Journal of the European Ceramic Society 20 (2000) 1587–1594

Polymeric stabilisation of aqueous suspensions of barium titanate. Part II: Effect of polyelectrolyte concentration

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Received 10 February 1999; received in revised form 30 August 1999; accepted 12 September 1999

Abstract

This article is the continuation of a study on the optimum conditions for deflocculation of aqueous suspensions of barium titanate powders with anionic and cationic polyelectrolytes. The effect of polyelectrolyte concentration on the stability of the suspension is described here, and stability maps are constructed at different pH values and polymer concentration. Defloculation is possible with 0.1 wt% of the anionic ammonium polyacrylate used (Dispex A40), at alkalyne pH. Maximum flocculation is obtained with this 0.5 wt% of this polymer at pH 4. At pH 6, stabilisation is possible with 0.4 wt% of this polymer. The use of the cationic quaternary alkylammonium polymers DP6 (Mw 150 000) and DPX-1 (Mw 7660) is not advantageous for the stabilisation of the suspension at any pH. At alkalyne pH, a concentration of 1 wt% of these polymers is able to decrease the yield stress and viscosity values, possibly through an electric effect of the adsorbed polymers. At pH 4, any concentration of these cationic polymers results in real yield stress values slightly higher than those corresponding to the suspension without polyelectrolytes, and green density values by slip casting are still low. On the other hand, green densities of 56.5% were obtained with the anionic polyelectrolyte at pH > 9. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$; Polyelectrolyte; Rheology; Suspensions

1. Introduction

This article is the second part of a study on the aqueous dispersion of barium titanate powders ($BaTiO_3$) using anionic and cationic polyelectrolytes. The first part [1] focussed on the effect of the pH on the dispersion. It was found there that the anionic polyelectrolyte used was effective at pH > 8, when the polyelectrolyte is fully ionised due to the electric repulsion created by the adsorbed polymer. At high pH and with the concentration of 0.1wt% used there, the cationic polyelectrolytes used were able to reduce the yield stress and viscosity of the suspensions, but not enough to impart stabilisation. At low pH they do not produce any significant improvement with respect to the suspension without polyelectrolytes.

The interparticle interactions previously found as a function of pH[1] can be modified with the concentration of polyelectrolyte. The effects of polyelectrolyte concentration on the stability have been described in detail.[2] An excess of free polymer in solution can cause depletion flocculation to an electrostatically stabilised suspension: the depleted concentration of polymer in the interparticle region generates an osmotic force, which causes formation of flocs.[2,3] In some cases, the opposite effect has been observed: i.e. deflocculation when the concentration of free polymer is very high and the interparticle distance very short, although this effect is not very common.[2,3] Some other times, when the polymer has low molecular weight, it is possible that the flocculation observed at low concentration of polymer is due to an incomplete coverage of the surface by the polyelectrolyte oppositely charged, and electrical attraction between "patches" of opposite charge in the particles.[4] In this case, an increase of concentration of polymer could result in its increased adsorption at the surface of the particles, creating therefore an interparticle repulsion of enough magnitude to deflocculate the suspension.[5] Molecular weight of the polymer, pH (which controls the degree of ionisation), and polyelectrolyte concentration, are, therefore, important variables related to the stabilisation.

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PII: S0955-2219(99)00241-1

The stability of the suspension can be related to the adsorbed fraction of polyelectrolyte.[6,7,12] Very few reports were found on the literature describing the behaviour of aqueous dispersion of $BaTiO_3$ powders with polyelectrolytes, and all of them were based on those polymers with an anionic character (acrylic type).[8–13] Depletion flocculation has been observed when an excess of polyacrylic acid (PAA) was added to a previously electrostatically stabilised suspension.[8] The maximum PAA adsorbed on $BaTiO_3$ particles was 0.4 or 0.45 mg m^{-2} at pH 8.8,[9–11] depending on the salt concentration of the medium. Other authors reported a lower limit of adsorption, 0.1 mg m^{-2}, at pH 10.5, and 10 times higher at pH 1.5.[12] A dependence on the amount of polyelectrolyte required with the pH has also been described with a related polyelectrolyte, consisting on the ammonium salt of polymethacrylic acid (PMAA).[13] In that case, ~1 mg m^{-2} was required for a monolayer of polyelectrolyte around the particles at pH 7.5, ~0.6 mg m^{-2} at pH 9.2, and ~0.4 mg m^{-2} at pH 12.0. These reports agree on that adsorption of these acrylic based polymers was very specific and followed the Langmuir equation.[10–13]

The aim of this article is to complete the study on the behaviour of $BaTiO_3$ powder suspensions describing the rheological behaviour found as a function of pH, with increasing concentrations of polyelectrolyte. The combination of both effects allows stability maps to be drawn.

