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The isoelectric point of $BaTiO_3$

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Abstract

The value of the isoelectric point (IEP) of $BaTiO_3$ is highly significant for the development of a fully rational basis for the successful processing of $BaTiO_3$ powder by aqueous routes. We report here experimental evidence that the true IEP value for $BaTiO_3$ is in the neutral pH range (6–7). However, Ba^{2+} ions are also selectively adsorbed at $BaTiO_3$ particle surfaces, raising the ζ-potential; IEP values greater than pH 7 can occur when the concentration of Ba^{2+} in the aqueous phase is high. Studies of the effects of Ba^{2+} and CO_3^{2-} additions on the ζ-potential of $BaTiO_3$ and on the rheology of aqueous suspensions, indicate that the reason for the wide range of ζ-potential and IEP values found for $BaTiO_3$ is in large measure the presence of impurity $BaCO_3$ in the $BaTiO_3$ powders used. Fully dehydrated $BaTiO_3$ powder has a low IEP value (~4), which slowly rises on ageing in water. The IEP appears not to be influenced by Nb_2O_5 doping at the levels normally used. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Isoelectric point; Suspensions; $BaTiO_3$; Perovskites

1. Introduction

The thin dielectric layers for multilayer capacitors are prepared by tape-casting of well dispersed barium titanate ($BaTiO_3$) powder slips. The suspending media have traditionally been organic solvents, such as toluene, tretrahydrofuran or azeotropic mixtures of alcohols [1]. A typical tape-casting formulation includes a plastic binder and additives such as dispersants and plasticisers. The burn off behaviour of these additives and that of the dispersion medium is an important processing factor.

Organic solvents have advantages compared to water in that they offer a wide range of vapour pressures and thus evaporation rates [2]. However, for economic and environmental reasons, there is now a move away from the use of organic solvents towards water, which has lead to a considerable interest in developing aqueous based tape-casting systems [3]. It has been possible to obtain high tape-casting rates with alumina powders by using high solids concentration slips and heating from underneath the tape [4], and the succesful preparation of $BaTiO_3$ dielectric layers from water based suspensions has also been reported [5]. However, the $BaTiO_3$ surface chemistry controlling the dispersion of $BaTiO_3$ powders in water is not fully understood, and the rational development of tape-casting formulations of controlled rheology is hindered.

It is clear that the optimization of the slip rheology and in particular, the deagglomeration of the $BaTiO_3$ particles are critical steps for preventing the development of microstructural heterogeneities in the sintered dielectric. The isoelectric point (IEP) of the powder is for both issues an important parameter, since particle flocculation is expected at that pH value, where Van der Waals forces predominate, while deflocculation occurs at pH values removed from it. Ceramic oxides generally have a well defined and characteristic IEP value, although some variations in the starting material or experimental conditions can lead a spread of values ranging ±2 units of pH [6,7]. However, the IEP values for $BaTiO_3$ reported in the literature differ widely (Table 1): an unusually broad range is covered from acidic (pH 4.3, 4.7) [8,9] to alkaline (pH ~ 10) [10–13]. Furthermore, there may be no IEP as is the case of acoustophoretic measurements [14,15]. The relatively new acoustophoretic technique is based on the measurement of a colloidal vibration potential [16]: its main advantage is that the ζ-potential can be measured on

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Table 1
Reported IEP values for $BaTiO_3$

IEP	Method	Ba/Ti ratio	Reference
4.3	Electrophoresis	0.991	[8]
4.7	Electrophoresis	1.0	[9]
6	Electrophoresis	1.0	[17]
7.7	Electrophoresis	0.99	[18]
8.5	Electrophoresis	1.07, –	[18,19]
9.9	Electrophoresis	1.1	[10–12]
10.2	Electrophoresis	–	[13]
None	Acoustophoresis	1.028	[14,15]

high solids concentration suspensions, as would be used for slip or tape-casting. The electrophoresis method, in marked contrast, requires the use of extremely dilute suspensions, and in order to predict slip behaviour, results need to be extrapolated to high solids concentration suspensions. It would be expected, however, that the IEP value, which should reflect only the solid–liquid interfacial chemistry, should be independent of the technique used to measure it.

Because of the lack of agreement in the IEP values for $BaTiO_3$, studies of the ζ-potential of $BaTiO_3$ and of the change of IEP with dispersion conditions, were considered necessary, if improved understanding of the rheology of $BaTiO_3$ aquoeus slips was to be obtained.

We report in this paper a definitive value for the IEP of $BaTiO_3$ in water, and suggest reasons why different values have been measured. The published literature concerning the dispersion behaviour of $BaTiO_3$ powders in water has been reviewed in a previous publication [17], which also included some preliminary finding of ζ-potential measurements on one of the $BaTiO_3$ powders used here.

2. Experimental

2.1. Materials

The materials used in this study are listed in Table 2. A and B were commercial powders: A was produced by solid state reaction between $BaCO_3$ and TiO_2 and B by the normal mixed oxalate decomposition method. Both powders were slightly titanium oxide rich. Powder A was a Nb-doped powder and B undoped. Powder A contained ~0.5% of SrO. Powder C was an undoped powder produced in the Department of Materials by a mixed oxalate route using high purity (AnalaR grade) reagents.

2.2. Experimental techniques

$BaTiO_3$ powders were weighed into polypropylene containers and deionised water added. The slips were thoroughly dispersed using an ultrasonic probe (Lucas Dawes Soniprobe, Solihull, UK) operated at full power for 5 min. pH adjustments were carried out using dilute aqueous AnalaR grade HCl or KOH, and values measured using a standard glass electrode pH meter. Aqueous potassium chloride solutions was used when control of ionic strength was required.

The ζ-potential of the $BaTiO_3$ particles were measured using a standard electrophoresis equipment (Zetasizer 4, Malvern Instruments, Malvern, UK). Very dilute suspensions (0.05 volume % solid) were prepared with deionised water. Ionic strengths were normally maintained constant by using 1 mmol dm^{-3} KCl, except in the cases where higher concentrations of barium chloride were being used to assess the influence of Ba^{2+} concentration behaviour. ζ-potentials were also measured using powders dispersed in the aqueous medium obtained from more concentrated suspensions (containing up to 20 vol %) of $BaTiO_3$. For this purpose, selected amounts of $BaTiO_3$ powder were equilibrated in deionized water, and the slip then centrifuged until the liquid phase was clear. Calibration of the instrument was carried out using dilute suspensions of a standard latex known to have an IEP at -55 ± 5 mV. Each ζ-potential value recorded was the average of 10 measurements.

Shear stress sweeps were applied on 20 vol % slips with a controlled stress rheometer (Carri-med SCL500 Rheometer Systems, Dorking, UK), and a concentric cylinder system geometry. Samples were presheared for 2 min at maximum stress, and then allowed to rest for 2 min before the shear sweep was commenced. With this rheometer, the true yield stress can be determined, as well as the extrapolated yield stress for systems that approximate Bingham behaviour.

