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Polymeric stabilisation of aqueous suspensions of barium titanate. Part I: Effect of pH

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Abstract

This article investigates the effect of the pH on the aqueous dispersion of barium titanate powders with anionic and cationic polyelectrolytes. The anionic polymer tested was an ammonium salt of polyacrylic acid (PAA) with molecular weight (M_w) ~4000, and the cationic were two quaternary alkyl ammonium derived polymers, with M_w ~150,000 and ~7600. The anionic polyelectrolyte has been found to be very effective in the alkalyne pH range, where the carboxylic groups are ionised. As result, the suspension is electrostatically stabilised, and the yield stress values and viscosities are very low. The adsorption and effectiveness of this polyelectrolyte could be reinforced by the presence of Ba^{2+} ions adsorbed on the surface of the $BaTiO_3$ particles. The cationic polyelectrolytes, on the contrary, are not effective stabilising the suspension: at alkaline pH, the long chain polymer has the tendency to bridge particles, and the short polymer does not generate ζ potential values high enough upon adsorption. At pH 4, their addition to the suspension is not of any advantage with respect to the suspension without polyelectrolytes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$; pH; Polyelectrolyte; Rheology; Suspensions

1. Introduction

Dielectric layers for multilayer ceramic capacitors are usually prepared by tape-casting of well dispersed barium titanate ($BaTiO_3$) powder suspensions. The suspending media are preferentially organic solvents.[1] There is, however, a recent interest in developing aqueous tape-casting, caused by the environmental needs of reducing organic wastage and by the industrial interest of lowering production costs.[2]

The dispersion of $BaTiO_3$ powders in water, although of great interest, was not well understood. We have shown that $BaTiO_3$ has an isoelectric point (IEP) at pH ~7.[3] However, when concentrated suspensions (as those required for ceramic processing) are used, an IEP at ~10.5 is observed.[3] This feature can only be explained taking into account that $BaTiO_3$ powders are contaminated with small amounts of $BaCO_3$.[4] It seems therefore that the adsorption of Ba^{2+} released by dissolution of $BaCO_3$ (more favourable than the hydrolysis of $BaTiO_3$)[5] is what is causing the shift on the IEP towards alkaline values observed when suspensions of higher solids volume fraction are used.

The aim of the present study was to find the optimum conditions for polymeric deflocculation of aqueous suspensions of the actual $BaTiO_3$ powders, within this framework. For this purpose, two water soluble polymers with similar charge density and containing active groups of different character (anionic and cationic) were tested and their effectiveness studied in a comparative way. Polyelectrolytes have the ability to modify interparticle forces through the action of adsorbed polymer or the presence of free polymer in solution. By studying their effect on sediment density, it has been shown that they are better dispersants for $BaTiO_3$ aqueous slurries than inorganic salts,[6] which, moreover, could leave harmful residues (e.g. Na^+, P) from the point of view of the electrical properties of the final ceramic.

Polyelectrolytes adsorbed at the surface of the particles can stabilise a colloidal suspension through a pure electrostatic effect of the adsorbed polymer, steric or a combination of both of them (electrosteric effect)[7]. When the chain is highly charged, the polymer will be stretched and, especially short polyelectrolytes, will adsorb in a flat conformation. The number of dissociated

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units (degree of ionisation) depends on the pH of the medium and their chemical nature. Their effectiveness as deflocculating agents might be affected not only by the pH, but also by their concentration in solution, in such a way that there is an optimum concentration of polymer and an optimum pH for stabilisation. In this work, the effect of pH has been studied at a fixed concentration of polyelectrolyte. Since the polymer concentration needed for stabilisation might change with the pH, the effect of polymer concentration at several fixed pH values has also been studied, and results are reported in the accompanying article,[8] which concludes with stability maps combining both effects (pH and polymer concentration).

The anionic polyelectrolyte used was a commercial ammonium salt of polyacrylic acid (Dispex A40). Dispersants based on carboxylic acid units are known to be effective in the stabilisation of concentrated suspensions of ceramic oxides. For instance, citric acid and a range of bezene aromatic compounds containing hydroxyl and carboxylic groups have been useful for the stabilisation of concentrated suspensions of Al_2O_3,[9] sodium and ammonium salts of polymethacrylic acid (PMAA) and polyacrylic acid (PAA) have also been described in the literature as good deflocculants for aqueous slurries of Al_2O_3[10–12] and TiO_2.[13] Moreover, carboxylic acid groups seem to have a great affinity for the $BaTiO_3$ surface[14–19] to the point that PAA is able to completely displace a commonly used binder such as polyvinylacohol (PVA) from the $BaTiO_3$ surface.[15] It has been shown too that PMAA is also a good deflocculant for $BaTiO_3$ aqueous suspensions.[20]

Nevertheless, it was initially thought that anionic polyelectrolytes, such as Dispex A40, might not be the most suitable dispersants for $BaTiO_3$ aqueous suspensions, because the presence of Ba^{2+} ions in solution (from dissolution of $BaCO_3$ impurity which accompanies $BaTiO_3$ powders)[4] could block and neutralise its negative charges. Cationic deflocculants were expected to be better dispersants because their active group was indifferent towards the suspected Ba^{2+} ions. It has been recently reported that other systems such as SiO_2 can be deflocculated with a cationic polyelectrolyte.[21] However, to the authors knowledge, they had never been tested before as dispersants for $BaTiO_3$.