2. Experimental

The barium titanate powder used was Nb-doped (Transelco-Ferro, USA). Characteristics of this powder can be found in previous publications.[1,14–16] The experimental procedure used involved ζ-potential and rheological measurements, using different concentrations of polyelectrolytes, and has been previously described.[1] Solids concentrations are given as vol% and the concentration of polyelectrolyte is expressed as wt% referred to the solids. Polyelectrolytes of anionic and cationic character were used: the anionic was an ammonium salt of PAA, with Mw ~4000, and the cationic, two quaternary alkylammonium chlorides, of Mw ~150 000 (DP6) and ~7660 (DPX-1), respectively. Their basic unit and details of the experimental procedure followed for electrokinetic and rheological measurements have been described before.[1] ζ -Potential measurements were carried out under two different conditions: diluted suspensions (0.05 vol% solids) and on the supernatant after centrifuging concentrated suspensions (20 vol% solids).

Green densities were measured on specimens obtained by slip casting suspensions under the conditions (concentration of polyelectrolyte and pH) that gave rise to the minimum yield stress observed. Two to three cubic centimetres of suspension were taken with the help of a syringe and poured through a glass tube on Plaster of Paris. The green density of the disc-shaped specimens obtained this way (dried for 48 h at 100°C) was measured by mercury immersion, and results are reported as % of the theoretical density of $BaTiO_3$ (6.02 g cm^{-3}).[17] The value plotted is an average of the green density measured with three specimens.

3. Results

3.1. Rheological measurements

Plots of viscosity as a function of shear rate show shear thinning behaviour (Fig. 1 and 2.). At pH 10, suspensions without polyelectrolyte and containing 1 wt% DP6 display the highest viscosity values, and with 1 wt% Dispex A40, the lowest (Fig. 1). The only difference from the behaviour of the suspension at lower polyelectrolyte concentration (see Fig. 7 in Ref.1) is the low viscosity achieved when 1 wt% of DPX-1 is used.

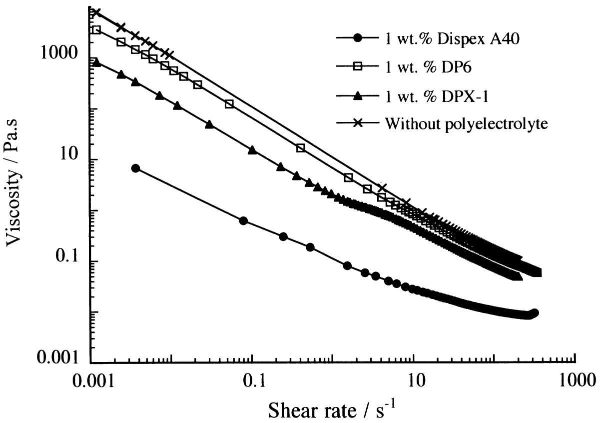

Fig. 1. Effect of 1 wt% concentration of polyelectrolytes on the viscosity of 20 vol% suspensions at pH 10.

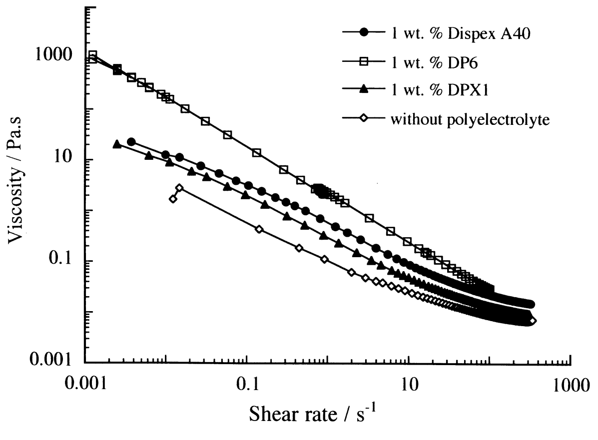

Fig. 2. Effect of 1 wt% concentration of polyelectrolytes on the viscosity of 20 vol% suspensions at pH 4.

