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The Properties of Aqueous Phase Suspensions of Barium Titanate

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Abstract

Recent literature is reviewed concerning the influence of suspension pH and ion concentrations on the zeta-potential of near-stoichiometric BaTiO₃ powders. New work is reported concerning the surface chemistry and rheology of BaTiO₃ powder in aqueous phase suspensions prepared without the use of surfactants or polyelectrolytes. © 1996 Elsevier Science Limited.

1 Introduction

Barium titanate ($BaTiO_3$) is a common component of electronic devices such as multilayer capacitors, communications filters, PTC thermistors and sensors. For many of these applications thin (< 100 μm) films of ceramic are required and the tape-casting of powder suspensions in non-aqueous media has traditionally been used as the forming operation. However, for environmental and economic reasons there is currently considerable interest in the replacement of the organic by an aqueous medium, and hence in the properties of aqueous suspensions of $BaTiO_3$ powders. A number of reports concern the properties of $BaTiO_3$ powders dispersed in water.[1-5] The preparation of stable dispersions of the $BaTiO_3$ powder is a critical step in the fabrication process, and an understanding of the surface chemistry of the $BaTiO_3$ particle is therefore a prerequisite to being able to control systematically the interparticle forces, which in turn control the tendency for agglomeration to occur and the rheological behaviour of the suspension. Commercial systems are generally very complex solid solutions or mixtures of, for example, titanates and zirconates, with a range of divalent cations. $BaTiO_3$ studied alone therefore is an idealized model system, and its examination provides an essential precursor to studies of more complex systems.

Earlier studies on $BaTiO_3$ suspensions examined their stability, assessed in terms of sediment volume, using a range of organic liquids of varying dielectric constant and capacity for hydrogen bonding. Contact angle has also been used as an indicator of the nature of the $BaTiO_3$–liquid interaction. A capacity for proton donation by the liquid appears to favour stability, and water has some advantages over liquids of lower dielectric constant, though precise quantitative correlations have been difficult to achieve.[1,2] It has generally been believed to be difficult to produce fully deflocculated aqueous slips of $BaTiO_3$ powder unless surfactants or polyelectrolytes are used. Attempts to produce stable, low-viscosity suspensions have entailed the use of surfactants such as sodium phosphate, of which 0·2% is sufficient to reduce the viscosity of a 22 vol% suspension and allow slip-casting.[3] High-molecular-weight sodium sulfonate has also been successfully used as a deflocculant.[4]

However, in order to optimize the electrical properties of barium titanate materials, elements such as Na and P are best avoided and non-ionic organic surfactants, or ammonium salts of organic acids, are preferable. Studies have been made on the use of acidic, non-ionic and basic organic polyelectrolytes.[1,3-5] Polyacrylic acid of molecular weight 5000 is an effective dispersant in basic solutions,[6,7] and the mechanism of suspension stabilization has been studied in some detail, focusing attention on the ionization of the carboxylic acid groups and their adsorption at the particle surface: at pH > 10 more than 95% coverage of the particle surface in a 48 vol% suspension is possible. Under acid conditions the carboxylic acid groups are uncharged and the consequent coiling of the polymer molecules inhibits surface coverage. Similar behaviour is shown by a standard commercial ammonium polyacrylate,[8] which becomes effective at pH > 7.

Tape-casting formulations also include organic binders such as polyvinylalcohol (PVA) and plasticizers, and the displacive interactions between these species and the dispersant at the particle

surface become important.[9,11] Although PVA itself is not effective as a dispersant–binder system, it is activated through copolymerization with carboxylic acid monomers. Block copolymers are effective dispersants and have been judged to be steric stabilizers, since they produce only small values of $BaTiO_3$ particle surface charge, and are insensitive to electrolyte concentration. Random copolymers, on the other hand, are susceptible to depletion flocculation and are not indifferent to electrolyte additions; in this case a combination of steric and electrostatic stabilization has been considered to be operative.[12]

A full understanding of the behaviour of $BaTiO_3$ powders in aqueous suspension in the presence of polyelectrolytes ideally requires the prior development of an understanding of the nature of the barium titanate particle surface in an aqueous environment in the absence of organic species. A programme of work has therefore been initiated into the behaviour of $BaTiO_3$ powders in water, in which the extent of flocculation is initially controlled by variation of pH. The programme has focused attention on the chemical stability of the $BaTiO_3$ particle and on the properties of concentrated suspensions of $BaTiO_3$ powder, using measurements of surface ζ-potential and suspension rheology. This paper reviews recent literature concerning $BaTiO_3$ stability and the influence of suspension pH and ionic concentration on the ζ-potential of near-stoichiometric powders, and reports new work concerning the surface chemistry of $BaTiO_3$ particles in aqueous suspensions prepared without the use of polyelectrolytes.

