirring the electrolyte whilst slowly adding the powder, pH was adjusted and more powder and electrolyte added sequentially until the required volume fraction and pH were obtained. The paste-like mixture was then treated with an ultrasonic horn of diameter 9·5 mm (Soniprep 150, MSE Scientific Instruments, UK). The samples were treated, at a maximum amplitude, in 2 min sequences until no large agglomerates could be detected visually. The sample beaker was kept in a cold water bath to prevent temperature rises and evaporation losses. Rheological experiments were carried out immediately.

Suspensions of a lower volume fraction ($\Phi = 0{\cdot}10$) were used for both rheological and electroacoustic measurements. 600 ml of a Ce-ZrO_2 suspension was prepared following the procedure above at the required pH, and left stirring overnight. Both the rheological and electroacoustic properties were determined as a function of pH and the amount of dispersant added. The dispersant was added in approximately 500 mg intervals, and stirred for 15 min with a magnetic stirrer whilst the pH was adjusted. Then the dispersion was subjected to 3 × 2 min intervals under the sonic probe followed by further magnetic stirring, for 5 min, whilst the pH was checked again. After this treatment, the dispersion was placed into the Acoustosizer sample holder and stirred continuously (300 rev min^{-1}) until the required temperature was achieved and a measurement could be performed. The rheological experiments were performed under the same conditions as previously reported.

3 Results and Discussion

3.1 Powder and dispersant characterization

The characteristics of the Ce-ZrO_2 (13 mol% CeO_2) powder are shown in Table 1. The bulk characteristics, which are taken from the manufacturer, indicated that the Ce-ZrO_2 powder only contains minor amounts of compounds other than CeO_2, ZrO_2 and HfO_2. The XRD results reveal that both the tetragonal and monoclinic zirconia phases were present in the powder, which is expected for this type of partially stabilized zirconia powder. The X-ray sedimentation results (Fig. 2) displayed an essentially submicrometre particle size distribution with a median particle size of 0·4 μm and a significant proportion (18 wt%) of particles smaller than 0·1 μm. SEM micrographs confirmed this particle size distribution, displaying a large amount of very fine particles and some large particles, probably agglomerates. The powder appears to be equiaxed. The multipoint BET measurement revealed a surface area of 21·4 m^2 g^{-1} (Table 1). It is believed that the high specific surface area can be related to the finest fraction which corresponds to the dominating number of particles and, thus, increases the specific surface area substantially above the value expected from the mean value of the volume particle size distribution.

Table 1. Characteristics of the Ce-ZrO_2 (Ce-TZP) powder

ZrO_2 + HfO_2 (mol%)	87·0 ± 1·0
CeO_2 (mol%)	13·0 ± 1·0
SiO_2 (wt%)	< 0·2
Al_2O_3 (wt%)	< 0·3
Fe_2O_3 (wt%)	< 0·01
Na_2O (wt%)	<0·05
CaO (wt%)	< 0·05
Density (g cm^{-3})	6·2
Particle size (μm)[a]	0·4
Specific surface area (m^2 g^{-1})[b]	21·4

[a] Sedigraph measurement.
[b] BET measurement.

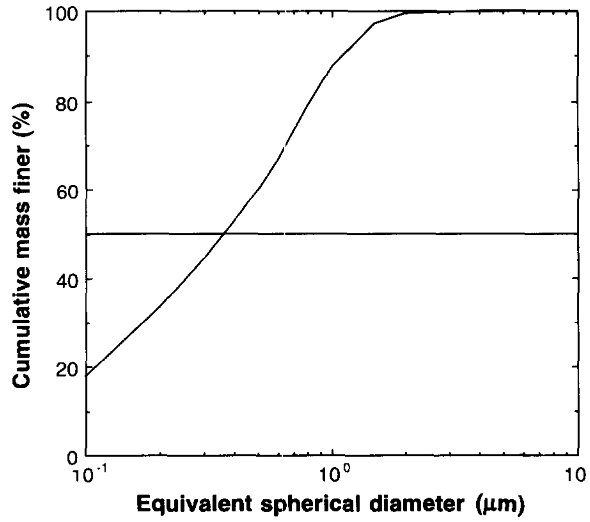


Fig. 2. Particle size distribution of Ce-ZrO_2 powder in water. The measurements represent a volume (or mass) based size distribution determined by X-ray sedimentation.