3. Results

3.1. Flow behaviour of $BaTiO_3$ aqueous slips

The systems were found to be shear thinning (pseudoplastic) with a yield stress value that varied with pH. The real yield stress (the minimum stress necessary for the system to begin flow) was recorded. This value is related to the state of deflocculation of the system, and Hunter [20] has provided a model relating it to the elastic properties and strength of the flocs. With A and B powders the higher yield stress values were obtained at pH ~ 11. For both powders the yield stress decreased at pH < 11 (Fig. 1), and for powder A the maximum was particularly sharp and strong at pH 11. At pH < 4 the yield stresses were very low, and the systems were almost Newtonian. These results show that it is possible to decrease the degree of flocculation of a concentrated aqueous $BaTiO_3$ slip by lowering the pH; the yield stress maxima seem to indicate that the system will have an IEP at pH~11.

Table 2
$BaTiO_3$ powders used

Powder	Manufacturer	Route	Mean particle size	TiO2/BaO ratio	Dopant
A	Transelco Ferro lot 219-3 (New York, USA), supplied by Beck Electronics (UK)	Solid state	1.5 μm	1.05	Nb_2O_5
B	TAM Ceramics (Niagara Falls, USA) HPB-MBB lot 10	Oxalate	0.5 μm	1.05	none
C	University of Leeds	Oxalate	10 μm	1.11	none

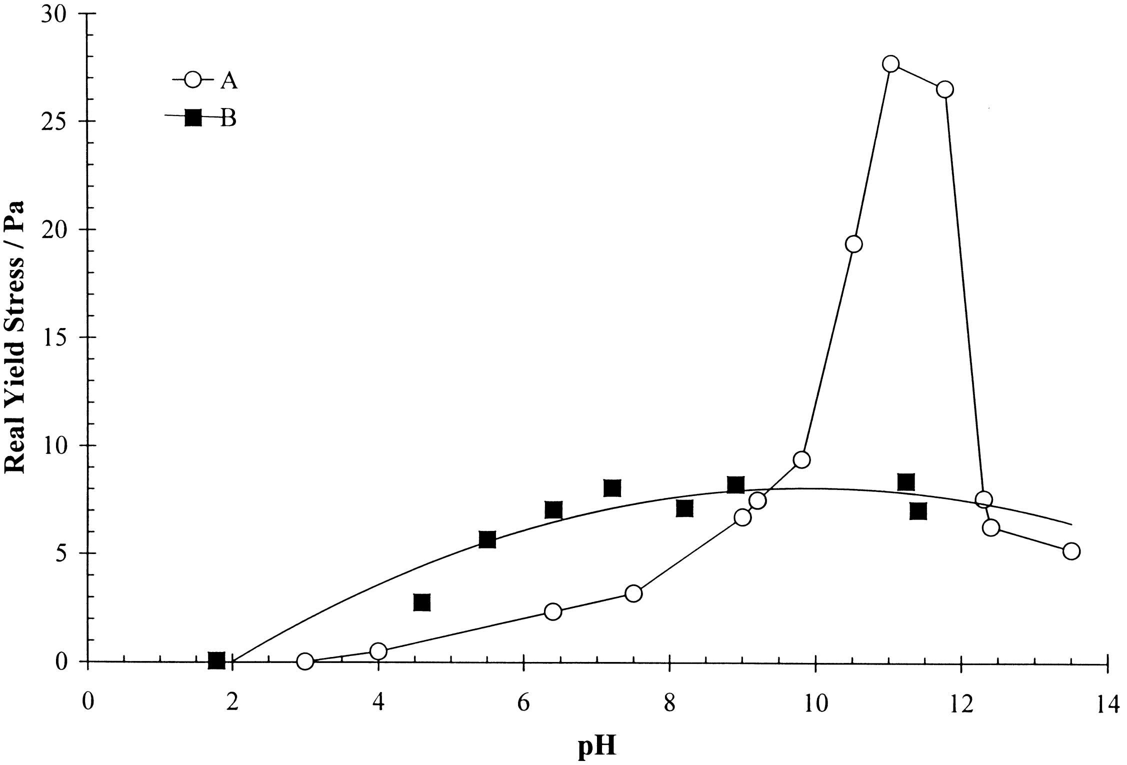

Fig. 1. Real yield stress of 20 vol % slips of powders A and B, as a function of pH.

3.2. ζ-Potential measurements

When electrophoretic measurements were carried out with diluted suspensions of powders A and B at constant ionic strength (0.05 vol % in 1 mmol dm^{-3} KCl) the IEP was at pH ~6.5 (Fig. 2), in apparent contradiction with the rheological data. However, when the measurements were repeated using the supernatant after centrifuging higher concentration slips, the ζ-potential curves were quite different, as shown in Fig. 3. Powder A had an IEP at pH 10 to 11, and the ζ-potential became increasingly positive as the pH decreased. This observation is more consistent with the rheological data, and is discussed in greater detail below. When electrophoretic measurements were made in a medium previously equilibrated with 10 vol % $BaTiO_3$, a lower IEP value (pH ~8–9) was obtained. This clearly indicates that the IEP is influenced strongly by the composition of the dispersing medium, which appears to change according to the solids concentration of the suspension in which the $BaTiO_3$ was first equilibrated. Similar trends were found with powder B, although no IEP was observed and the ζ-potential remained positive over the entire pH range (3–11) investigated (Figs. 2 and 3).

Fig. 4 shows the variation of the IEP observed for several solids conditions. It was found that the IEP increased with increasing solids concentration, and data could be approximated to a straight line. With the aim of clarifying this dependence of the IEP on $BaTiO_3$