In this comparative study, the effectiveness of anionic and cationic polyelectrolytes was assessed through sediment density, electrophoresis and steady shear flow measurements at different hydrogen ion concentrations.

2. Experimental

2.1. Materials

Powder used in this study was commercial Nb-doped $BaTiO_3$ powder, produced by Transelco-Ferro USA (lot 219-3) through solid state reaction between $BaCO_3$ and TiO_2. This powder had a specific surface area (BET) of 1.1 $m^2\ g^{-1}$, mean particle size ~1.5 μm and was slightly TiO_2-rich (TiO_2/BaO ratio was 1.05).[5] Its IEP was ~7.[3]

The polyelectrolytes used (ammonium polyacrylate, Dispex A40, and two quaternary alkylammonium chlorides, DP6 and DPX-1) were supplied by Allied Colloids, Bradford, UK. It is know that the molecular weight of the polymer affects the interparticle interaction. Optimum efficiency was found with PAA of Mw 400 on the surface of TiO_2,[13] and the most commonly used PAA and PMAA, have M_w between ~100 and ~10000.[9,10,14,20] The commercial ammonium polyacrylate Dispex A40 used in this work had a M_w within that range (~4000). The cationic alkyl ammonium chloride was supplied as two experimental grades, called DPX-1 (M_w ~7660) and DP6 (M_w~150 000), respectively, which offer the possibility of observing the effect of the polymer chain on the interparticle interactions. The structures of these polymers and are shown in Fig. 1.

The degree of dissociation of the ammonium polyacrylate groups in Dispex A40 increases gradually from the acid range to pH 10. Its pK_a is ~4.5, where 50% of the COOH groups are dissociated. At pH = 7, there is still a significant number of undissociated COOH groups present. However, DP6 and DPX-1 are strong polyelectrolytes, and they will be therefore dissociated over the whole pH range covered.

2.2. Methods

Powder was weighed into polypropylene containers and the polyelectrolyte solution was added then. The slip was dispersed using an ultrasonic probe (Lucas Dawes Soniprobe) operated at full power. pH adjustments were carried out afterwards using diluted HCl or KOH.

A Zetasizer 4 (Malvern Instruments, Malvern, UK) was used to measure the ζ-potential of the particles in the aqueous suspension by electrophoresis. Deionised water was used for the preparation of the suspensions, which were left equilibrating over night. The ionic strength was adjusted to 1 mmol dm^{-3} of KCl. Two

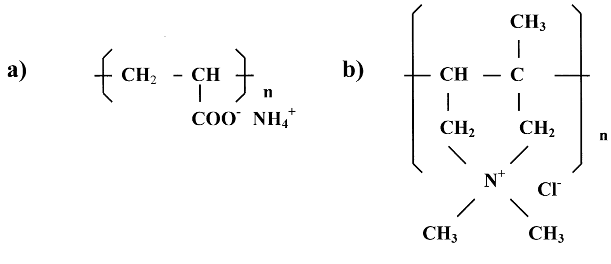


Fig. 1. Polyelectrolytes used in this work: (a) Dispex A40, and (b) DP6 and DPX-1.

solids concentrations were used: 0.05 vol% (diluted) and 20 vol% (concentrated). The diluted suspensions were left to settle over night, and the ζ-potential was measured on the supernatant liquid. Concentrated suspensions were centrifuged until the supernatant was a clear liquid. The Zetasizer uses the Smoluchowski equation to convert electrophoretic mobilities (u_E) into ζ-potential values:

$$u_E = \frac{v_E}{E} = \frac{\zeta\varepsilon}{\eta} \tag{1}$$

where v_E is the velocity of the surface relative to stationary liquid; E, the electric field strength; ζ, the zeta potential: η the viscosity of the medium and ε, the permittivity of the electrolyte medium. It is generally considered[22] that this equation is valid when $\kappa a > > 1$ (a is the radius of the particle and κ^{-1}, the thickness of the double layer) and it was estimated that the suspensions used here to measure ζ-potentials met that requirement. ζ-potential values would be then a function of amount of polyelectrolyte adsorbed, the degree of dissociation, and the surface charge of the bare particle.[10] In this equipment, the position of the stationary layers in the electrophoresis cell are found by alignment of a laser beam using suspensions of a latex standard known to have a ζ-potential of -55 ± 5 mV. The value plotted is the average of 10 measurements.

Shear stress sweeps were applied on 20 vol% suspensions with a controlled stress rheometer (Carri-med SCL500 Rheometer Systems, Dorking, UK), and a concentric cylinder system was the geometry used. In order to ensure a shear history independent of handling, the samples were presheared for 2 min at the maximum shear stress used for every experiment and were subsequently left unstirred for 2 min before the stress sweep was applied. The real yield stress (minimum stress needed by the system to begin flow) is proportional to the degree of agglomeration of the system,[23] and was used as parameter to evaluate the efficiency of the polyelectrolytes as dispersants for $BaTiO_3$ aqueous suspensions with the pH. Twenty vol% was the solids concentration selected for all rheological measurements, to be able to compare the performance of all polyelectrolytes tested here. In some cases, however, higher volume fractions could be used.

Twelve vol% suspensions were prepared for sediment density experiments. Suspensions were left standing for a week in 25 cm^3 cylinders, and the volume of the sediment was recorded then. Results are expressed as % of the theoretical density for $BaTiO_3$, which was taken as 6.02.[24]

The concentration of polyelectrolyte is expressed as weight % (wt%), referred to the solids loading, and the $BaTiO_3$ powder concentrations are given in volume % (vol%).