Table 2. ESCA analysis results of the Ce-ZrO_2 (Ce-TZP) powder

Element	*Line spectrum*	*Atomic concentration (%)*
Zr	Zr 3*d*	21·1
Ce	Ce 3*d*	3·3
La	La 3*d*	2·3
O	O 1*s*	62·9
C	C 1*s*	10·4

In the ESCA analysis of the Ce-ZrO_2 powder (Table 2), five different elements could be identified: Zr, Ce, O, C and La. Carbon is always found on powders which have been exposed to the atmosphere owing to contamination of carbon-containing species, but the lanthanum was somewhat unexpected. Also, no hafnium could be detected. The ratio of atomic concentration in the surface film of ceria to that of zirconia is 0·156, which is in the range of the expected value from the bulk composition of the powder, calculated from the data in Table 1. These results show that there is no surface enrichment of the zirconia or ceria in the powder.

The characterization of the Dispex A40 using GPC, NMR and elemental analysis suggests that this commercial dispersant is an ammonia-neutralized polyacrylic acid with a molecular weight, M_w, of about 10000 and a polydispersity M_w/M_N, of 1·56. The structure is shown in Fig. 3. The characterization of the Duramax D3007 indicated a much more complicated structure, see Fig. 3. The GPC measurements resulted in a molecular weight of about 10 000 and a polydispersity of 1·55, hence similar to the Dispex A40 dispersant. The ^{13}C NMR analysis of the Duramax D3007 revealed three different types of C=O groups in the polymer, suggesting

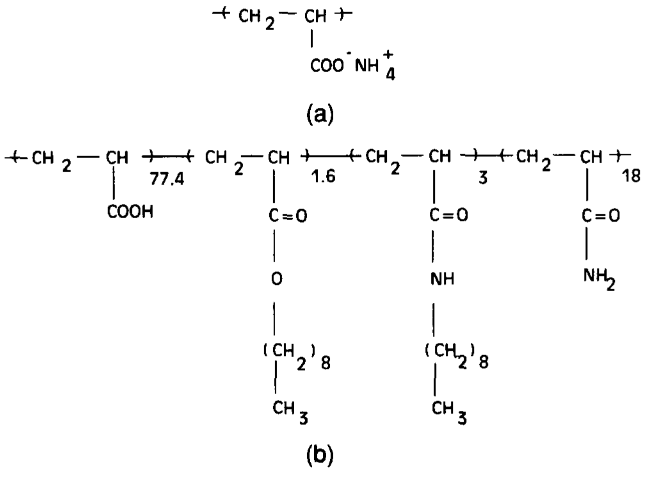


Fig. 3. Molecular structure of (a) Dispex A40 and (b) Duramax D3007.

a copolymer of acrylic acid, an amide and an ester. A further ^{1}H NMR analysis revealed the existence of several alkyl chains. Integration of the ^{1}H NMR peaks enabled the ratio of the ester and the amide groups and the length of the alkyl chains to be established. The relatively long alkyl chains bonded to the polymer backbone suggest that the water-soluble polymer might display an associative behaviour. This suggestion is supported by the more viscous nature of the Duramax D3007 solution compared with the Dispex A40 solution at similar concentrations. The elemental analysis implied a larger amount of nitrogen in the structure, which indicates the presence of acrylamide monomer in the structure. Since the pH of the polymer solution is low, pH = 3–4, the polymer is probably present in the undissociated form. The suggested structure of the Duramax D3007 dispersant is shown in Fig. 3.

3.2 Solubility

From the ICP results, the cerium dissolution rate of dilute Ce-ZrO$_2$ suspensions is shown in Fig. 4. The results show that it is only at low pH (pH = 3) that the powder displayed any significant dissolution. At the higher pH values (pH = 5·3–5·6), only small amounts (1–2 mg l^{-1}) of cerium were dissolved. Under near neutral and basic conditions (pH = 6–9) there was no dissolution based on the limit of sensitivity (≈ 0·5 mg l^{-1}) of the analysis method. Analysis of the supernatants showed no significant dissolution of the zirconia over time at any pH value investigated. It was noted that at the two pH extremes investigated, pH = 3 and 9·1, the pH of the samples tended to drift faster towards neutrality over a period of time. Also, at about pH = 8, the suspension always flocculated and displayed rapid settling, whereas the other suspensions remained homogeneous with only slight settling. This observation is an indication that the point of zero charge of the powder is close to pH = 8.