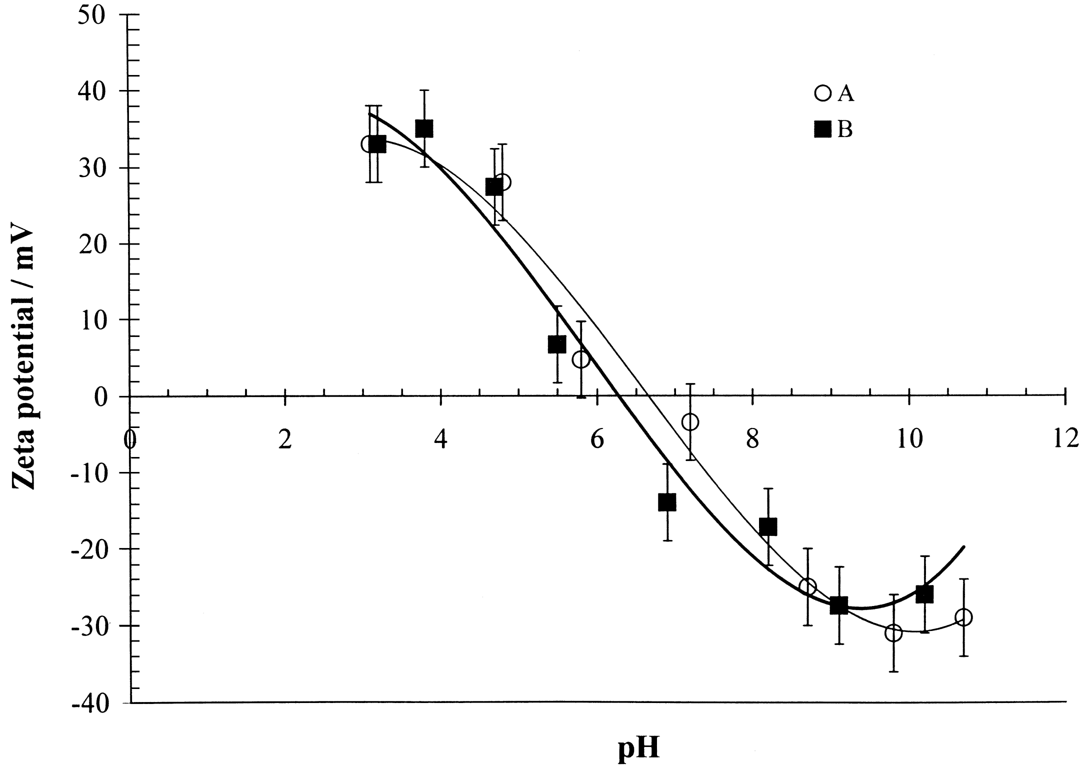

Fig. 2. ζ-Potential of 0.05 vol % suspensions of powders A and B in deionized water, as a function of pH.

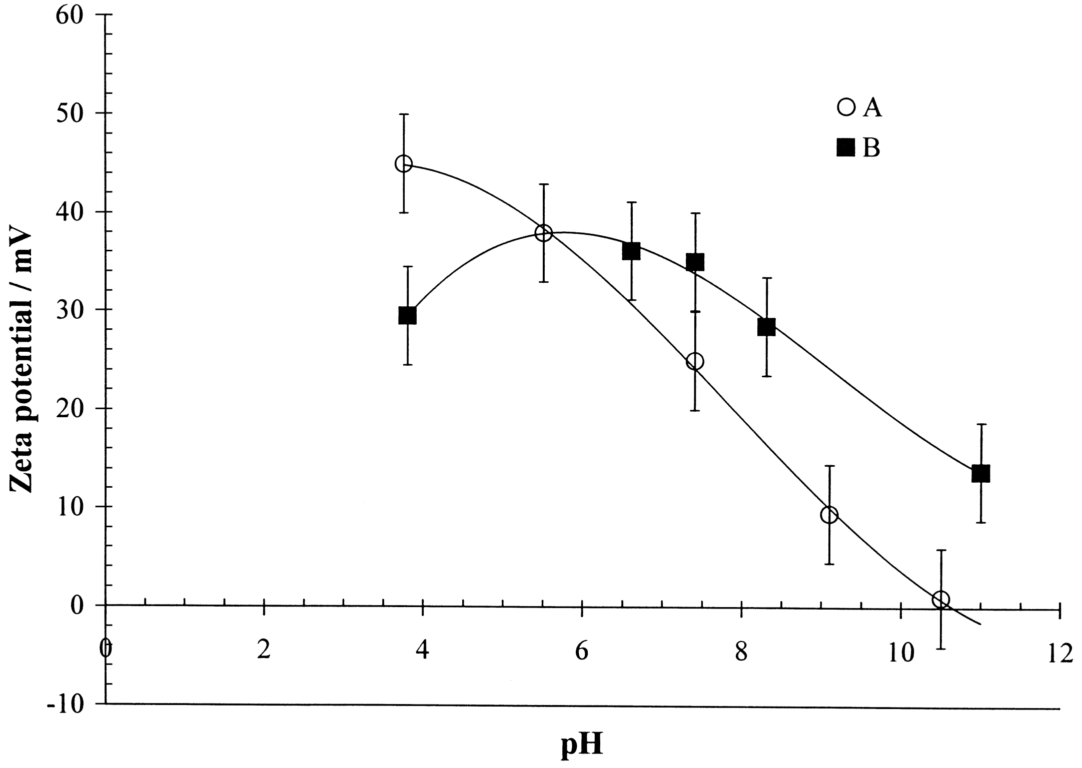

Fig. 3. ζ-Potential of powders A and B measured in the supernatant fluid obtained from a 20 vol % suspension of $BaTiO_3$, as a function of pH.

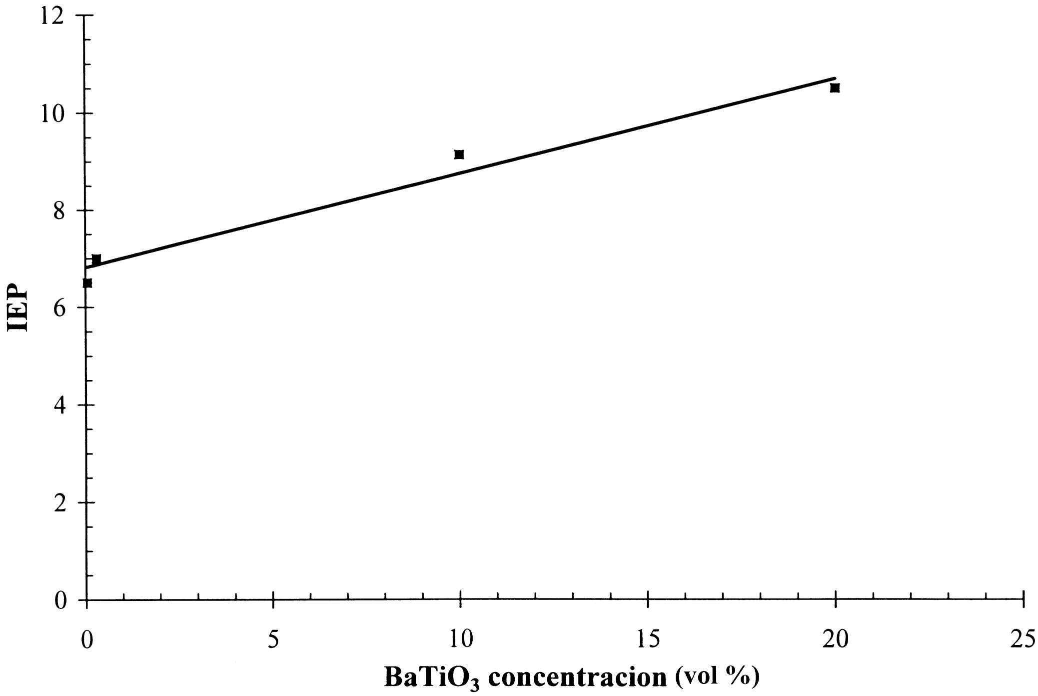

Fig. 4. IEP of powder A, as a function of the barium titanate slip concentration from which the supernatant fluid was obtained.

concentration in the slip, a series of experiments was carried out on $BaTiO_3$ powder suspensions in water containing a range of concentrations of Ba^{2+} and CO_3^{2-} ions by studying separately the effect of adding Ba^{2+} and CO_3^{2-} ions to the $BaTiO_3$ powder suspensions.