3. Results

3.1. Sediment density

Initial dispersion studies showed that the sediment density curves obtained with 12 vol% suspensions with and without the use of 0.2 wt% of cationic polyelectrolyte are very similar. The only differences are values slightly higher with the cationic polyelectrolytes at low pH (<7) (Fig. 2). It was observed too that the suspensions with cationic polyelectrolytes at pH$>$7 sedimented leaving a cloudy supernatant. On the other hand, the curve for the anionic Dispex A40 has an "S" shape with very low values (poor dispersion) at low pH, and increasing suddenly at pH$\sim$7 to reach a plateau at pH$>$8 with high values (53%) of the theoretical density. These high sediment densities are achieved when the suspension is stabilised (particles pack in a low sediment volume), whereas an unstable or flocculated system originates low sediment values (primary particles are attracted to each other and form loose flocs of subsequent low packing density).[25] This indicates that Dispex A40 is an effective deflocculant under alkaline conditions.

3.2. ζ-potential measurements

The modification of the electrophoretic behaviour induced by the polyelectrolytes is shown in Figs. 3–5. ζ-potential measurements were carried out in the presence of 0.1 wt% of polyelectrolyte both with a dilute suspension (0.05 vol% solids) and with the supernatant obtained after centrifuging a concentrated (20 vol%) suspension. This was necessary because it has been found that there is not correlation between ζ potential values obtained with diluted suspensions and rheological measurements,[3] mainly as a consequence of the dissolution of $BaCO_3$ present as impurity, in the presently available $BaTiO_3$ powders.[4] Ba^{2+} ions released and

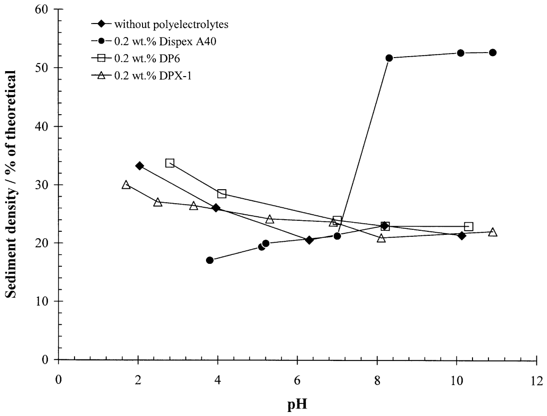


Fig. 2. Effect of polyelectrolytes on the sediment density of a 12 vol% solids suspension of $BaTiO_3$ powder.

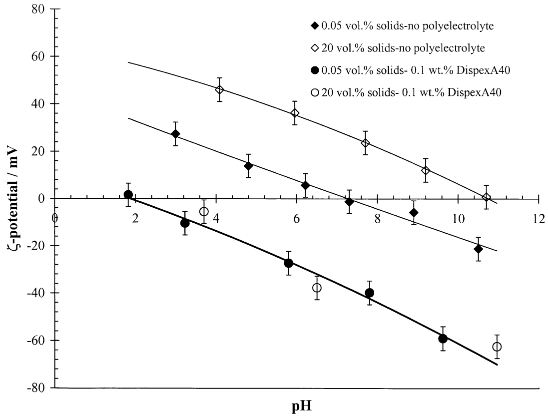


Fig. 3. Effect of Dispex A40 on the ζ-potential of $BaTiO_3$ particles in a 0.05 vol% solids concentration (filled symbols) and on the ζ-potential of particles in the supernatant obtained by centrifuging a 20 vol% solids suspension (open symbols).

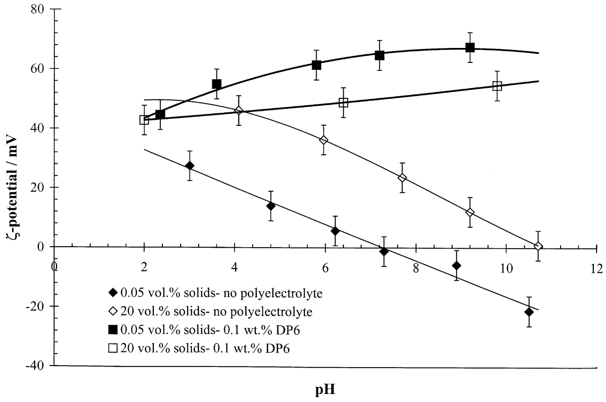


Fig. 4. Effect of DP6 on the ζ-potential of $BaTiO_3$ particles in a 0.05 vol% solids concentration (filled symbols) and on the ζ-potential of particles in the supernatant obtained by centrifuging a 20 vol% solids suspension (open symbols).

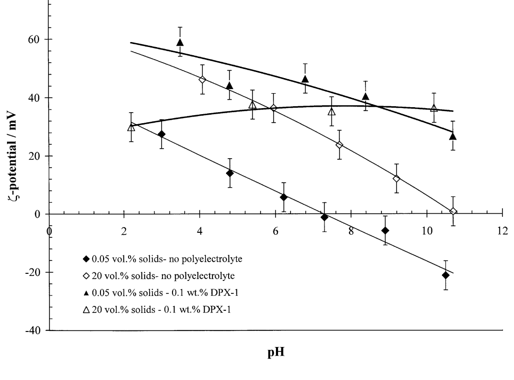


Fig. 5. Effect of DPX-1 on the ζ-potential of $BaTiO_3$ particles in a 0.05 vol% solids concentration (filled symbols) and on the ζ-potential of particles in the supernatant obtained by centrifuging a 20 vol% solids suspension (open symbols).

readsorbed on the surface of $BaTiO_3$ originate a shift of the ζ-potential curve to upper values, with an IEP at ~10.5, indicating clearly that the surface under those conditions has a more positive character than that under diluted conditions. This curve has been included in Figs. 3–5 to better compare the results.