2 The Chemistry of BaTiO₃ in Water

$BaTiO_3$ is not thermodynamically stable in aqueous media of pH less than ~12, and theoretically will undergo hydrolysis according to reactions of the type:

$$BaTiO_3 \text{ (s)} + H_2O$$
$$= Ba^{2+} \text{ (aq.)} + TiO_2 \text{ (rutile)} + 2OH^- \text{ (aq.)} \quad (1)$$
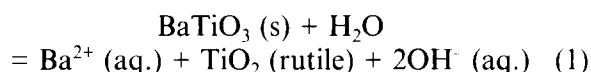
This particular reaction has been studied extensively for titanate minerals with the $BaTiO_3$ perovskite structure.[13,14] Although rutile is thermodynamically the most stable phase of TiO_2, under certain conditions titanium hydroxo complexes can also exist in solution.[15] Under acidic conditions, reaction (1) can be written:

$$BaTiO_3 \text{ (s)} + 2H^+ \text{ (aq.)}$$
$$= Ba^{2+} \text{ (aq.)} + TiO_2 \text{ (rutile)} + H_2O \quad (2)$$
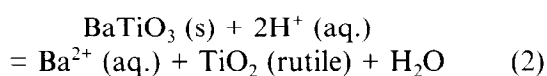
Setting the activities of solid and neutral species equal to 1 allows an estimate to be made of Ba^{2+} concentration as a function of pH, since:

$$[Ba^{2+}][OH^-]^2 = K \quad (3)$$

and

$$\log K = \log [Ba^{2+}] - 2\log [OH^-] \quad (4)$$

or

$$\log [Ba^{2+}] = 20 \cdot 08 - 2pH \quad (5)$$

on the basis of published standard Gibbs function data.[16,17] This shows that the equilibrium concentration of Ba^{2+} (and hence solubility of $BaTiO_3$) should be very low for all normal pH values. A theoretical stability diagram for the system $Ba–Ti–H_2O$ has been derived which indicates that $BaTiO_3$ can only exist in equilibrium with Ba^{2+} (aq.) and TiO_2 (s) under strongly alkaline conditions.[18] It is therefore likely that in practice particles of $BaTiO_3$ will release Ba^{2+} up to the point when the particle surface assumes a 'TiO₂-like' character. Further Ba^{2+} release should then be controlled by the slower diffusion of Ba^{2+} through the surface film, until solution saturation with Ba^{2+} is attained.

However, in normal environments the situation is in reality more complicated because of the general presence of carbon dioxide in the atmosphere and in solution in water. A second equilibrium:

$$BaTiO_3 \text{ (s)} + CO_2 \text{ (soln)}$$
$$= BaCO_3 \text{ (s)} + TiO_2 \text{ (rutile)} \quad (6)$$
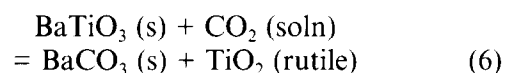
has to be taken into account; this has the effect of increasing $BaTiO_3$ solubility unless p_{CO_2} (and thus $[CO_2 \text{ (soln)}]$) is extremely low. The theoretical phase equilibrium diagram for the system $Ba–Ti–CO_2–H_2O$[19] shows that $BaTiO_3$ is only stable in contact with water at pH < 12 for $\log[p_{CO_2}/\text{bar}]$ < −4·5. At higher pressures of CO_2 and for pH > 7 barium carbonate is the stable phase. Barium carbonate would itself be expected to have significant solubility under higher pressures of CO_2 under neutral to alkaline conditions because of the formation of the hydrogen carbonate anion (HCO_3^-), the overall effect then being to further enhance the extent of solution of $BaTiO_3$. It has to be noted, however, that these equilibria may in practice be slow to be attained at room temperature, and that the rate is likely to depend in part on solid-state diffusion processes occurring in the subsurface regions of the barium titanate particle.