3.3. Ba^{2+} additions

Fig. 5 shows the effect of $BaCl_2$ on the ζ-potential of powder A, and the marked shift of the IEP towards higher pH values with increasing Ba^{2+} concentration (in these experiments no attempt was made to control ionic strength by addition of KCl). In the presence of 0.1 mmol dm^{-3} Ba^{2+}, the IEP was at pH~9, and the ζ-potential values at pH higher than the IEP were significantly less negative than those of suspensions without added Ba^{2+}. At higher concentrations of Ba^{2+}, an inflexion point developed at pH 9–10; there was no IEP, and the ζ-potential remained positive over the pH range 3–11.

Fig. 6 shows rheological data obtained using concentrated (20 vol %) $BaTiO_3$ slips. A sharp decrease in the real yield stress of the suspension with increasing concentrations of Ba^{2+} for $pH < 7$ is observed, and small values of yield stress (approximating to those of the suspension without Ba^{2+} additions) at $pH < 7$. Fig. 7 shows apparent viscosity at a shear rate of 20 s^{-1} as a function of Ba^{2+} concentrations, at pH 10 and pH 4. At pH 10, high concentrations of $BaCl_2$ decrease considerably the apparent viscosity appreciably. In contrast, at pH 4 increasing the Ba^{2+} concentration caused a small increase in apparent viscosity.

3.4. CO_3^{2-} additions

A study of the effect of carbonate ion concentration on ζ-potential was considered to be important because $BaCO_3$, which has appreciable solubility in water, is a common impurity in $BaTiO_3$ powders [21]. For this purpose, the ζ-potentials were measured on 0.05 vol % suspensions of $BaTiO_3$ powder A, with the addition of a range of volumes of aqueous Na_2CO_3 up to a concentration of 10 mmol dm^{-3}. Increasing the concentration of CO_3^{2-} automatically had the effect of increasing the pH, and it was therefore no necessary to further control the pH with aqueous KOH. It has been suggested in other studies [22,23] that the CO_3^{2-} concentration in deionised water exposed to normal laboratory atmospheres is ~0.01 mmol dm^{-3}. The presence of the added CO_3^{2-} did not influence significantly the ζ-potential of this $BaTiO_3$ powder in the pH range 8.5–11, which was almost constant at ~ −30 mV (Fig. 8).

3.5. Effects of heat treatment and ageing

The electrophoretic mobility of powder B was measured in the "as received state", and after heating in air for 12 h at 800°C. ζ-potential data for dilute suspensions of powder in 1 mmol dm^{-3} KCl are shown in Fig. 9.

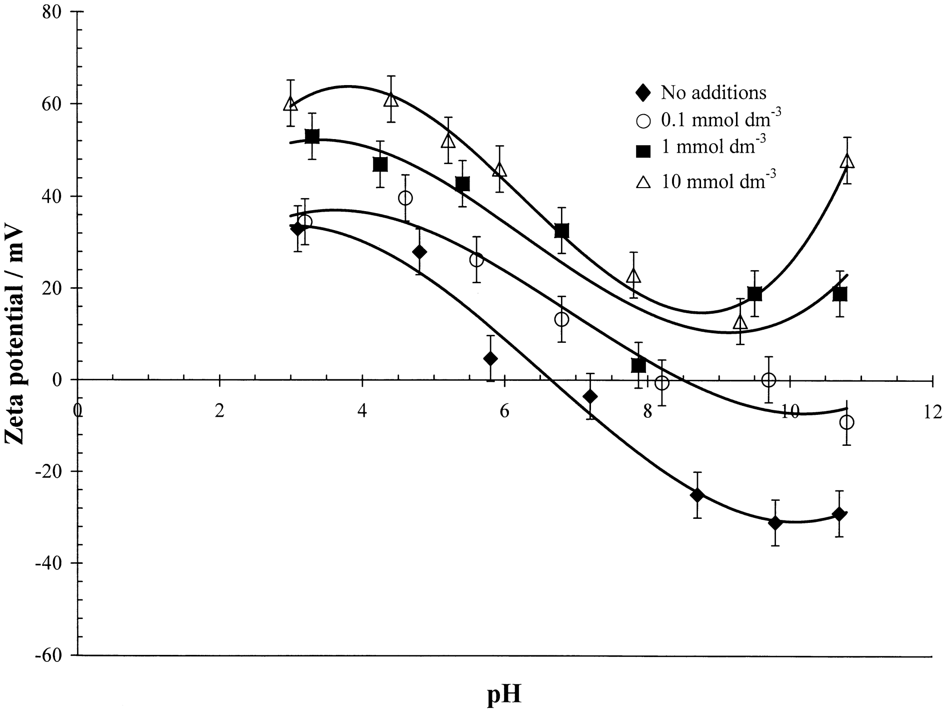

Fig. 5. Effect of adding Ba^{2+} on the ζ-potential of 0.05 solids vol % suspensions of $BaTiO_3$ powder A.

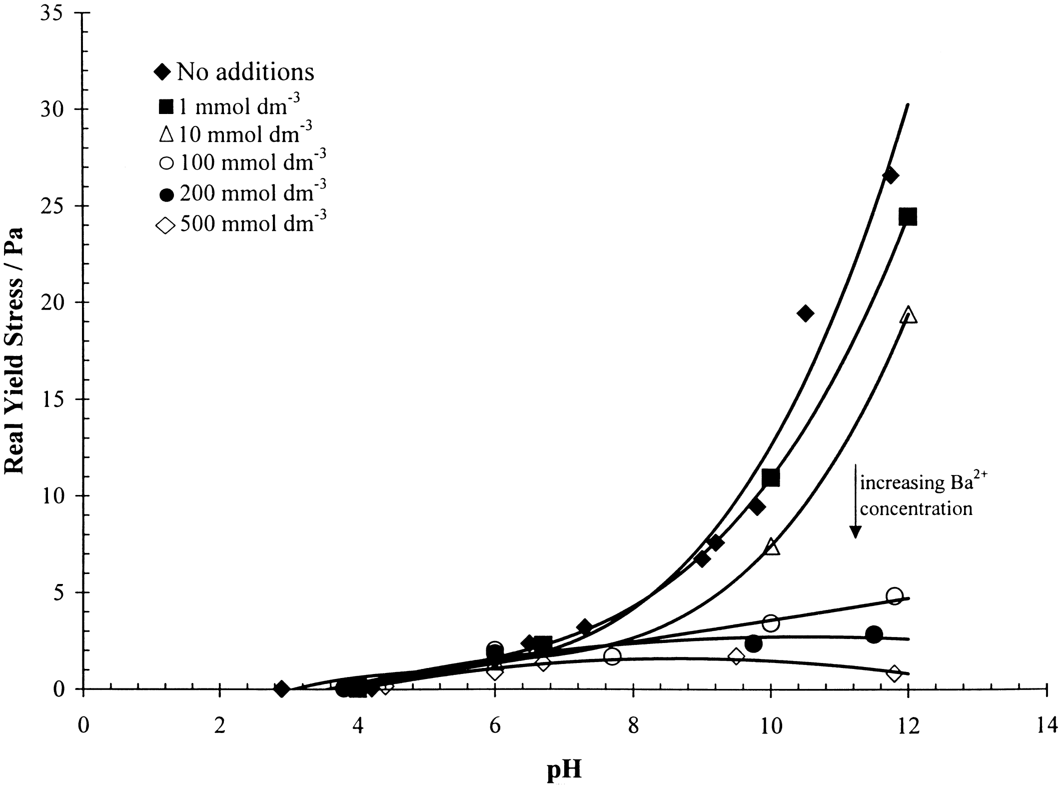

Fig. 6. Real yield stress of 20 vol % slips of $BaTiO_3$ powder A, as a function of pH, with $BaCl_2$ additions to 10 mmol dm^{-3}.