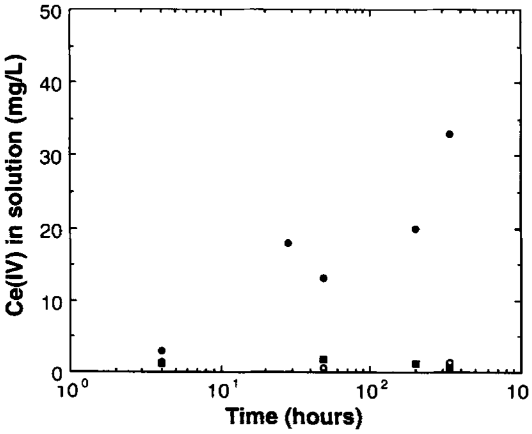


Fig. 4. Dissolved amount of Ce(IV) versus time of a Ce-ZrO$_2$ powder at three different pH-values: ●, 3·0; ○, 5·3; ■, 5·6.

3.3 Suspension properties

3.3.1 Rheology at $\Phi = 0{\cdot}25$

The suspensions at pH = 8·3 and 9·3 show a strongly shear thinning behaviour while the suspension at pH = 5·2 displays a substantially lower viscosity at low shear rates. From these experiments and visual observations — all of the suspensions were paste-like — it can be concluded that all of these suspensions are flocculated, i.e. the suspensions are characterized by attractive particle interactions. Since the particle interactions have a strong influence on the steady shear properties at low shear rates, the viscosity at a shear rate of 1·84 s^{-1} is plotted as a function of suspension pH in Fig. 5. There is a definite maximum at about pH 8, indicating strong flocculation. However, nearly all of the suspensions display such a high viscosity, η = 50 to 300 Pa s, at this moderate solids concentration (Φ = 0·25) that no suspension, except maybe the suspension at pH = 4·1, is colloidally stable. Hence, the double-layer repulsion created by the charge on the particle surface in this pH range is insufficient to overcome the large van der Waals' forces and create a stable suspension. Although the suspension at pH = 4·1 displays the lowest viscosity, indicating a higher degree of colloidal stability, we know from the solubility studies that the powder will slowly dissolve, which may cause unwanted ageing effects in this acidic range.

3.3.2 Electroacoustics and rheology at $\Phi = 0{\cdot}10$

For electrostatic stabilization it is vital to know the position of the isoelectric point (iep) of the powder so a pH region can be identified where there is sufficiently high surface charge density to generate a strongly repulsive double-layer force. Electroacoustic measurements were performed using a sample at Φ = 0·10, starting at basic conditions and reducing the pH, then increasing the

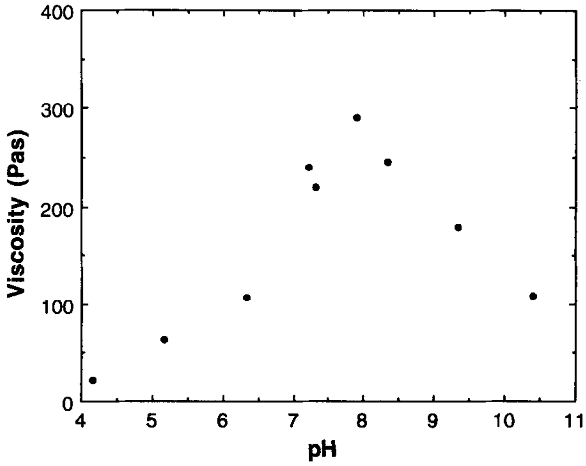


Fig. 5. Steady shear viscosity versus pH for a Ce-ZrO$_2$ aqueous suspension at Φ = 0·25 at γ = 1·84 s^{-1}.

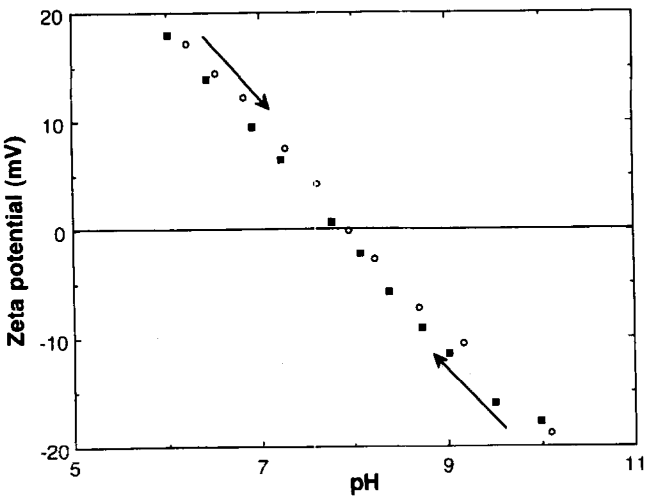


Fig. 6. Zeta potential versus pH of a Ce-ZrO_2 suspension at $\Phi = 0{\cdot}10$. The open symbols indicate increasing pH whilst the filled symbols indicate a decreasing pH.