At pH 4 (Fig. 2) high viscosity is observed with Dispex A40. The addition of DPX-1 and DP6 increases the viscosity (in this order), and the only difference from values obtained at low concentrations (Fig. 8. in Ref.1) is the higher viscosity of the suspension with cationic polymers when compared to the suspension without polyelectrolytes. It can be observed that the viscosity curve obtained for the suspension without polyelectrolytes at pH 4 is very similar to that of Dispex A40 at pH 10.

These effects can be seen also with the Real Yield Stress values at pH 10 (Fig. 3.) and at pH 4 (Fig. 4). At pH 10, 0.1 wt% of Dispex A40 reduces sharply the yield stress of the suspension, which is kept at almost 0 values with increasing concentrations (Fig. 3). Small amounts of DP6 produce a minimum in the yield stress, which increases again at higher concentrations. A second minimum is attained at around 1 wt%. Additions of DPX-1 produce a continuous decrease in yield stress, to a minimum at 1 wt%. Increasing concentrations increase further the yield stress. The yield stress values obtained with the cationic polyelectrolyes are not as low as those obtained with Dispex A40 at any case.

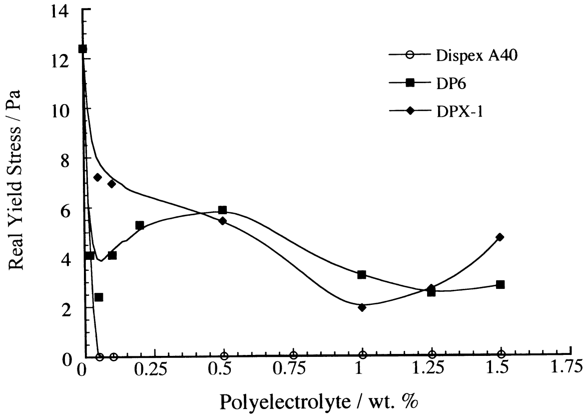

Fig. 3. Effect of polyelectrolyte concentration on the real yield stress of a 20 vol% suspension at pH 10.

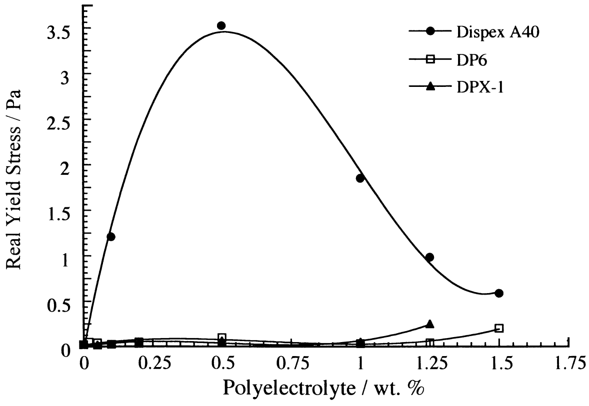

Fig. 4. Effect of polyelectrolyte concentration on the real yield stress of a 20 vol% suspension at pH 4.

At low pH, addition of Dispex A40 produces a maximum on the yield stress at concentrations of 0.5 wt%, with decreasing values for higher concentrations (Fig. 4). Both cationic polymers behave similarly, destabilising slightly the suspension as their concentration increases with respect to the suspension with no polyelectrolytes (Fig. 4).

3.2. ζ-*Potential measurements*

Fig. 5. shows that at pH 10, very small amounts of Dispex A40 (0.1 wt%) are required to provide the surface with a ζ-potential value of -50 mV. The ζ-potential the increases slightly to -60 for 0.4 wt%. Only 0.1 wt% of DP6 is required to give a plateau at $+65$ mV, and 0.05 wt% for DPX-1 for a plateau at $+35$ mV. Fig. 6 shows that at pH 4, 0.1 wt% of Dispex A40 is necessary for a plateau at -18 mV and 0.05% of each cationic polyelectrolyte is necessary for a similar charge of $\sim$60 mV.