After calcination at 800°C there was a slight decrease in the IEP to pH ~5. The electrophoretic mobility of powder C immediately after calcination at 700°C corresponded to an IEP of pH 3–4, with a ζ-potential of only +10 mV at pH 3 (Fig. 10). Since the rehydration of the surface of dehydrated oxides has been reported to be slow [24], calcined powder was aged in contact with deionized water for 3 months, and the

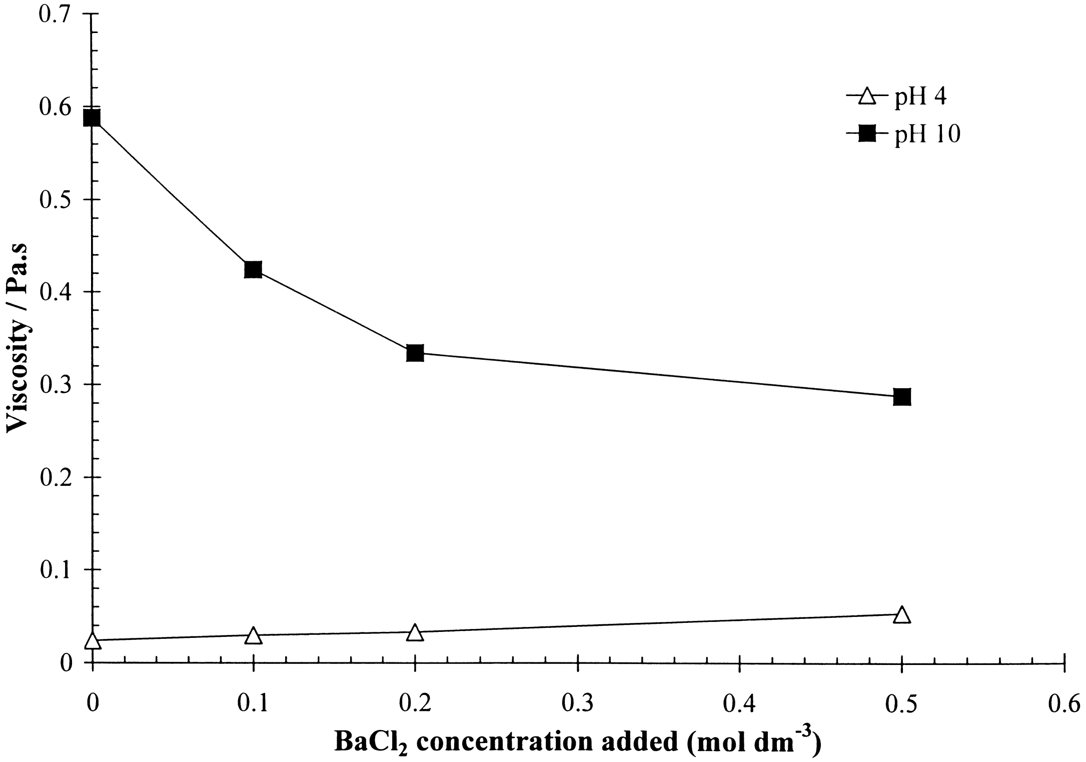

Fig. 7. Apparent viscosity at pH 4 and 10 of 20 vol % suspensions of powder A as a function of $BaCl_2$ concentration.

ζ-potential then redetermined. The rehydrated IEP value was at pH ~5.5, and did not change with further ageing (to a total of 6 months), suggesting that this was the equilibrium value.

4. Discussion

4.1. *Deflocculation of $BaTiO_3$ aqueous suspensions*

The IEP represents the pH value at which the charge at the Stern layer is zero, and the electrostatic repulsion between the double layer of the particles is eliminated. Under these conditions, Van der Waals forces (attractive) are the only contributions to the total potential energy of the system, and cause flocculation. High shear stresses are necessary to overcome the attraction forces between flocs and particles, and the suspension shows high viscosity. It is clear from the rheological data that the concentrated $BaTiO_3$ slips are deflocculated at low pH (Fig. 1). It is assumed that this is because of the high ζ-potential values (>30 mV) reached under acidic conditions (Fig. 3), and which in this case may simply reflect the protonation of the $BaTiO_3$ particle surfaces, and electro-stabilisation. On the other hand, an important contribution to the positive ζ-potential seems likely to be provided by the specific adsorption of Ba^{2+} ions. Whatever the origin of the positive potential, a strong electrostatic repulsion between the particles will prevail when the ionic strength is low, as predicted by the DLVO theory of colloid stability. On the basis of the ζ-potential values measured for the dilute suspensions (shown in Fig. 2), yield stress plotted as a function of pH would be expected to be fairly symmetrical curve with a maximum at the IEP (pH 6.5). The experimentally determined yield stress curve (Fig. 1) is very different from that predicted from the ζ-potential measurements, and suggests that the IEP must be nearer to pH 11.

In order to explain this lack of match between observed and expected rheological behaviour, it is necessary to consider the different mechanisms of surface potential development [25], which give rise to the ζ-potential values measured. Generally, *insoluble oxides* acquire a surface electrical potential through protonation or deprotonation of surface hydroxyl groups and H^+ and OH^- are the potential determining ions. The surface concentration of these groups depends in turn on the extent of surface hydrolysis. In the case of slightly *soluble inorganic salts* (AgI being the classic example [26]) the lattice forming ions are the major potential determining species. The case of $BaTiO_3$ is more complex. The results presented here show clearly that $BaTiO_3$ is behaving both like a simple insoluble oxide, and partially soluble inorganic salt. The ζ-potential is determined both by H^+ and Ba^{2+}. ζ-potential as a function of pBa (-log 10 [Ba^{2+}]) is shown in Fig. 11 for pH 4 and 10. The contribution made by Ba^{2+} to the