pH back to the original value. After each pH adjustment the sample was subjected to 2 × 3 min under the sonic probe. This procedure yielded reproducible results with a small degree of hysteresis, and it can be seen from Fig. 6 that both the increasing and decreasing pH curves reveal a $pH_{iep} = 7{\cdot}9$. Initial measurements using only the stirrer in the sample cell to mix and disperse the suspension resulted in significant hysteresis. It is believed that the treatment with the sonic probe before each measurement assisted in creating a more reproducible state of the suspension, mainly due to breaking up of the flocs. The obtained iep for the investigated Ce-ZrO_2 powder ($pH_{iep} = 7{\cdot}9$) is substantially higher than earlier reported values, where Bleier *et al.* obtained $pH_{iep} = 6{\cdot}9$ for a Ce-ZrO_2 powder[37] using microelectrophoresis.

The surface charge on the particles is also reflected in the rheological behaviour (Fig. 7) with a viscosity maximum between pH 7·5 and 8·5. At the low shear rate, where the particle interactions affect the response more, some minor hysteresis can still be observed since the suspensions prepared at a high and low pH display a maximum in viscosity at pH ≈ 8·5 and pH ≈ 7·7, respectively.

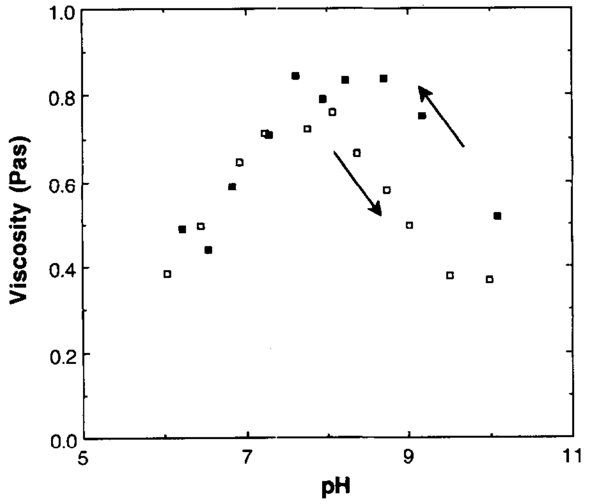


Fig. 7. Steady shear viscosity at $\gamma = 18{\cdot}4\ s^{-1}$ versus pH of a Ce-ZrO_2 suspension at $\Phi = 0{\cdot}10$. The open symbols indicate increasing pH whilst the filled symbols indicate a decreasing pH.

Attempts were also made to use microelectrophoresis to determine the iep. It was found that the problems of attaining an equilibrium state of a slightly soluble powder like Ce-ZrO_2 makes electrophoresis measurements of (very) dilute suspensions subjected to short equilibration times highly susceptible to errors in determining the iep. The electroacoustic measurements on concentrated suspensions show a much better correlation to the colloidal stability and rheological response of the concentrated Ce-ZrO_2 suspensions as shown above. Further evidence for an iep near to pH 8 was noted from the pH = 8·0 sample in the solubility measurements, which always settled out the quickest.

3.4 Effect of dispersants

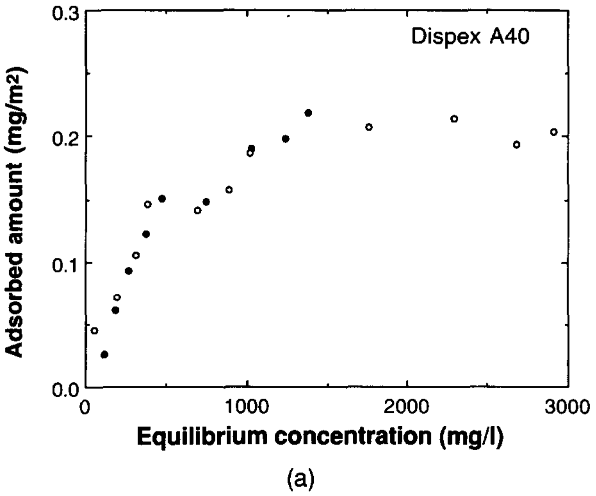
3.4.1 Adsorption isotherms

The effect of dispersant addition on the properties of Ce-ZrO_2 suspensions was investigated at two basic pH values, pH = 8·3 and 9·5. The acidic range was avoided due to dissolution of the powder. Polyelectrolyte dispersants, like the Dispex A40 and the Duramax D3007, are charged polymers. Polyelectrolytes containing ionizable groups, such as carboxylic groups and primary and secondary amines (see Fig. 3), will change their degree of ionization with pH and ionic strength. As the fraction of ionized monomers increases, the polyelectrolyte charge density increases from neutral to highly charged. For polyelectrolytes based on carboxylic acid monomers, e.g. polyacrylic acids (PAA) such as Dispex A40, the negative charge density increases with increasing pH. The ionization properties of PAA have been extensively studied and previous work has shown that low-molecular-weight PAA ($M_w \approx 2600$) is completely ionized at pH > 8.[38] Hence, at the two investigated pH values, pH = 8·3 and 9·5, Dispex A40 is completely ionized.