These results obtained with suspensions of very low solids loading (0.05 vol%) seem to indicate that the ζ-potential values do not increase further with increasing concentrations of polyelectrolyte. Few experiments were

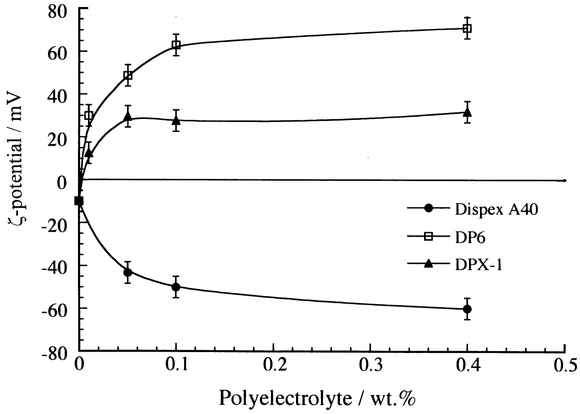

Fig. 5. Effect of polyelectrolyte concentration on the ζ-potential of a 0.05 vol% suspension at pH 10.

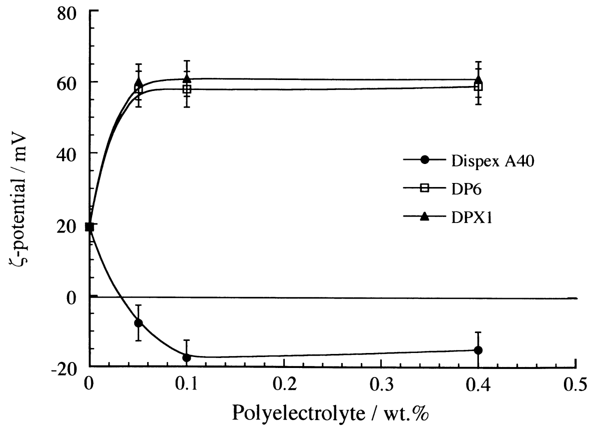

Fig. 6. Effect of polyelectrolyte concentration on the ζ-potential of a 0.05 vol% suspension at pH 4.

repeated with the supernatant after centrifuging the high solids suspension used for rheological measurements (i.e. 20 vol%). ζ-potential values obtained with concentrated suspensions and 0.1 wt% of polyelectrolytes were reported and commented in Ref. 1. With 0.4 wt%, the curves were practically coincident with those shown in Figs. 3, 4 and 5 of Ref. 1. Using 1 wt% of each polyelectrolyte, the results are as follows: no changes were found for Dispex A40, as compared with the results in Fig. 1, with the diluted suspensions; however, some differences were found with the cationics: ζ-potential was now sligthly lower with DP6 (~45 mV) and slightly higher than before with DPX-1 (~50 mV). These values are consistent with the variation of yield stress observed in Fig. 1.

3.3. Slip-casting green densities

Suspensions for slip casting were prepared with 0.1 wt% Dispex A40 at pH 10. With DP6 and DPX-1, the minimum yield stress values were obtained at pH 4, but they were not at any moment lower than those of the suspension without polyelectrolytes. Some specimens were cast at pH 4 with and without these polyelectrolytes. The polyelectrolyte concentrations used was also 0.1 wt% DP6 and DPX-1. The maximum solids concentration was considered the highest concentration before a sharp increase in viscosity is produced, and was 30 vol% with the anionic Dispex A40, and 20 vol% with the cationics and without polyelectrolytes at pH 4. Higher solids concentration limit (40–45 vol%) was found with a submicron $BaTiO_3$ powder and 0.1 wt% Dispex A40.[18]

The green densities calculated under the conditions described before are shown in Table 1. The highest values were obtained with 0.1 wt% Dispex A40 at pH 10 (56.5%). At pH 4 with DPX-1 and without polyelectrolytes only ~42% of the theoretical density was attained, and ~39% with DP6.