Negative ζ-potential values were obtained with Dispex A40, and positive with the cationic polyelectrolytes used, over the whole pH range. With Dispex A40, there is an IEP at pH 2, and values are more negative with increasing pH. No significant differences on the ζ-potential with either high or low solids concentration conditions are observed (Fig. 3). On the contrary, it seems that the cationic polyelectrolytes DPX-1 and DP6 are not adsorbed at $pH < 4$, when the suspension has a high solids concentration, since no increase in ζ-potential values is observed (Figs. 4 and 5). However, they are adsorbed, in all pH range under diluted conditions, and at $pH > 4$ (DP6) and $pH > 6$ (DPX-1) with concentrated suspensions (Figs. 4 and 5).

3.3. Rheological measurements

Flow curves were obtained at different pH values using suspensions containing 20 vol% $BaTiO_3$ powder and 0.1 wt% of polyelectrolyte. Under these conditions, the yield stress decreases with decreasing pH for the cationic polymers, and increases with decreasing pH for the Dispex A40 (Fig. 6). The curves obtained are pseudoplastic (shear thinning). The changes in viscosity with shear rate for every polymer at pH 10 and 4 are shown in Figs. 7 and 8, respectively. 0.1 wt% of Dispex A40 decreases considerably the viscosity and eliminates the yield stress of the slip at alkaline pH (Fig. 7). At $pH > 9$ DP6 decreases the yield stress and viscosity significantly, but these are not reduced to the limit attainable with Dispex A40. At low pH, both Dispex A40 and DP6 increase the viscosity, although the effect is lesser for the latter (Fig. 8). DPX-1 at the concentration considered here (0.1 wt%) does not seem to have any effect on the viscosity (Figs. 7 and 8).

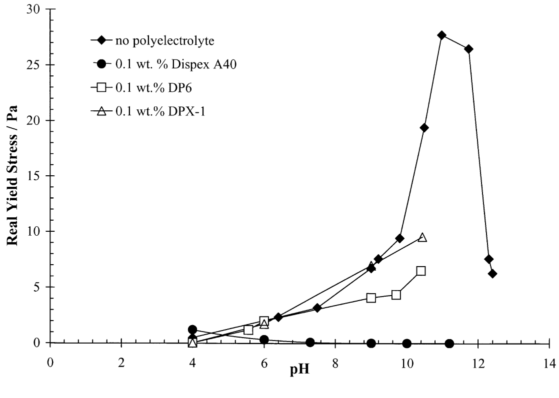


Fig. 6. Effect of 0.1 wt% of polyelectrolyte on the yield stress of 20 vol% $BaTiO_3$ powder suspensions.

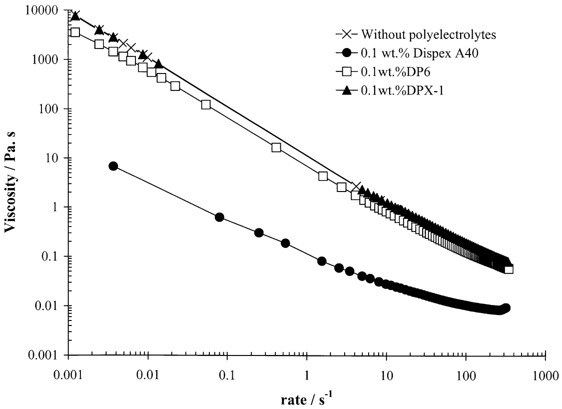


Fig. 7. Effect of 0.1 wt% of polyelectrolyte on the viscosity of 20 vol% $BaTiO_3$ powder suspensions at pH 10.

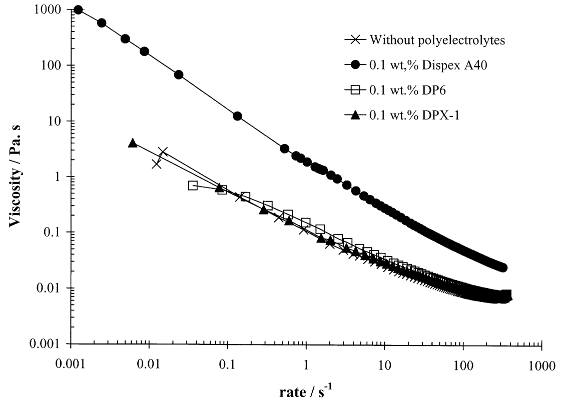


Fig. 8. Effect of 0.1 wt% of polyelectrolyte on the viscosity of 20 vol% $BaTiO_3$ powder suspensions at pH 4.

3.4. *Effect of adding Ba^{2+}*

Ba^{2+} ions were added to the suspension, in order to check the possible blocking of the active sites of the anionic polymer. Addition of $BaCl_2$ in 1:1 equivalent ratio relative to the polyacrylate groups (0.5 mmol dm^{-3}) has very little effect on the sediment density of the suspension (Fig. 9), but flocculation occurs when higher concentrations (1:10 polymer to Ba^{2+}, 5 mmol dm^{-3}) were used.