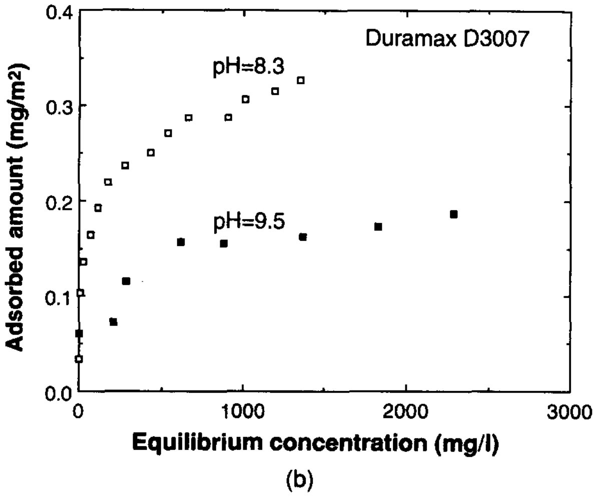
The adsorption of a polymer from solution onto a surface is determined by a number of factors including the solution properties of the polymer, the monomer–surface interaction and the surface–solvent interaction. Hence, the adsorption of dispersants will also be affected by the surface charge on the particle surfaces. The lower pH value, pH = 8·3, is just above the iep of the powder (Fig. 6), which means that the powder surface is slightly negatively charged. At pH = 9·5, the negative charge on the powder is larger.

The nearly identical isotherms of Dispex A40 on Ce-ZrO_2 at pH = 8·3 and 9·5 in Fig. 8(a) show that the difference in the surface charge density of the powder does not affect the adsorption to any great extent. The area per ionized acrylic acid monomer was estimated to be 70 Å^2 from the plateau value of the adsorption isotherms (0·22 mg Dispex A40/m^2 powder area). This value corresponds rather well to estimations of the cross-sectional area of the acrylic acid monomer, thus indicating that the polyelectrolyte adsorbed in a flat conformation on the powder surface. A fully ionized polyelectrolyte with such small monomer units as PAA (Dispex A40) will attain a relatively rigid, extended conformation in solution and the polyelectrolyte will usually adsorb flat on a surface with essentially no parts of the polyelectrolyte extending into the solution.

The Duramax D3007, on the other hand, displays a significantly higher adsorption at pH = 8·3 than at pH = 9·5 [Fig. 8(b)]. The structure of the Duramax D3007 is much more complicated compared with Dispex A40 (Fig. 3). The structure of the dispersant is dominated by the acrylic acid monomers but it also contains a smaller degree of ester, amide and acrylamide monomers, hence the Duramax D3007 can be characterized as a zwitterionic polyelectrolyte containing both anionic and cationic monomers. The nitrogen-containing monomers (which consist of primary or secondary amine groups) will be positively charged at low pH values and neutralize at high pH values, while the carboxylic groups will be ionized at high pH. The charge density of the Duramax D3007 might become significantly more negative at pH = 9·5 than at pH = 8·3 since most of the amine groups are expected to be neutralized at pH = 9·5. At this high pH value the adsorption behaviour of the Duramax D3007 is similar to that of Dispex A40, which might be explained by the ionized carboxylic acid groups dominating the interaction with the Ce-ZrO_2 powder surface. The significantly higher adsorption at pH = 8·3 of the Duramax D3007 shows that the dispersant does not adsorb flat in a monolayer on the powder surface. The increase in adsorbed amount may be explained by some self-association of the Duramax D3007 dispersant due to interactions between the negatively and positively charged groups or some hydrophobic association by the alkyl chains. This type of associative behaviour (indicated by the more viscous properties of the Duramax D3007 solutions as mentioned previously) may result in multilayer adsorption.



(a)



(b)

Fig. 8. Adsorption isotherms of (a) Dispex A40 and (b) Duramax D3007 on Ce-ZrO_2 at pH = 8·3 (○,□) and pH = 9·5 (●,■), respectively.