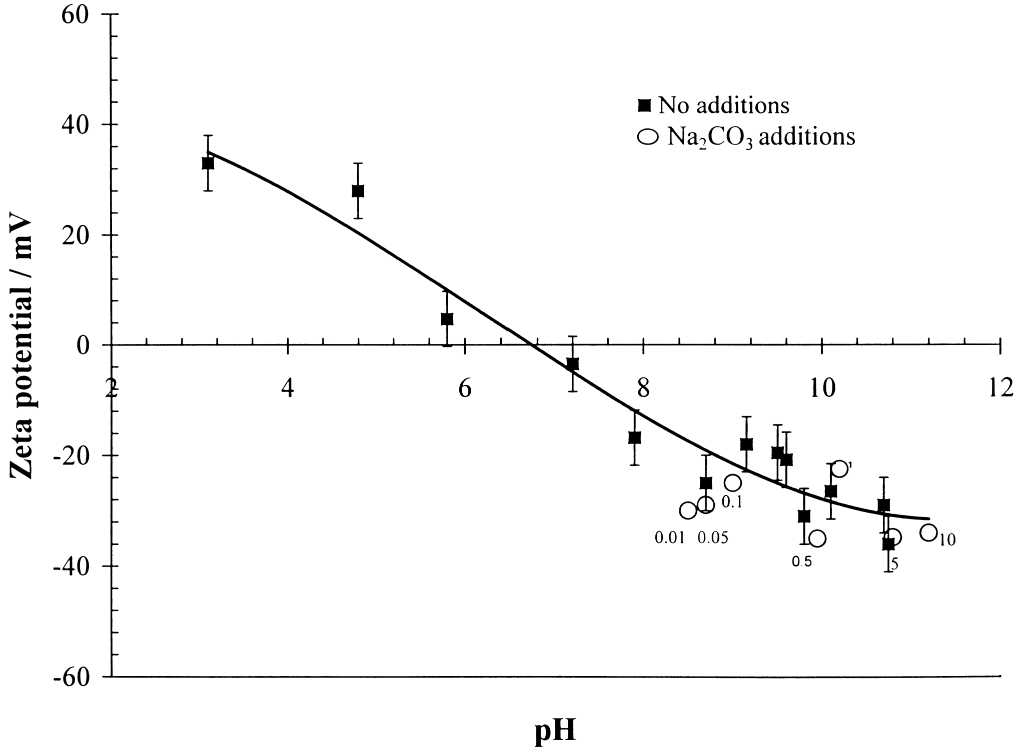

Fig. 8. ζ-Potential of 0.05 volume % suspensions of powder a as a function of pH, and in the presence of 0.01 to 10 mmol dm^{-3} sodium carbonate.

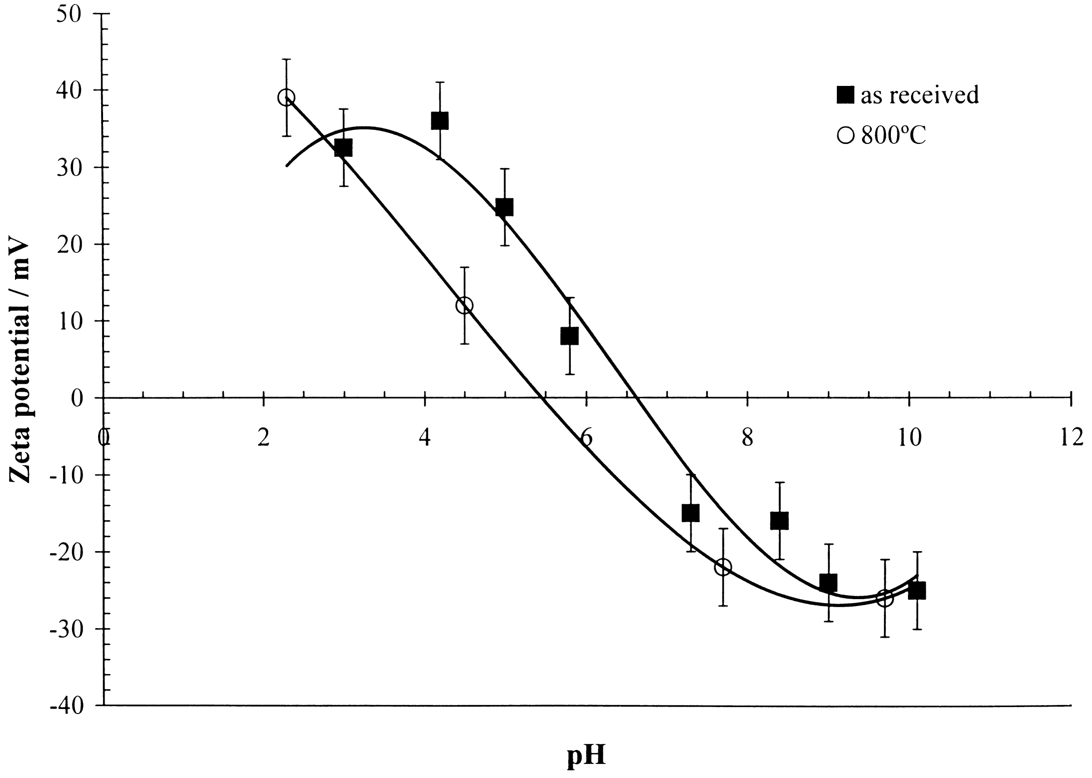

Fig. 9. Effect of a heat treatment (800°C, 12 h) on the ζ-potential of 0.05 vol % suspensions of powder B.

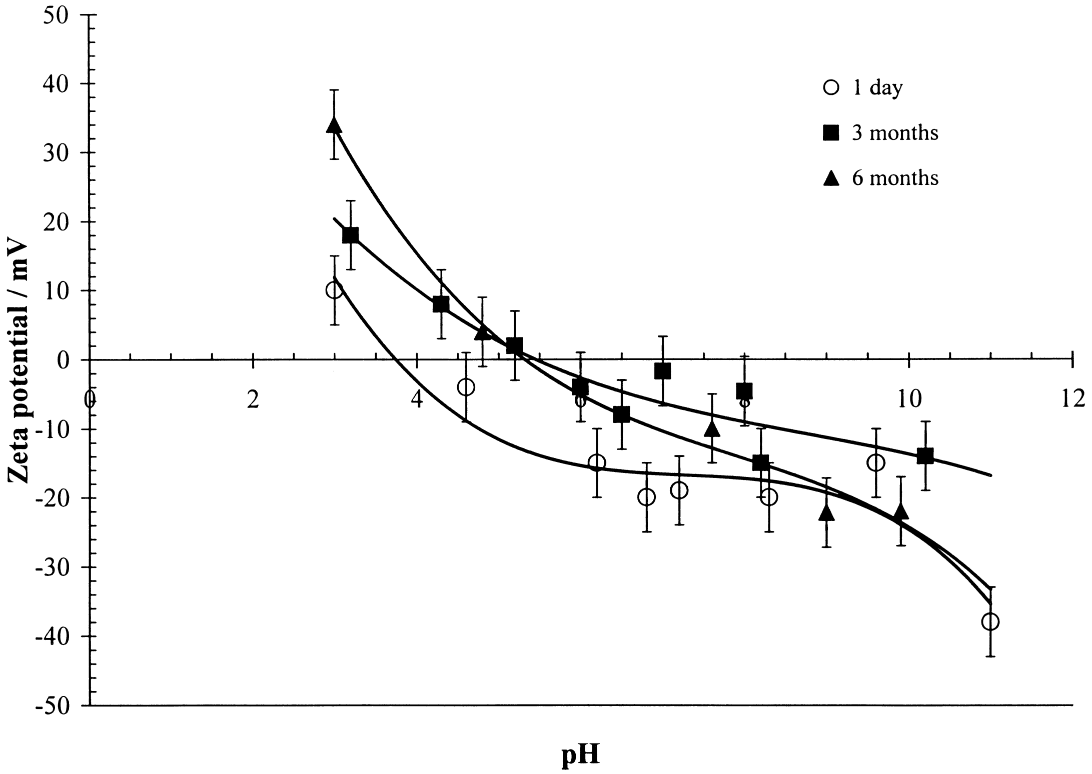

Fig. 10. ζ-Potential of 0.05 vol % suspensions of powder C calcined at 700°C and then aged for 1 day, 3 months and 6 months.

surface charge is considerable, and appears to be most marked at lower pH values.