4. Discussion

4.1. *Anionic polyelectrolyte Dispex A40*

The differences between the ζ-potential curve obtained under diluted and concentrated conditions in absence of polyelectrolytes are mainly related to the differences on concentration of Ba^{2+}. Ba^{2+} acts as a potential determining ion, as explained in detail in Ref. 3. When Dispex A40 is used (Fig. 3), there is no significant difference between the ζ-potential values obtained with diluted suspensions or after centrifuging those with high solids loading (20 vol%). These negative ζ-potential values are evidence of that there is an important number of dissociated sites negatively charged along the polymer molecule even at low pH values (where the degree of dissociation is lower), and of polymer adsorption at the surface of $BaTiO_3$ particles.

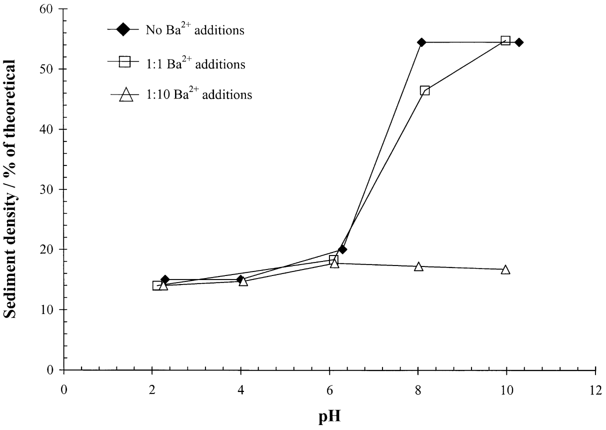


Fig. 9. Effect of $BaCl_2$ additions on the sediment density of 12 vol% solids suspension of $BaTiO_3$ powder.

It can also be observed in Fig. 3 that adsorption of Dispex A40 still occurs when $BaTiO_3$ and Dispex A40 are both negatively charged (i.e. $pH > 7$, with diluted suspensions). Thermodynamic theories explain adsorption in this case as a process which lowers the free energy of the system,[26] and predict that the conformation adopted by the polymer at the surface of the particles consists in more segments in loops, and fewer in trains.[26–27] However, it is very unlikely that highly charged short chains adsorb in a loop-train-tail conformation because of their high degree of stretching, and we can assume then a flat conformation for Dispex A40 chains at the surface of the particle.

In the case of $BaTiO_3$ high solids concentration suspensions, polymer and particle surface are always oppositely charged, and adsorption of polymer is enhanced then by a favourable electrostatic energy contribution. The conformation of polymer on the surface of the particles will consist mainly on trains, with shorter loops and tails, and it would be maximised at pH 9–10 when the degree of dissociation is 1.[26]

An IEP at pH 2 was found (Fig. 3), corresponding to a situation for which the adsorbed polymer has neutralised the positive charge with residual negative charges or has screened completely the positive surface charge of the particles. The absence of electrical repulsion leads to a flocculated system because it is dominated by the attractive Van der Waals forces. Larger flocs are formed, giving rise to lower sediment density (Fig. 2), and higher viscosity (Fig. 8) and yield stress (Fig. 6) than the suspension without Dispex A40. It is possible that, at these low pH values, higher concentrations of Dispex A40 are required for stabilisation. The effect of polyelectrolyte concentration with pH is discussed in Ref.8.

The polymer charge increases with the pH because the degree of dissociation of the carboxylic acid groups also increases. The electrostatic stabilisation of the adsorbed polymer becomes effective only at pH > 8 (Figs. 2 and 6), when a ζ-potential value of ~45 mV is reached, and most of the carboxylic groups are dissociated.[14] It seems therefore that this electrical charge originates a repulsion potential high enough to prevent particles from forming agglomerates, and this results in very low yield stress values and low viscosity under alkaline conditions (Figs. 6 and 7).

Deflocculation was then observed, in spite of the possibility of blocking the polyelectrolyte carboxlylic groups by Ba^{2+} ions present in solution.[5] This means that an excess of polymer concentration (over the minimum required to reach the adsorptium equilibrium value at the particle surface) is required, since some Dispex A40 molecules will be forming complexes with Ba^{2+} ions in solution. The effect of Ba^{2+} concentration was still checked with increasing concentrations of Ba^{2+} in solution by means of $BaCl_2$ additions. It is important to consider that there will be also adsorption equilibrium for Ba^{2+} at the $BaTiO_3$ particle surface, causing the surface charge to be less negative.[3] Moreover, the presence of Ba^{2+} at the surface of the $BaTiO_3$ particles could increase the adsorption level of Dispex A40 by forming a barium carboxylate complex at the surface. With a similar polyacrylate, the bond between PMAA and Ba^{2+} ions at the surface of $BaTiO_3$ particles has been detected by means of infrared spectroscopy.[20] This could reinforce the attraction between polymer and surface, as it was observed with Ca^{2+} when the adsorption of a sodium polyacrylate onto calcium phosphate particles was studied.[28] It was also observed there that polyelectrolyte adsorption increased when the Ca^{2+} concentration increased.[28] With further additions of $BaCl_2$, the ionic strength is too high, the interparticle distance is shortened, and the system flocculates. As a result, low sediment density values are obtained (Fig. 9).