Ba^{2+} is leached from $BaTiO_3$ powder during milling in water in the presence of ammonium polyacrylate dispersant, and the concentration is increased by the addition of binders such as PVA. Sintering of this powder gave exaggerated grain growth, which was attributed either to redeposition of the Ba^{2+} ion on the particle surfaces during drying or to creation of a TiO_2-rich surface phase

(since the same effect was observed after filtering and washing the powder to remove dissolved barium[20]). X-ray photoelectron spectroscopy (XPS) studies of the results of long-term (8+ days) leaching of titanate powders with water at temperatures up to 350°C show significant changes in particle surface composition: there was a marked decrease in M^{2+} $2p$ contribution, and increase in the Ti $2p$ contribution to the spectrum, indicative of loss of M^{2+} cation to the aqueous phase.[14]

Commercial 'barium titanate' powders are themselves chemically complex; they are normally deliberately slightly non-stoichiometric with respect to Ba and Ti, but they will also contain small amounts of unreacted $BaCO_3$ and TiO_2 if calcination of the starting materials has been incomplete. Studies using such powders need to take these facts into account. There is also good evidence for the presence of thin films of $BaCO_3$ on the surface of $BaTiO_3$ particles through normal contact with air, and which it has been claimed may not be readily removed by washing with acidified water (pH 4.5).[21,22] Varying amounts of $BaCO_3$ are likely to influence the reproducibility of the sintering of a $BaTiO_3$ powder, and it has therefore been considered advisable to take steps to remove the $BaCO_3$ early in the fabrication process, particularly because the subsequent loss of gaseous CO_2 during sintering is likely also to impair the densification characteristics of a powder.[22,23]

Because of the theoretical lack of stability of $BaTiO_3$ in contact with water and the varying composition of commercial powders, it is not surprising that the values reported for the ζ-potential isoelectric point (iep) of powders in aqueous suspension vary considerably. Using the standard electrokinetic mobility technique (EM) the values extend from pH 4·7 to 9·9; no iep was found for concentrated $BaTiO_3$ suspensions using acoustophoretic titration (ACT).[6,7] A summary of literature data for barium titanate powders is shown in Table 1.

Although the use of concentrated suspensions for measurements of this type seems sensible, because they might be considered to be better representative of those most likely to be used in commercial practice, values of ζ-potential mea-

sured with concentrated suspensions will not necessarily agree with those obtained on very dilute suspensions of fine powder, for which the partitioning of the surface Ba^{2+} ions would favour the aqueous phase rather than the solid. In order to interpret more precisely the measured ζ-potential value, a full history of the $BaTiO_3$ powder is required, together with experimental details of the conditions of measurement, but in most cases the production and subsequent processing and measurement conditions have not been reported.

3 Experimental

Barium titanate powder (Transelco, PA, USA; stated (Ba + Sr)O/TiO₂ molar ratio of 0·996) was dispersed in deionized water in a polypropene container under normal laboratory atmosphere with ultrasonic vibration at a range of pH values measured by a standard glass electrode (Corning 220, Ciba Corning Diagnostics Ltd, Sudbury, UK) controlled by the addition of dilute hydrochloric acid. At least 10 min was allowed for stabilization of the suspension conditions before taking measurements. Ba^{2+} concentrations in the aqueous phase were measured by atomic absorption spectroscopy after sedimentation of the powder by centrifuging. Chemical analysis for Ba, Ti and other major impurities or additives in the $BaTiO_3$ powder was carried out using a standard X-ray fluorescence technique on a fused glass disc.

Rheological properties (yield stress and viscosity, as functions of shear rate) were determined by a variable stress rheometer (Carri-Med SCL 500, Rheometer Systems, Dorking, UK). To ensure reproducibility, the suspension was sheared at the maximum stress applied for 2 min, allowed to equilibrate for 5 min, and the shear stress sweep started with 2 min increasing rate, 2 min hold and 2 min decreasing rate. ζ-potential was measured (Malvern ZetaSizer, Malvern, UK) on dilute suspensions, buffered to a constant ionic strength by addition of 5 mmol dm⁻³ potassium chloride. Additional Ba^{2+} was added as barium chloride (AR grade).

Powder surfaces were examined using XPS (Vacuum Generators, ESCA, LAB/SIMS).