There has been discussion about the origin of the Ba^{2+} ions in the aqueous phase of $BaTiO_3$ powder suspensions. Our recent work [27] has shown that the most important source is the hydrolysis of the $BaCO_3$ impurity present in commercial $BaTiO_3$ powders, and that the release of Ba^{2+} from the $BaTiO_3$ itself is probably relatively slight (in part because of the suppression of the process by the Ba^{2+} ions released by the more soluble $BaCO_3$).

Measurements made of the $BaCO_3$ content of a number of commercial and laboratory prepared $BaTiO_3$ powders suggest that 1–5% is probably a normal level, unless special preacutions have been taken [21]. Contamination by $BaCO_3$ is generally very hard to avoid because of its high thermodynamic stability with respect to $BaTiO_3$ [28]. $BaCO_3$ is significantly soluble in cold water (20 mg dm^{-3}) and like all carbonates, tends to become increasingly soluble as the pH is reduced [29]. The hydrolysis reaction for $BaCO_3$ can be written:

$$BaCO_{3(s)} + H_2O_{(l)} = Ba^{2+}_{(aq)} + HCO_3^- + OH^-_{(aq)} \qquad (1)$$

In the pH range 6.3–10.3 HCO_3^- is the predominant aqueous phase ion [23]. In the present study, the ability of Ba^{2+} ions to adsorb on the surface of $BaTiO_3$ particles to act as potential determining ions, and therefore able to control the rheology, has been tested and confirmed (Fig. 5). The presence of the $BaCO_3$ and its solubility, to provide a source of Ba^{2+} is the explanation for the lack of correlation between electrokinetic measurements made on suspensions of very low solids concentration (0.05 vol %, Fig. 2) and rheological measurements made on very high (20 vol %, Fig. 3) solids concentrations.

The relationship found between the ζ-potential values and the slip concentrations at which the powder were equilibrated can be explained on the basis of the different equilibrium concentrations of Ba^{2+} in the fluid medium. The apparent discrepancies between IEP and yield stress maxima are simple and direct consequence of the higher concentrations of impurity $BaCO_3$ available to the liquid phase, when a higher concentration of $BaTiO_3$ is used in the initial slip. For example, a $BaTiO_3$ powder containing 1% $BaCO_3$ will release 0.2 mmol dm^{-3} of Ba^{2+} into a 0.05 vol % suspension on adjustment of the pH to 4 by hydrochloric acid (giving complete dissolution of the carbonate). For the more concentrated $BaTiO_3$ slips used for rheological measurements (20 vol %) the concentration of Ba^{2+} would have been 80 mmol dm^{-3}. Under the conditions of temperature and time used for the measurements, equilibrium should be reached between Ba^{2+} in solution and Ba^{2+} adsorbed on the $BaTiO_3$ particle surface. An increase in $BaTiO_3$ (and hence $BaCO_3$) concentration results in an increased degree of Ba^{2+} adsorption, and

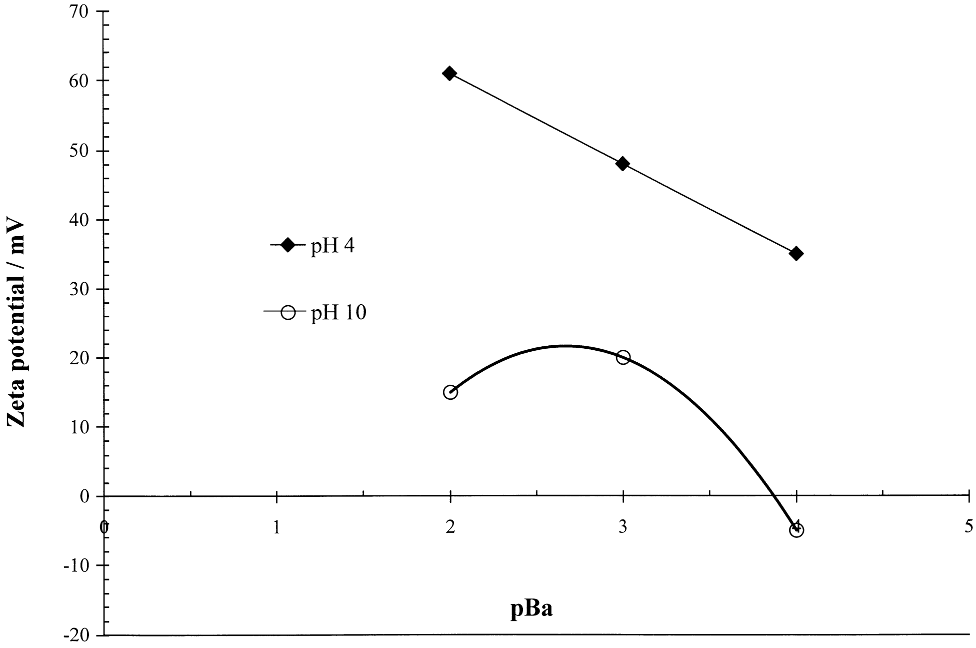

Fig. 11. Zeta potential of 0.05 volume % suspensions of powder A at pH4 and 10 as a function of pBa.

thus more positive ζ-potential values found for the more concentrated $BaTiO_3$ slips.

Because of the almost inevitable presence of the $BaCO_3$ impurity in the $BaTiO_3$ powder, the *true* IEP of $BaTiO_3$ can only be obtained by extrapotaltion to zero $BaCO_3$ concentration. Fig. 4 shows that the IEP of $BaTiO_3$ is 6.5, slightly higher than that of TiO_2 [6,7]. This is not surprising because the IEP is related to the arrangement of ions at a particle surface. The surface analyses of these $BaTiO_3$ powders have shown that they are slightly deficient in Ba, and the surfaces can therefore be considered chemically to be "TiO_2-like" [27,30].

The presence of varying amounts of $BaCO_3$ impurity in $BaTiO_3$ powder is therefore the most likely reason for the different IEP values reported for $BaTiO_3$, or the absence of an IEP and its replacement by an inflexion point when measuremets are made by acoustophoresis on slips of very high concentration (Table 1). The ζ-potential curves obtained here using 1 or 10 mmol dm^{-3} $BaCl_2$ (Fig. 5) are similar in form to those reported earlier [14,15] and with a similar point of inflexion.