Although it is known that $BaTiO_3$ hydrolysis is thermodynamically favourable,[29] we have shown that the main source of Ba^{2+} in solution is the $BaCO_3$ present in the current $BaTiO_3$ powders.[4] The partial hydrolysis of $BaTiO_3$ would not be a problem anyway when working with this polyelectrolyte, because the operative pH range with Dispex A40 is alkalyne pH, and dissolution is minimised then. It might be possible too that the dissolution process would be prevented by the polymer present at the surface, where Ba^{2+} is adsorbed, blocking the process of Ba^{2+} ion interchange with the medium, which is necessary for dissolution to progress. It is justified then its inclusion in currently used water based tape-casting formulations.[30]

4.2. Cationic polyelectrolytes DP6 and DPX-1

The quaternary alkylammonium chloride groups are strong electrolytes, and therefore it is expected that they will be fully dissociated over the whole pH range.

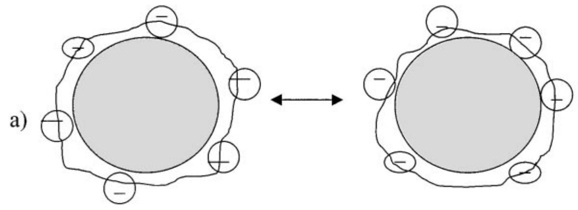
At pH > 7, electrostatic attraction between the polymer and the negatively charged $BaTiO_3$ particles in the low solids concentration suspensions occurs. This could result in bridging flocculation with DP6, since the ability of quaternary ammonium salts to bridge negative particles is well known, and has allowed their commercial development as flocculants.[31,32] For example, a quaternary almmonium sulphate has been used with success for the flocculation of colloidal silica.[31]

In concentrated suspensions, bared $BaTiO_3$ particles had very low positive ζ-potential values at pH > 10–11, as previously discussed.[3] Under these conditions, it is observed that adsorption of cationic species such as DP6 or DPX-1 takes place on the positively charged surface, because the magnitude of the ζ-potential is higher (Figs. 3, 4). The ζ-potential values found for DP6 (~50 mV) are higher than those obtained with DPX-1 (~35 mV) and higher than those of the suspension without polyelectrolytes (~50 mV), in agreement with the sequence of yield stress values (Fig. 6). It seems then that DPX-1 adsorbed on the surface of the $BaTiO_3$ particles at these alkaline pHs is not able to create an energy barrier high enough to provide electrostatic stabilisation. With respect to DP6, it is surprising to find that yield stress and viscosity are still high, whereas ζ-potential values were of the order of those found with Dispex A40, giving rise to electrostatic stabilisation. A possible explanation is that the ζ-potential values measured with DP6 correspond in reality to clusters of particles bridged by the polymer, and not broken when the particle is forced to move under the electric field. This hypothesis is supported by the cloudiness observed at the top part of the graduated cylinders used for the sedimentation experiments, or even at the surpernatant after centrifuging the suspensions. It seems therefore that the tendency to bridge particles of this long chain cationic polymer predominates over any other effect, and this is why the viscosity and yield stress of the suspensions are still high. It is possible that ζ-potential values calculated with the Smoluchowski equation are overestimated, and some corrections (e.g. viscosity of the medium) would be necessary.

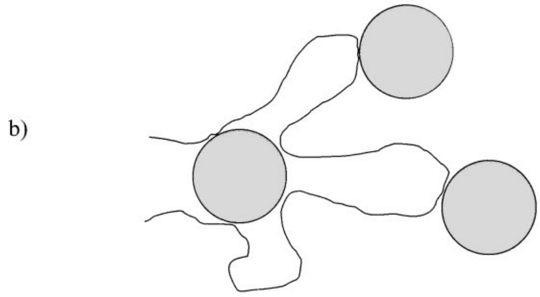
At pH 4, both the polymer and $BaTiO_3$ particle surface are positively charged, and there is electrostatic repulsion between polymer and particle surface. However, polymer adsorption still occurs for particles in the diluted suspension, as seen by the change in ζ-potential values, from ~30 (suspension with no polyelectrolytes) to ~50 with DP6 and to ~57 with DPX-1, at pH 4 (Figs. 4 and 5). In diluted suspensions with DPX-1, the ζ-potential values tend to decrease from ~60 mV at pH

3 to $\sim$30 mV at pH 11. Comparison with the reference curve seems to indicate decreased adsorption of this cationic polymer as the pH decreases due probably to the electrostatic repulsion. The DP6 ζ-potential values, however, increase from $\sim$45 mV at pH 3 to $\sim$70 mV at pH 9. The difference between these two polymers in low solids suspensions could be due to an effect of the longer chain, which results in higher repulsion with positively charged particles and less adsorption. A similar ζ-potential curve was obtained with a cationic polyelectrolyte based on the acidic form of polyethylenimine and M_w 50 000.[21] This type of polymer have however been proved to be good deflocculants for α-SiO_2 (which had an IEP at pH$\sim$2).[21]