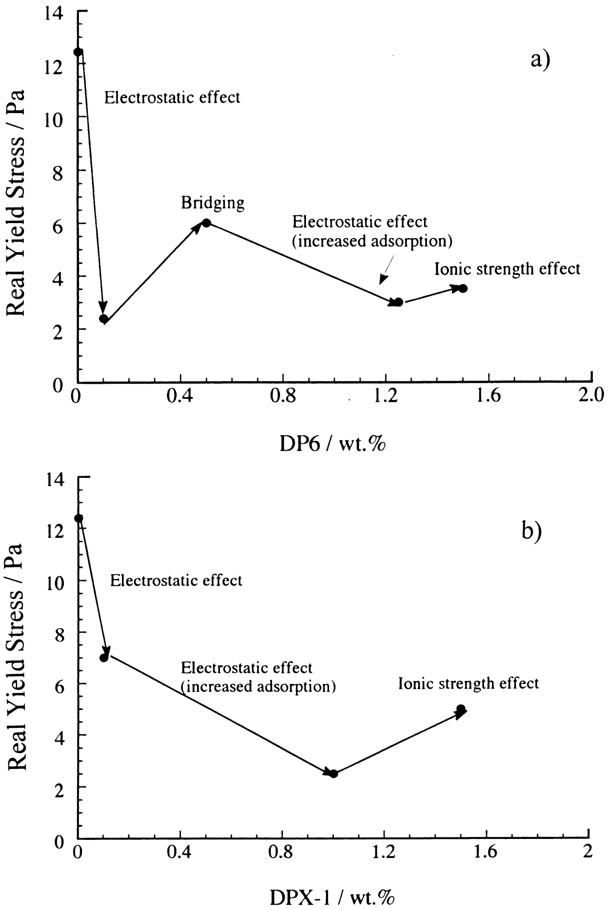

Fig. 7. Schematic representation of the effect of additions of (a) DP6 and (b) DPX-1 on the stability of barium titanate suspensions (20 vol%) at pH 10, based on the yield stress values from Fig. 5.

4. Discussion

4.1. Polyelectrolyte additions at pH 10

At high pH, increasing concentrations of Dispex A40 above a critical concentration of 0.1 wt% do not

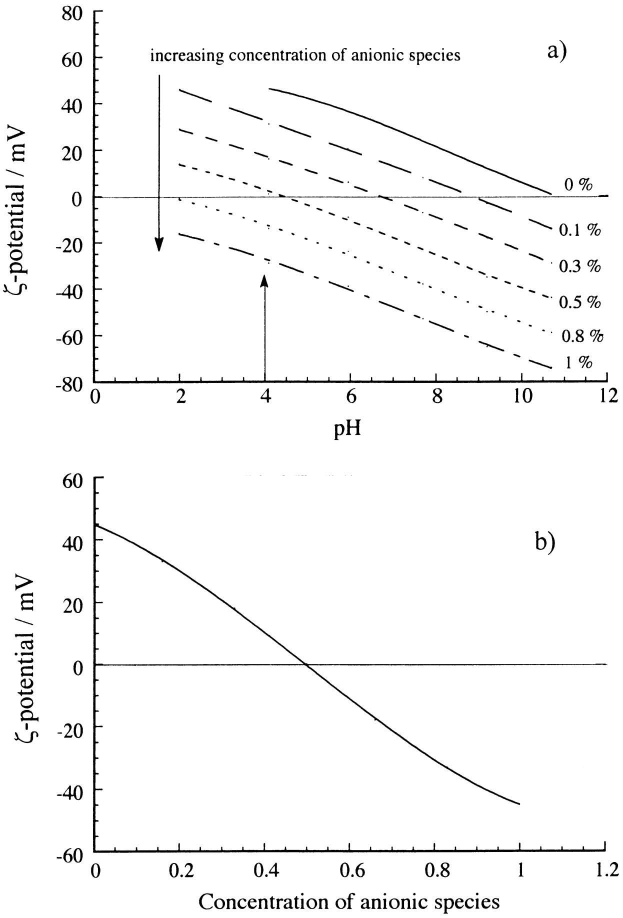

Fig. 8. (a) Schematic representation of the effect of increasing concentration of anionic species on the ζ-potential of $BaTiO_3$ when specific adsorption occurs; (b) Schematic representation of the change on the ζ-potential at pH 4 for the situation in (a).

Table 1
Green densities obtained by slip-casting

	Dispex A40 (0.1 wt%) 30 vol% solids	DP6 (0.1 wt%) 20 vol% solids	DPX-1 (0.1 wt%) 20 vol% solids)	No polyelectrolytes (20 vol% solids)
pH4	–	39.8	41.5	42.3
pH10	56.5	–	–	–

improve further the stability of the suspension: the high solids content suspension has low viscosity (Fig. 1) and low yield stress values for polymer concentrations (0.1 wt% (Figs. 1 and 3). This behaviour could be directly related to the electrical contribution of the adsorbed polymer to the deflocculation mechanism, and once a ζ-potential value >45 mV is reached (Fig. 5) an electrostatic force strong enough to prevent flocculation is created.