3.4.2 Electroacoustics and rheology

The steady shear rheology of a Ce-ZrO_2 suspension as a function of the amount of Dispex A40 added is shown in Fig. 9. The results display an abrupt change from a shear thinning behaviour at low additions to a Newtonian behaviour with a very low viscosity (η = 4 mPa s) at higher additions of the dispersant. The strongly shear thinning

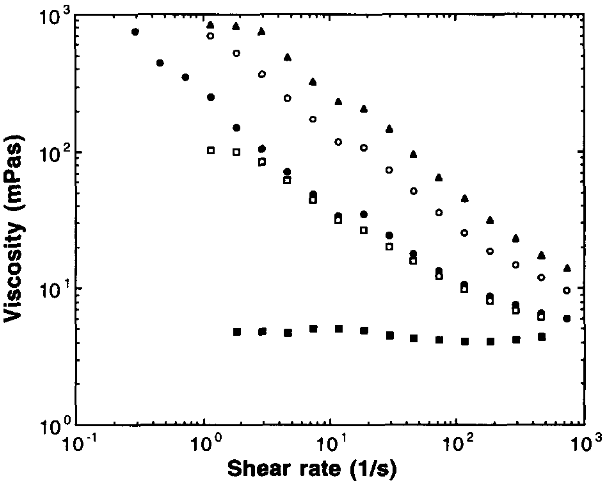


Fig. 9. Steady shear viscosities for a Ce-ZrO_2 aqueous suspension at Φ = 0·10 and pH = 8·3 at different dispersant additions of Dispex A40: (▲) 0·078, (○) 0·105, (●) 0·151, (□) 0·249 and (■) 0·278 mg dispersant/m^2 of powder.

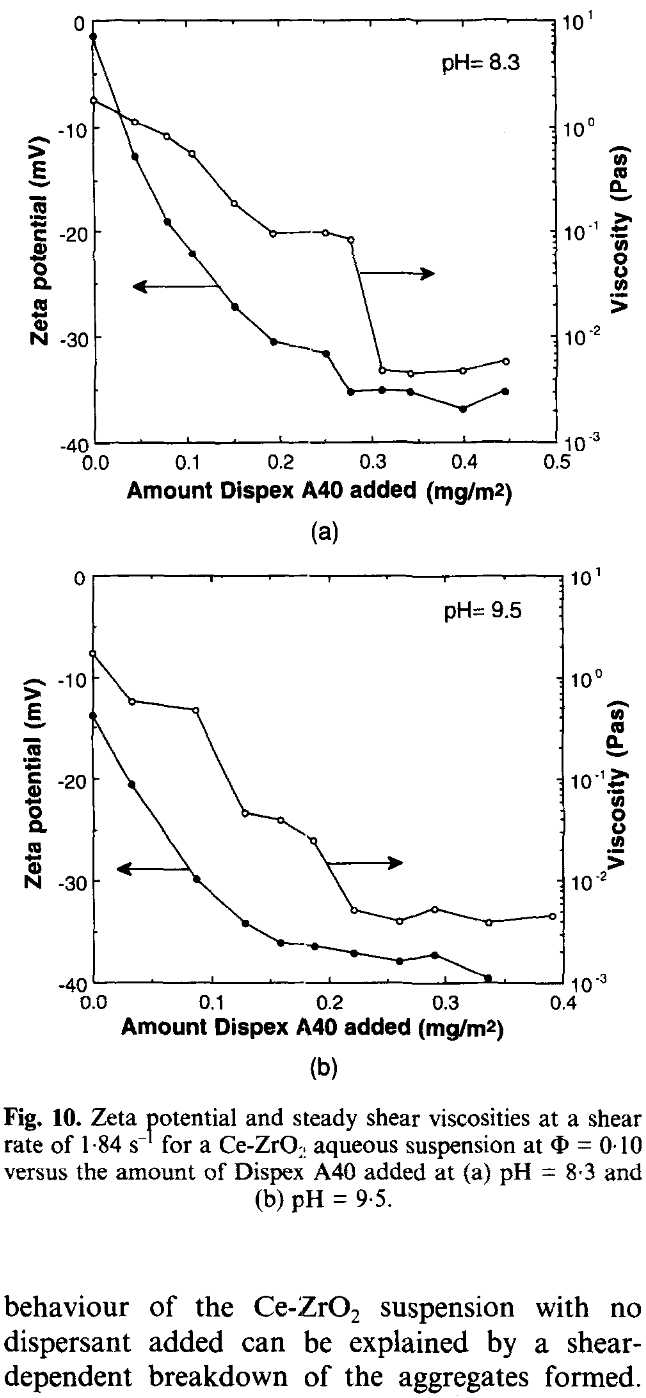


Fig. 10. Zeta potential and steady shear viscosities at a shear rate of 1·84 s^{-1} for a Ce-ZrO$_2$ aqueous suspension at Φ = 0·10 versus the amount of Dispex A40 added at (a) pH = 8·3 and (b) pH = 9·5.