Table 1. Reported iep values for $BaTiO_3$

Ba/Ti	d(μm)	aₛ (m² g⁻¹)	iep pH	Method[a]	Ref.
0·90	0·6	1·7	7·7	EM	8
1·0	<<1	—	4·7	EM	24
0·92	0·5	2·1	8·5	EM	8
1·1	3	—	9·9	EM	10,11
—	5·6	1·06	8·5	EM	20
'1·8% excess Ba'	0·75	2·5	none	ACT	6
1·028	0·75	2·9	none	ACT	7

[a]EM, electrokinetic mobility; ACT, acoustophoretic titration.

4 Results

The characteristics of the commercial $BaTiO_3$ powder used in this section of the study are given in Table 2.

The Ba^{2+} release behaviour of powder suspensions at 23°C is illustrated by Fig. 1, showing the

Ba^{2+} concentration in equilibrium with a 0·5 vol% suspension over 48 h as a function of pH. The maximum concentration of Ba^{2+} released is influenced by pH; acid conditions favoured surface solution, qualitatively consistent with the phase diagram predictions. There was a clear tendency for the pH of the suspension to drift towards a value in the region of 8 to 10, as shown in Fig. 2 for 12 vol% BaTiO$_3$ in water equilibrated over a period of 7 days. This observation is consistent with the occurrence of the BaTiO$_3$ particle surface hydrolysis reaction and the release of OH ion [eqn (1)]. A more detailed analysis of the behaviour of the powder is provided by Ba^{2+} release rate data, illustrated in Fig. 3 for a suspension maintained at pH 4. The concentration of ~160 ppm Ba^{2+} reached after 5 h corresponded in this

instance to the solution of 4·8 mg Ba^{2+}, or 0·82% of the BaTiO$_3$ present in the suspension.

EM ζ-potential measurements made on very dilute suspensions indicated an iep value in the region of 6, and significantly lower than values obtained by this technique with other powders. The plots of ζ-potential as a function of pH for the as-received BaTiO$_3$ powder showed values in the range +20 to –40 mV over the pH range 3 to 11 (Fig. 4). Calcination of the powder in air at 500°C for 24 h appeared to have no effect on surface properties. In contrast, leaching with dilute hydrochloric acid at pH 4 for 16 h at 23°C had a marked influence on particle surface composition, shifting the whole curve towards more negative charge values and giving an iep value of pH ≈ 4·5. The change in the nature of the particle surface was confirmed by the changes in XPS peaks for Ba, Ti and O, and their intensities, before and after acid leaching, as shown in Table 3.

Two types of oxygen were provisionally identified by excitation energy in the as-received powder: one oxygen peak and the carbon peak became markedly weaker after leaching, suggesting that these might have been those of surface carbonate;