When low concentrations of the cationic polyelectrolyte DP6 and DPX-1 are added at pH 10, the viscosity (Fig. 1) and yield stress of the suspension are only slightly reduced with respect to the initial suspension (Fig. 3). DPX-1 has a significant effect lowering the viscosity and yield stress at a concentration of 1 wt% (Figs. 1 and 3) reasonably assumed to be due to adsorption of positively charged polymer molecules. Comparison between the behaviour of the DP6 and the related low molecular weight DPX-1 might be useful to distinguish between effects due to the electrical charge (qualitatively similar for both of them) and to the length of the chain: the slight decrease in yield stress at low concentrations (0.1–0.2 wt%) was observed in both cases (Fig. 3) and can be correlated to the ζ-potential values ($\sim$55 mV for DP6 and 38 mV for DPX-1) and is due therefore to adsorption of the positively charged polymer on the $BaTiO_3$ particle surface. These values can be responsible for some repulsion, as compared with the system without polyelectrolyte additions at that pH, which corresponds to the IEP.[16]

A maximum in yield stress was found with DP6 at 0.5 wt% concentrations, but not with DPX-1 (Fig. 3). This may be related to the chain length, since the long chain cationic polymer DP6 has a great tendency to bridging. This mechanism would not available for the short chain polymer DPX-1, and the yield stress of the suspension decreases with concentrations of this polymer up to 1 wt%.

The decrease in yield stress values with increasing concentration of these cationic polyelectrolytes is accompanied by higher ζ-potential values, and is therefore related to higher degree of adsorption. Results obtained with low solids concentration suspensions (0.03 vol%, Fig. 5) point towards a plateau of adsorption with 0.1 wt% of DP6 and 0.05 wt% with DPX-1. However, ζ-potential values measured in the supernatant after centrifuging the high solids concentration suspensions with 1 wt% of these polyelectrolytes (+45 mV DP6 and +50 mV DPX-1) are more related to the rheological behaviour found. It is known that large concentrations of polymer can stabilise a system that was initially flocculated by bridging, through an effect involving adsorption of more polymer at the particle surfaces[5]. When a polymer has a lower molecular weight and does not cover completely the opposite charged surface, restabilisation of the flocculated system is possible when an excess of polymer is used, by simply electrical repulsion between particles that are now fully coated and uniformly charged.[5] These two cases could be applicable to DP6 and DPX-1, respectively, to explain the decrease in yield stress observed for concentrations higher than 0.5 wt%.

However, the relative stabilisation observed with high concentrations of these polymers at pH 10 does not reach the level attained with Dispex A40. As was discussed in Part I,[1] this is not well understood, because ζ-potential values are similar in both cases. It is possible that some degree of bridging flocculation is still important with the high molecular weight polymer. The effect of additions of the cationic polymers tried at pH 10 is summarised in Fig. 7, which shows schematically the effects involved, based on the values of the yield stress obtained.

4.2. Polyelectrolyte additions at pH 4

At pH 4, $BaTiO_3$ particles in the aqueous suspension without polyelectrolytes have high ζ-potentials,[16] and the suspension has low viscosity and Real Yield Stress values[16] (Figs. 2 and 4).

At pH 4, increasing concentrations of Dispex A40 move the IEP towards lower values, as indicated schematically in Fig. 8 for anionic species adsorption in general. At a fixed pH (pH4), the ζ-potential as a function of concentration of polymer would be given by a curve similar to the situation shown in Fig. 8(b). This would be due to the specific adsorption of the polymer at the surface of the particles in the concentrated suspensions. A maximum yield stress with a concentration of 0.5 wt% was observed here, corresponding to ζ-potential values close to 0. The adsorption of Dispex A40 on the surface of positively charged particles may be at a maximum, by attraction between residual negative charges of the polymer chain and particles, which are positively charged. Experimental evidence can be found in the literature.[12] It seems then clear that the maximum in the yield stress could correspond then to the zero ζ-potential value. A decrease at higher concentrations of polymer could be explained as a progressive increase of negative potentials beyond this point as polymer is added, as it is shown schematically in Fig. 8.