The extent of the scatter in all ζ-potential measurements with 0.05 vol % suspensions is believed to be caused by the heterogeneous character of the powder with respect to particulate $BaCO_3$ contaminant; this feature becomes increasingly important when very small sample sizes (~mg) are used. The actual form of the $BaCO_3$ contaminant in $BaTiO_3$ powder has been examined in detail [21]; it appears to be present largely as descrete $BaCO_3$ particles. At high pH the measured ζ-potential values will therefore be the mean of those of the $BaCO_3$ and the $BaTiO_3$ particles, but because 95% or more of the powder is $BaTiO_3$, the measured values will represent closely those of a $BaTiO_3$ particle (and in any case, as is discussed below, the two values appear not be very different). The proportion of the $BaCO_3$ present as a film on the $BaTiO_3$ particle surface in aqueous suspension is believed to be small, but this is not to say that an outer layer of thickness corresponding to only one or two unit cell dimensions might under certain compositions not approximate in composition to $BaCO_3$. The change in the slope observed (increasing ζ-potential values at pH 9) under those conditions could be due to the beginning of the precipitation of $Ba(OH)^+$ ions on the partcle surface, as is seen also for Ba^{2+} adsorption on TiO_2 with the same range of pH value and Ba^{2+} concentration [31].

It is theoretically possible that dopants (such as the Nb_2O_5 in powder A) could also modify the ζ-potential and the IEP. However, the dilute suspensions of both powder used here behaved similarly under electrophoresis (Fig. 2), and small differences were detected only when high solids concentrations were used (Fig. 3). It is more probable that the origin of these differences lies in the different concentration of impurity $BaCO_3$ present [27], than in differences in the composition of the $BaTiO_3$ itself. It can therefore be concluded that the Nb_2O_5 dopant at the level used in this powder does not affect the IEP significantly. Again, this result is consistent with $BaTiO_3$ particle surface analyses, which showed similar characteristics for both type of powder [27,30].

4.2. Effect of Ba^{2+} and CO_3^{2-} ion additions on rheology

In order to test the effect of aqueous Ba^{2+} concentration on particle surface chemistry using rheological measurements, higher concentration of Ba^{2+} must be used, because of the larger total $BaTiO_3$ surface area in the 20 vol % suspensions. The decrease in yield stress with increasing Ba^{2+} concentration is very sharp for pH >8 (Fig. 6). Viscosity also decreases considerably with increasing Ba^{2+} concentration (up to 500 mmol dm^{-3}, as is shown in Fig. 7), indicating that the electrical charge generated by adsorption of Ba^{2+} is sufficient to allow electrostatic stabilisation. The deflocculating effect of Ba^{2+} ions adsorbed on the surfaces of $BaTiO_3$ particles might simultaneously be used to improve sintering behaviour, according to a model that has been proposed for sintering [32]. On the other hand, at pH 4 the suspensions were already stabilised. The high ζ-potential values required are probably initially achieved by adsorption of H^+, and then further increased by the specific adsorption of Ba^{2+}, provided by the complete solution of the $BaCO_3$ impurity. In this case, further addition of $BaCl_2$ (up to 500 mmol dm^{-3}) will simply have the effect of compressing the double layer (through the high concentration of Cl^- counter ions), to lower the potential barrier to flocculation, and allowing the attractive forces dominate and accounting for the steady increase in viscosity observed (Fig. 7).

CO_3^{2-} additions on the other hand, do not produce such strong effects on the slips. It has been reported that it is possible to observe precipitation of $BaCO_3$ on the surface of barite (mineral $BaSO_4$) at pH 10.3 with only 0.8 mmol dm^{-3} added carbonate. This is believed to be because the adsorbed CO_3^{2-} ions produce reversal of charge, and give rise to an abrupt change to negative ζ-potential values [22]. However, it has not been possible to confirm the precipitation of $BaCO_3$ on the surface of $BaTiO_3$ particles suspended in H_2O in this way, because the ζ-potential values for $BaTiO_3$ and $BaCO_3$ [22] are similar over the pH range (>9) for which the carbonate remains partly soluble (Fig. 8). It is possible that in aqueous suspensions at high pH a thin $BaCO_3$ layer covers the $BaTiO_3$ particle surface, and which so far as surface potential is concerned, will therefore behave more or less like $BaCO_3$ particles.

4.3. Effect of calcination and ageing

The electrophoretic behaviour and IEP of an oxide can be changed if the concentration of active sites on the surface (–OH) groups is altered by a heat treatment. Fig. 9 shows that for powder B, the IEP has moved to pH 4.5 after calcination at 800°C for 12 hours. Immediately after calcination at 700°C, the laboratory produced powder C also shows an IEP in the acidic range at pH ~3.5–4.0 (Fig. 10). A similar effect was seen in the case of hydrothermally prepared powder [9], reported to have an IEP at ~4.7. Therefore, calcined $BaTiO_3$ powders seem generally to have IEP values in the acidic range, as a result of the partial alimination of the surface amphoteric –OH groups.

Rehydration for 3 months of powder C moved the IEP from ~3.7 to ~5.5, but there was no further change after longer increasing exposure (Fig. 10). The general shift of the ζ-potential curve may be the result of the reestablishment of the amphoteric sites, permitting a greater extent of electrical charge development through protonation.

5. Conclusions

All the IEP values reported in the literature, acidic (~4) for dehydrated surfaces, alkaline (8–10) or even no IEP for high concentrations slips, can be explained. Because Ba^{2+} is specifically adsorbed on $BaTiO_3$ surfaces, the IEP value is strongly dependent on Ba^{2+} ion concentration and thus on the amount of contaminant $BaCO_3$ in $BaTiO_3$ powder. The true IEP value for $BaTiO_3$ of ~6.5 is obtained by extrapolation to zero $BaCO_3$ contamination. $BaTiO_3$ thus behaves simultaneously as an *insoluble oxide*, and as *partially soluble inorganic salt*. In this model the *insoluble oxide* can be approximated to the TiO_2 component, and the *salt* to the BaO component of the $BaTiO_3$ structure.

It is possible to deflocculate a high solids concentration $BaTiO_3$ aqueous slip by reducing the pH to 3–4. This effect is the result of an electrostatic repulsion force created by the large positive ζ-potential developed at the particle-solution interface. The surface positive charge arises from two sources: protonation of the amphoteric oxide groups, and the adsorption of the Ba^{2+} ions provided by the dissolution of contaminat $BaCO_3$. Because the $BaTiO_3$ surface has a strong affinity for Ba^{2+} this ion has a marked effect in the rheology of the slip and at pH >7 high Ba^{2+} concentrations can result in deflocculation. At pH 4, the system is already largely deflocculated, and high concentrations of Ba^{2+} ion simply compress the double layer and through the increase of interparticle attraction cause slight flocculation.

High concentrations of Ba^{2+}, depending on the conditions, either shift the IEP to more alkaline values, or provide the surface with high positive charge over the entire pH range. In the limit, a condition of no IEP is possible.

Dehydration of the powder through high temperature calcination affects the surface charge developed and the position of the IEP.

No influence of dopant Nb_2O_5 on the behaviour of $BaTiO_3$ suspensions was detected with the dopant levels present.

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