Table 2. BaTiO$_3$ powder characteristics

(BaO + SrO)/TiO$_2$ molar ratio	0·968
SrO	0·56 % (by weight)
Nb$_2$O$_5$	0·23 % (by weight)
Particle size (Coulter)	2·0 μm
Specific surface area (BET)	1·3 m^2 g^{-1}
Density	5·949 g cm^{-3}
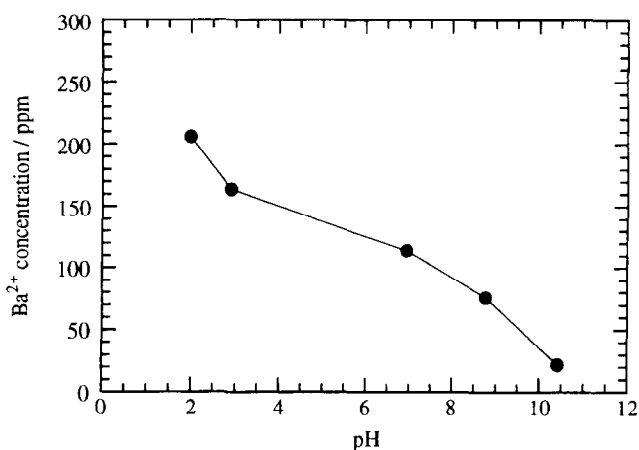
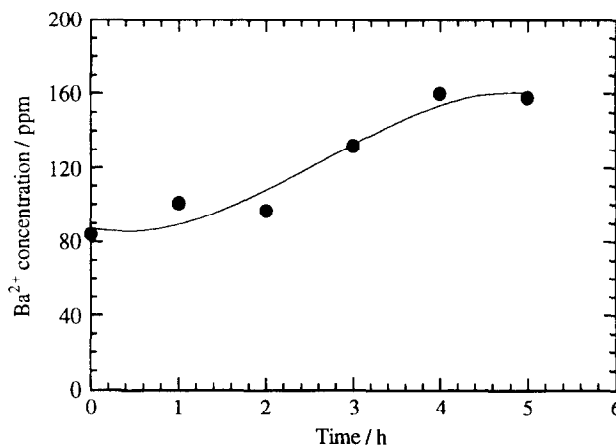**Fig. 1.** Barium ions released from a 0·5 vol% suspension of BaTiO$_3$ over 48 h, as a function of pH.
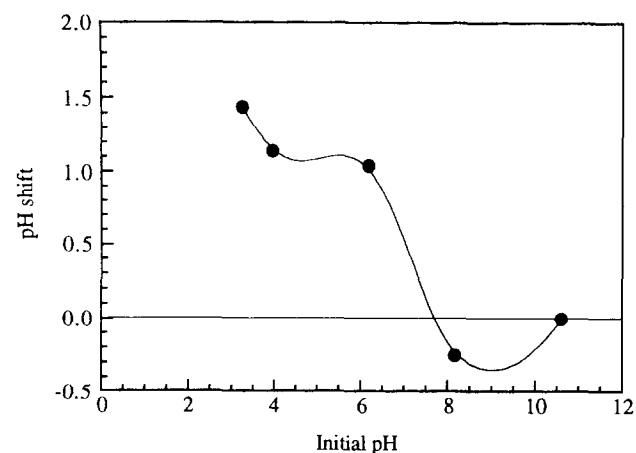
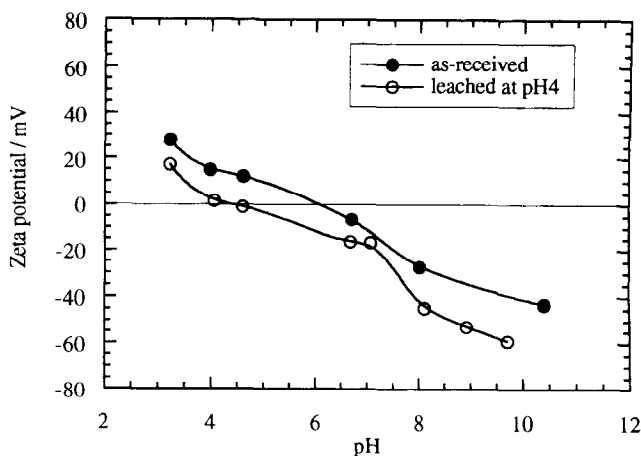**Fig. 2.** pH shift over 7 days for a 12 vol% suspension of BaTiO$_3$, as a function of initial pH.

**Fig. 3.** Barium ions released at pH 4 from a 0·5 vol% suspension of BaTiO$_3$ at pH 4.

Fig. 4. ζ-potential as a function of pH, for as-received and acid washed powders.

simultaneously the barium peak weakened slightly. However, because it is difficult to avoid contamination of sample surfaces by carbon in high-vacuum systems, further work is being carried out to confirm these observations. There was only one titanium peak, which appeared to correspond to that of $BaTiO_3$.
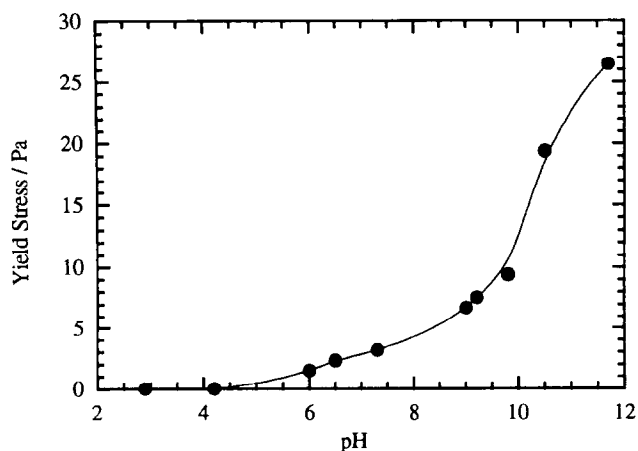
The magnitude of the EM ζ-potential values suggested that satisfactory electrostatic dispersion of particles should have been possible under either strongly acidic or strongly alkaline conditions, with extensive flocculation at pH values in the region of 5 to 7. Viscosity as a function of shear rate plots for 20 vol% suspensions showed, how-