At pH 4, increasing concentrations of the cationic polymers have only the effect of a small increase in yield stress and viscosity (Figs. 2 and 4), as compared with the suspension without polyelectrolytes. Although with diluted suspensions, an increase in ζ-potential values as compared with the suspension without polyelectrolytes is observed, the ζ-potential values found with concentrated suspensions are very similar to those of the suspension without polyelectrolytes.[1] This fact added to the observation of no decrease in yield stress and viscosity (Figs. 2 and 4) seems to indicate that no stabilisation due to adsorbed polymer is present at any concentration of DP6 and DPX-1. It seems that the only effect of these cationic polyelectrolytes in solution at pH 4 is due to an effect of the free polymer. The small increase in yield stress and viscosity observed is due to the higher ionic strength. Depletion flocculation might contribute too to destabilisation.

4.3. Stability diagrams

Stability maps plotting pH against polyelectrolyte concentration were constructed on the basis of the real yield stress values (the minimum shear stress required for the suspension to begin flow). The criterion applied to consider that the suspension was "stable" (deflocculated) for the construction of stability maps was real yield stress value < 0.05 Pa. The stability map for Dispex A40 (Fig. 9) shows a large area of stability starting at very low concentrations of Dispex A40 (0.05 wt%) at alkaline pH. Higher concentrations of this polyelectrolyte (> 0.4 wt%) are required as pH moves down to 6. Dispex A40 has been found very efficient imparting stability to the system at pH > 6, provided that concentration of Dispex A40 is higher than 0.5 wt%. At that pH, it is possible that the slipping plane is shifted outwards by the adsorbed polymer with still enough groups ionised, enhancing electrostatic repulsion. This type of stabilisation is not possible at lower pH, where the electrical charge is not enough. This diagram is very similar to that obtained for PAA and Al_2O_3[6,7] and for PMAA with $BaTiO_3$.[13]

Although some differences were found between both cationic polymers, the stability diagram constructed with the criterion explained above (Fig. 10.) is similar for both. This way, suspensions can be considered "stable" only in a small area at pH < 4 up to 0.15 wt% of these cationic polyelectrolytes, although yield stress values found under these conditions were slightly higher than those for the suspension without polyelectrolytes. The addition of those cationic polymers is not advantageous for the system because at those low pH values the viscosity and yield stress of the suspension were already low. Although they are able to decrease the yield stress at pH 10, the yield stress and viscosity values are still of importance at that pH, and therefore there is not a stability region in that area.

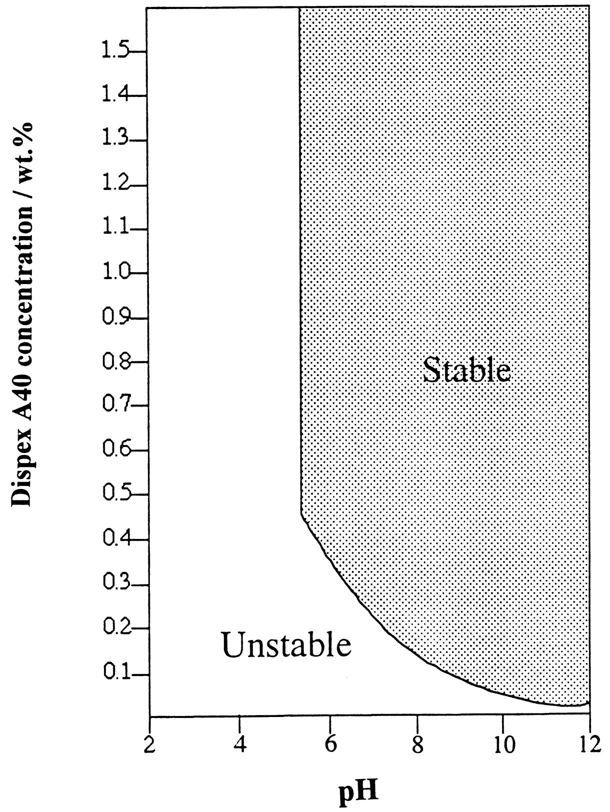

Fig. 9. Stability diagrams for the anionic Dispex A40.