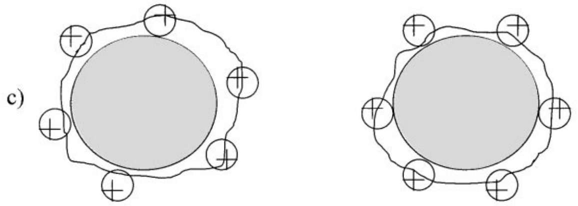
At pH 4, ζ-potential values obtained for the particles remaining in the supernatant after centrifuging the high solids concentration suspension with these cationic polymers are very close to those of the suspension in the absence of polyelectrolytes (Figs. 4 and 5). At that pH and lower, adsorption of cationic polymers is minimised, due to repulsion between strongly positively charged particles and polymer. In fact, viscosity, yield stress and sediment density values are very similar to those of the suspension without polyelectrolytes, which were already low. However, it is not well understood why while the magnitude of the ζ-potential value and viscosity found in this case is similar ($\sim$45 mV) to what was found when 0.1 wt% Dispex A40 was used at pH 10, the sediment density values are not. With respect to the suspension without polyelectrolytes, a drift towards the IEP value was observed[33] during the 7 days allowed for the sedimentation experiment. These could explain the low values found. In order to explain the behaviour found with the suspension with polyelectrolytes, it could be thought that the stabilisation observed with Dispex A40 is not only a consequence of the electrical charge, and the adsorbed polymer would be adding some steric contribution to the stabilisation. This is generally accepted for the stabilisation of $BaTiO_3$ aqueous suspensions with PAA[14] and PMAA.[20] It is possible then that the cationic polymers are not contributing to the steric repulsion, and the electrical charge developed is not enough. However it is very unlikely to have a steric effect with Dispex A40, since the ionisation of carboxylic groups and its short chain are more favourable for a flat conformation upon adsorption.



Electrostatic stabilisation with Dispex A40



Bridging flocculation with DP6



Adsorption of DPX-1. The electrical charge is not enough for electrostatic stabilisation

Fig. 10. Schematic representation of the predominant effect of Dispex A40, DP6 and DPX-1 on the dispersion of the $BaTiO_3$ powder suspension: (a) electrostatic stabilisation of Dispex A40 at pH $>$ 8; (b) bridging flocculation with DP6; (c) the electrical charge developed by DPX-1 adsorbed at the surface of $BaTiO_3$ particles is not enough for electrostatic stabilisation at alkalyne pH. At acidic pH no stabilisation is observed.

More information about the interaction of the polyelectrolytes used here with the $BaTiO_3$ particle surface in aqueous solution is required to fully understand these effects. Although some facts remain still unexplained, it can be concluded that the lowest yield stress and viscosity are achieved with these cationic polymers when working at acidic pH (pH$\leqslant$4), but in reality, they do not add any favourable contribution to the stability of the suspension. Yield stress is slightly higher, due probably to the higher ionic strength involved. Higher polymer concentrations could modify the effects described here, and this aspect is discussed further in Ref. 8.

Fig. 10 summarises schematically the predominant effect of the polyelectrolytes tried on the $BaTiO_3$ aqueous suspensions.

5. Conclusions

The anionic polyelectrolyte tested here (Dispex A40) is very effective as dispersant for aqueous $BaTiO_3$ powder suspensions. It is adsorbed over the pH range from 2 to 11. At pH $>$ 8 it is adsorbed on the surface of the particles, developing a highly negative ζ-potential value. The stabilisation provided is of electrostatic nature. Contrary to what was suspected, the Ba^{2+} ions present do not block the active sites of the polymer, and could enhance the adsorption of the polymer on the surface of the particles. Both cationic polymers tried, in turn, although adsorbed on the surface of the $BaTiO_3$ particles, do not appear very effective for the deflocculation. The long chain DP6 is likely to produce bridging flocculation, forming networks of particles that are not completely broken by the shear field during rheological measurements. The shorter chain version (DPX-1) has not that tendency, but at the concentration used here (0.1 wt%) does not seem to develop a ζ-potential high enough for an electrostatic type of stabilisation. Higher concentrations were investigated in the accompanying article.[8] At low pH the viscosity and ζ-potential values are very similar to those of the suspensions without polyelectrolytes, and the addition of the polymer does not produce any improvement on the deflocculation. Direct correlation between sediment density results, ζ-potential and rheological measurements obtained with different solids volume fraction could not always be made.

Although the powder used for this study was Nb-doped, it has been shown that rheological behaviour does not depend on the Nb-doped character of the powder,[3] and therefore, results obtained here can be generalised to undoped $BaTiO_3$ powders.