ever, (Fig. 5) low values for pH 4 and values higher by one to two orders of magnitude at pH 11·8, with no maximum in the neutral pH range. 35 vol% suspensions of pH 4 were very fluid and suitable for slip-casting. The similar sensitivity of yield stress to pH is shown in Fig. 6 for a 20 vol% suspension; from a very low value at pH 4 the yield stress increases steadily for pH values > 7, without the expected maximum at the iep (pH $\approx$ 6). There is thus a clear discrepancy between the observed rheology of these suspensions and the behaviour predicted on the basis of the measured ζ-potential values, which indicate that there should be a viscosity maximum in the region of pH from 4 to 6.

Because of the rapid release of Ba^{2+} ions by the $BaTiO_3$ powder, the effect of added Ba^{2+} on $BaTiO_3$ suspensions was examined. At low concentrations (0·1 mmol dm^{-3}) Ba^{2+} appeared to be strongly adsorbed on particle surfaces, and the ζ-potential shifted to higher values, as shown by Fig. 7. The effect on rheology of Ba^{2+} ion additions at concentrations corresponding to those released naturally is shown in Fig. 8 for a suspension of pH 10: there are small but significant decreases in yield stress and viscosity.

Table 3. XPS data for $BaTiO_3$ powder before and after acid leaching

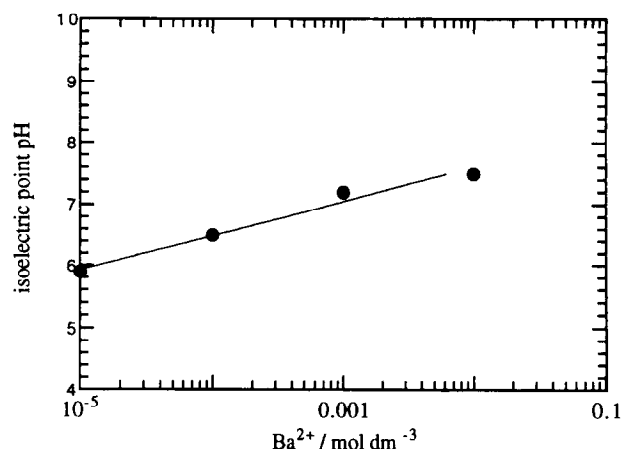| Element peak	Centre eV		Peak intensity (kcounts eV s⁻¹)	
	before	after	before	after
Ba	782·8	782·4	6·03	5·47
Ba*	784·4	—	1·16	0·00
O	533·5	533·0	1·94	2·57
O*	535·7	535·4	1·89	2·54
Ti	462·1	461·7	1·36	1·40
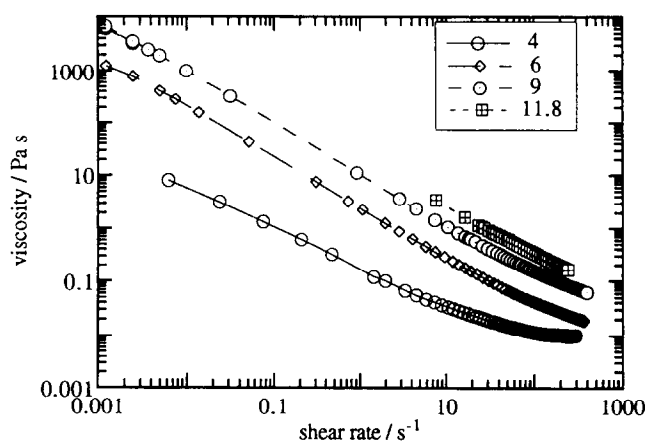
Fig. 5. Viscosity as a function of shear rate, of 20 vol% suspensions of $BaTiO_3$, for pH values in the range 4 to 11·8.
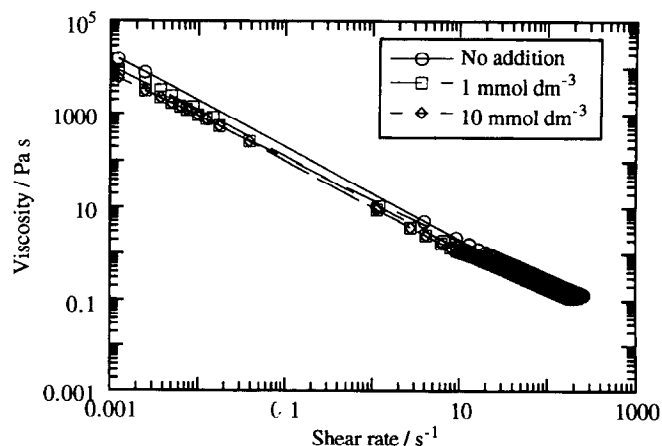

Fig. 7. ζ-potential isoelectric point as a function of barium ion concentration.