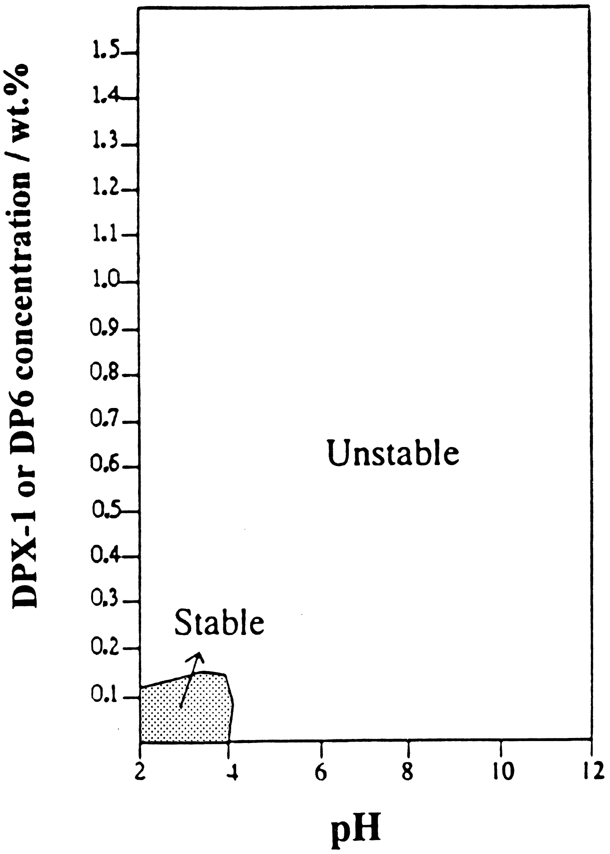

Fig. 10. Stability diagrams for the cationics DP6 and DPX-1.

4.4. Green densities

Green density values obtained here by slip casting suspension with Dispex A40 at pH 10 (56.5%) is very similar to those reported for $BaTiO_3$ suspensions with PAA at pH 10.5.[12] As it was discussed in Ref. 1 with respect to the sediment density results, it is not well understood why green density values obtained at pH 4 are not as high as those obtained with Dispex A40 at pH 10 since the suspensions have comparable viscosity and yield stress. With respect to the cationic polyelectrolytes, it is known that adsorption of these polymers is at a minimum at $pH < 4$. Therefore, results seem to support the hypothesis that the electrical charge is not enough and some additional polymeric contribution would be required for full deflocculation, as previously discussed.[1]

5. Conclusions

The short chain length anionic ammonium polyelectrolyte Dispex A40, is a very effective deflocculating agent for aqueous suspensions of $BaTiO_3$ powders at alkaline pH through an electrostatic mechanism. At these pH values, most of the carboxylic groups are ionised, markedly increasing the repulsion term in the balance of forces of the system. For $pH > 9$, 0.1 wt% of polyelectrolyte is enough to achieve slip cast green densities of the order of 56.5% of theoretical. 30 vol% could be used, while maintaining adequately low viscosities and yield stresses. At pH values between 6 and 8, deflocculation can be achieved provided that higher concentrations of Dispex A40 are used (> 0.4 wt%). At acidic pH (pH 4), the anionic polymer is still adsorbed, but now reduces the electrical potential at the particle surface, and the system flocculates. Maximum flocculation is found with 0.5 wt% of Dispex A40 at pH 4, corresponding to the IEP for that concentration. It is expected that green bodies obtained with Dispex A40 would leave a clean burn out, and no harmful residues that could affect the electrical properties of the final ceramic will remain.

Cationic polymers are able to decrease the yield stress of the suspension at high pH, but only at the high concentrations of 1 wt%. Concentrations of 1 wt% can induce relative stabilisation by an electrostatic effect due to the larger extent of adsorption. However, yield stresses and viscosities are still high and the system is not fully deflocculated. ζ-potential electrokinetic values obtained are difficult to interpret. At low pH, when both polymer and particle surface are positively charged, no stabilisation is observed because adsorption of the ionised polymer on the surface of particles with the same electrical charge has been reduced or eliminated. Green densities obtained at low pH with 0.1 wt% of DP6 and with 1 wt% DPX-1 are still low, and of the same values as those obtained from suspensions without polyelectrolytes at pH 4. However, it is not well understood why green density values for the suspension without polyelectrolytes are not as high as those values obtained with Dispex A40 at pH 10, while the suspensions had similar viscosity and yield stress.

From this work, we can conclude that research for effective dispersants for $BaTiO_3$ should focus on a wider range of anionic polyelectrolytes. COOH groups have been found to be suitable for the deflocculation of this aqueous system.

Acknowledgements

This work was supported by the Commission of the European Communities by a Human Capital and Mobility Fellowship (Contract No. ERBCHB1CT941697).

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