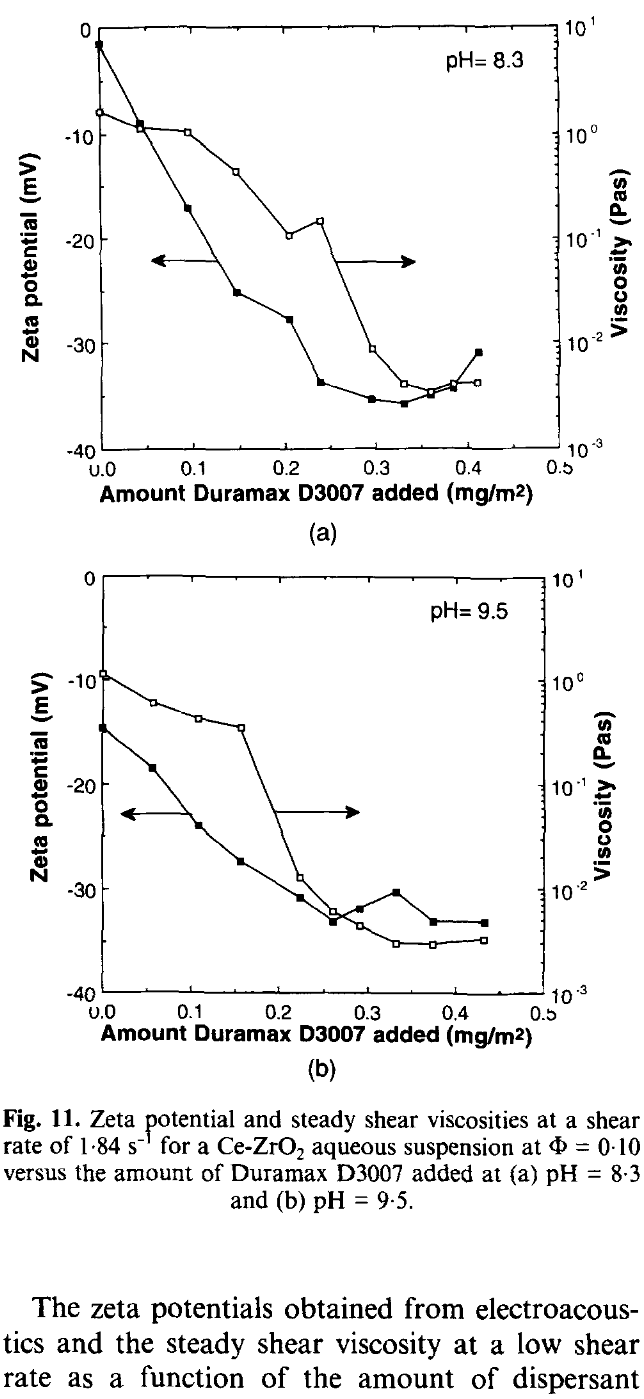


Fig. 11. Zeta potential and steady shear viscosities at a shear rate of 1·84 s^{-1} for a Ce-ZrO$_2$ aqueous suspension at Φ = 0·10 versus the amount of Duramax D3007 added at (a) pH = 8·3 and (b) pH = 9·5.

behaviour of the Ce-ZrO$_2$ suspension with no dispersant added can be explained by a shear-dependent breakdown of the aggregates formed. With increasing shear rate, the viscous forces tend to reduce the size of the aggregates and release liquid immobilized in the aggregates, thus facilitating flow.[39] It has been demonstrated that a concentrated suspension becomes more and more severely shear thinning with an increase in the magnitude of the interparticle attraction.[40] The decrease in viscosity and degree of shear thinning with the addition of more Dispex A40 implies that the degree of flocculation decreases. At a critical addition of dispersant the viscosity is at a minimum and the suspension becomes Newtonian, implying the powder is now colloidally stable. This transition from a shear thinning, flocculated behaviour to a Newtonian, colloidally stable behaviour at a critical amount of added dispersant was found for both Dispex A40 and Duramax D3007.