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References

1. Moreno, R., The role of slip additives in tape-casting technology: part I — solvents and dispersants. *Am. Ceram Soc. Bull.*, 1992, **71**(10), 1521–1531.
2. Mistler, R. E., Tape-casting: past, present, potential. *Am. Ceram. Soc. Bull.*, 1998, October, 82–87.
3. Blanco López, M. C., Rand, B. and Riley, F. L., The isoelectric point of $BaTiO_3$. *J. Eur. Ceram. Soc.,* 2000, **20**(10), 1587–1594.
4. Blanco López, M. C., Fourlaris, G., Rand, B. and Riley, F. L., Characterization of barium titanate powders: barium carbonate identification. *J. Am. Ceram. Soc.*, 1999, **82**, 1777–1786.
5. Blanco López, M. C., Fourlaris, G. and Riley, F. L., Interaction of barium titanate powders with an aqueous suspending medium. *J. Eur. Ceram. Soc.*, 1998, **18**, 2183–2192.
6. Itoh, H., Parish, M. V. and Bowen, H. K., Particle packing of $BaTiO_3$ powders in aqueous solutions. *Materials Science and Engineering*, 1987, **96**, 303–310.
7. Hunter, R. J., *Foundations of Colloid Science.*, Clarendon Press. Oxford, 1987, Vol. I.
8. Blanco López, M. C., Rand, B. and Riley, F. L., Polymeric stabilisation of aqueous suspensions of barium titanate. Part II: effect of polymer concentration. *J. Eur. Ceram. Soc.*, in press.
9. Hidber, P. C., Grauler, T. J. and Gauckler, L. J., Competitive adsorption of citric acid and poly(vinyl alcohol) onto alumina and its influence on the binder migration during drying. *J. Am. Ceram. Soc.*, 1995, **78**, 1775–1780.
10. Cesarano, J. and Aksay, I. A., Processing of highly concentrated aqueous α-alumina suspensions stabilized with polyelectrolytes. *J. Am. Ceram. Soc.*, 1988, **71**, 1062–1067.
11. Cesarano, J., Aksay, I. A. and Bleier, A., Stability of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, 1988, **7**, 250–255.
12. Weim, J. W., Lu, S. J., Wei and Yu, Y. B., Characterization of submicron alumina dispersions with poly(methacrylic acid) polyelectrolytes. *J. Eur. Ceram. Soc.*, 1995, **15**, 155–164.
13. Foissy, A., El Attar, A. and Lamarche, J. M., Adsorption of polyacrylic acid on titanium dioxide. *J. Coll. Interface Sci.*, 1983, **96**, 275–287.
14. Chen, Z., Ring, T. A. and Lemaître, J., Stabilisation and processing of aqueous of aqueous $BaTiO_3$ suspensions with polyacrylic acid. *J. Am. Ceram. Soc.*, 1992, **75**, 3201–3208.
15. de Laat, A. W. M. and Derbs, W. P. T., Colloidal stabilisation of $BaTiO_3$ with poly(vinyl alcohol) in water. *Colloids and Surfaces*, 1993, **A 71**, 147–153.
16. de Laat, A. W. M. and Van den Heuvel, G. L. T., Competitive and displacement adsorption of poly(vinyl alcohol) and the ammonium salt of a polyacrylic acid on $BaTiO_3$. *Colloids and Surfaces*, 1993, **A 70**, 179–187.
17. de Laat, A. W. M., de Bruijn, A. W. and Van den Heuvel, G. L. T., The adsorption of polyvinyl alcohols with caboxylate groups on $BaTiO_3$. *Colloids and Surfaces*, 1994, **A 82**, 99–110.
18. de Laat, A. W. M. and van den Heuvel, G. L. T., Molecular weight fractionation in the adsorption of polyacrylic acid salts onto $BaTiO_3$. *Colloids and Surfaces*, 1995, **A 98**, 53–59.
19. de Laat, A. W. M., van den Heuvel, G. L. T. and Bohmer, M. R., Kinetic aspects in the adsorption of polyacrylic acid salts onto $BaTiO_3$. *Colloids and Surfaces*, 1995, **A 98**, 61–71.
20. Jan-Ho, J. and Hong-Ren, W., Dispersion of aqueous barium titanate suspensions with ammonium salt of poly(methacrylicacid). *J. Am. Ceram. Soc.*, 1998, **81**, 1589–1599.
21. Baklouti, S., Pagnoux, C., Chartier, T. and Baumard, J. F., Processing of aqueous α-Al_2O_3, α-SiO_2 and α-SiC suspensions with polyelectrolytes. *J. Eur. Ceram. Soc.*, 1997, **17**, 1387–1392.
22. Shaw, D. J., *Colloid and surface science*. Butterworth-Heinemann Ltd, Oxford, 1992 p. 200-202.
23. Hunter, R. J., The elastic flow model. *Adv. Coll. Interface Sci.*, 1982, **17**, 197–211.
24. Weast, R. C., *Handbook of Chemistry and Physics*, 64th edn. CRC Press, Boca Raton, FL 1983, p. B-74.
25. Ottewil, R. H., in *Solid and Liquid Dispersions*, ed. Th. F. Tadros. Academic Press, London 1987, pp. 163–181.
26. Hesselenik, F. Th., In *Adsorption from Solution at the Solid–Liquid Interface*, ed. G. D. Parfitt and C. H. Rochester. Academic Press, London, 1983, pp. 377–412.
27. Papenhuijzen, J., Van der Schee, H. A. and Fleer, G. J., Polyelectrolyte adsorption I. A new lattice theory. *J. Coll. Interface Sci.*, 1985, **104**, 540–552.
28. Robb, I. D. and Sharples, M., The adsorption of poly(acrylic acid) onto insoluble calcium salts. *J. Coll. Interface Sci.*, 1982, **89**, 301–308.
29. Lencka, M. M. and Riman, R. E., Thermodynamic modelling of hydrothermal synthesis of ceramic powders. *Chemistry of Materials*, 1993, **5**, 61–70.
30. Hui, A., Bloomfield, D., Bell, A. and Chu, M., Water based binder systems for tape-casting of MLC dielectrics. In *Proc. 3rd European Capacitor and Resistor Technology Symposium*. Component Technology Institute, Amsterdam, 1989, pp. 78–85.
31. Iler, R. H., Relation of particle size of colloidal silica to the amount of a cationic polymer required for flocculation and surface coverage. *J. Coll. Inter. Sci*, 1971, **37**, 264–273.
32. Gregory, J., In *Solid and Liquid Dispersions*, ed Th. F. Tadros. Academic Press, London, 1987, pp. 163–181.
33. Blanco Lopez, M. C., Rand, B. and Riley, F. L., The properties of aqueous phase suspensions of barium titanate. *J. Eur. Ceram. Soc.*, 1997, **17**, 281–287.