The zeta potentials obtained from electroacoustics and the steady shear viscosity at a low shear rate as a function of the amount of dispersant added are shown in Figs 10 and 11. At pH = 8·3 the zeta potentials of the dispersion with no dispersant present were very close to zero; again this is further evidence that the isoelectric point is about pH 8. In all the electroacoustics experiments addition of the polyelectrolyte caused an increase in the zeta potential (i.e. became more negative), which is expected, as at these pHs the polyelectrolyte is negatively charged and hence imparts a higher charge density on the particles when adsorbed. The zeta potential gradually increases with addition until a plateau region is reached where further addition of the dispersant did not affect the zeta potential.

The values of the amount of dispersant corresponding to monolayer coverage from the adsorption isotherms (Fig. 8) are compared with the

Table 3. Monolayer coverage of dispersants from adsorption isotherms compared with minimum addition to obtain maximum zeta potential and minimum viscosity for concentrated suspensions

Dispersant/pH	*Isotherms (mg m^{-2})*	*Electroacoustics (mg m^{-2})*	*Rheology (mg m^{-2})*
Dispex A40/ pH = 8·3	0·22	0·28	0·31
Duramax D3007/ pH = 8·3	0·32	0·33	0·35
Dispex A40/ pH = 9·5	0·21	0·25	0·25
Duramax D3007/ pH = 9·5	0·2	0·25	0·30

additions required to produce minimum viscosity or maximum zeta potential using steady shear and electroacoustic measurements (Figs 10 and 11) in Table 3. The adsorption isotherm estimate for monolayer coverage is always lower than the addition needed for minimum viscosity or maximum zeta potential. This can be explained by the amount of dispersant needed in solution to reach maximum adsorption. The adsorption isotherms (Fig. 8) show that 0·1–0·2 wt% (1000–2000 mg l^{-1}) of dispersant in solution is needed. This amount of dispersant in solution corresponds to approximately 0·07 mg m^{-2} at a solids concentration of Φ = 0·10. Taking this effect into account, the results display an excellent agreement between the amount needed for monolayer coverage and the minimum amount of dispersant needed to reach minimum viscosity and maximum zeta potential for the different suspensions. Hence, the use of rheology and electroacoustic measurements is a very powerful combination, since information regarding the flow properties as well as the zeta potential of the suspended particles can be obtained in concentrated suspensions.

4 Conclusions

Ceria will dissolve out of the Ce–ZrO_2 (Ce-TZP) powder under slightly acidic conditions. The dissolution of such polyvalent cations must be avoided if a colloidally stable suspension is to be prepared. No dissolution of ceria or zirconia was found under basic conditions. It was concluded that a pH value above pH = 6 must be chosen when preparing suspensions of this powder.

Rheology and electroacoustics experiments on concentrated suspensions resulted in a pH_{iep} = 7·9. Microelectrophoretic measurements showed a significantly lower iep. This difference in iep with solids concentration may be related to the difference in the complex surface reactions, e.g. dissolution, dissociation, adsorption and possibly hydration, that will depend on the surface-to-volume ratio of the system. We have established an experimental procedure, using ultrasonication to obtain a reproducible state of the suspension, which gave good correlation between electroacoustic and rheological measurements at moderate volume fraction of solids. These results illustrate the importance of electroacoustics as an excellent technique for studying complex suspensions of slightly soluble powders at high volume fractions. It is often problematic to use electrophoresis data alone and extrapolating the results to higher volume fractions when studying ceramic suspensions.

The two dispersants studied (Dispex A40 and Duramax D3007) are both capable of dispersing the powder to produce a low viscosity slip under basic conditions. These favourable suspension properties could not be produced at basic pH values without the addition of dispersants. The adsorption isotherms of the two polyelectrolyte dispersants were discussed in relation to the molecular structure. It was suggested that the zwitterionic nature and the existence of hydrophobic parts of the Duramax D3007 can result in an associative behaviour, leading to multilayer adsorption.

The amount of dispersant required for monolayer coverage from the adsorption isotherms and zeta potential measurements using electroacoustics correlate very well with the amount required for reaching the minimum in viscosity. So, it can be concluded that minimum viscosity occurs at monolayer coverage of the polyelectrolytes on the powder, which corresponds to highly charged polyelectrolyte-coated particles. This implies that the dominating mechanism for colloidal stability is electrostatic. Steric effects probably play only a minor role. We found that electroacoustics can be used as a convenient and simple method to obtain information regarding the change in zeta potential with the addition of dispersant, making it possible to screen many dispersants in a rather short time. The results in this study also illustrate how the powerful combination of rheology and electroacoustics can be utilized in the investigation and optimization of the effect of different dispersants on the properties of concentrated ceramic powder suspensions.

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