Fig. 6. Yield stress as a function of pH, for a 20 vol% suspension.

Fig. 8. Influence of added barium ion on the yield stress of a 20 vol% suspension at pH 10.

5 Discussion

This examination underlines the importance of the intrinsic thermodynamic instability of $BaTiO_3$ in aqueous media on the behaviour of powder suspensions. At pH 4 the measured equilibrium concentration of ~160 ppm of Ba^{2+} corresponds to a ~1 mmol dm^{-3} solution. It is clear that under acid conditions an outer film of each $BaTiO_3$ particle tends to lose Ba^{2+} to assume structural characteristics close to those of TiO_2; this view is supported by the observation that the iep value measured is closely similar to reported values for TiO_2.[25] This effect is likely to be accentuated because the instrument used to measure ζ-potential required only very small concentrations of powder, obtained in practice by prolonged settling and then rejection of relatively coarse (~2 μm) particles. The acid leach treatment has a demonstrably more intense effect on the Ba content of the surface, and the iep value was reduced even further. An estimate based on the amount of Ba^{2+} released from a suspension indicates that on average a particle surface layer ~3 nm thick becomes depleted of Ba^{2+}; this indicates that a particle 6 nm or smaller would have been, effectively, completely converted to TiO_2. The data in Table 1 show, as expected in view of the instability of $BaTiO_3$ in an aqueous environment, that there is no obvious correlation between Ba/Ti ratios departing only marginally from stoichiometry, and iep value. At higher pH values the outer surface film would also be slightly barium deficient, though now it would be expected to be more readily able to accept readsorbed barium ions because of the approach of the system to the conditions of pH and Ba^{2+} ion concentration under which the $BaTiO_3$ crystal structure is stable. A tendency for Ba^{2+} ion adsorption to occur is suggested by the observed strong influence of low concentrations of added Ba^{2+} ion on ζ-potential, and thus isoelectric point. At pH values higher than the maximum (11·8) used here, and in the presence of normal levels of dissolved CO_2, the particle surface theoretically should be $BaCO_3$. The $BaTiO_3$ particle surfaces may, to a first approximation, therefore be considered to be predominantly TiO_2 in character at pH < 6, and predominantly $BaCO_3$ in character as the pH approaches 12. The XPS data of Table 3 also support a view that in the dry state the $BaTiO_3$ particle surface consists partially of $BaCO_3$.

The rheological characteristics of the $BaTiO_3$ powder do not match those expected from the ζ-potential measurements; the viscosity and yield stress would have been expected to show maxima in the vicinity of pH 6, corresponding to strong flocculation of the uncharged particles caused by the van der Waals' forces of attraction. Instead a steadily increasing viscosity and yield stress is seen with increasing pH, with the more marked rise at pH > 8. The low viscosities and yield stress values at pH 4 might just be explicable in terms of electrostatic repulsion resulting from the ~20 mV positive surface charge. The complete absence of correlation at pH > 8 suggests that the surface charge of particles in a 20 to 30 vol% suspension used for the rheological measurements is not the same as those of the particles in the extremely dilute suspensions needed for ζ-potential measurements, and supporting the view that the surface (if not the internal) composition of these finer particles approximates to TiO_2.

The significant influence of Ba^{2+} at concentrations approximating to those released by the powder (~1 mmol), in reducing viscosity and yield stress under conditions where the flocculated particle surfaces are likely to be negatively charged, suggests that as counter-ions they are adsorbed at the particle surfaces and contribute to a breakdown of a flocced structure. The mechanism of this effect is not clear, though a parallel may be seen in the effects of large salt concentrations on the behaviour of deflocculated suspensions of aluminium oxide powder.[26] In the present case it might be supposed that adsorption of very large hydrated Ba^{2+} ions may prevent close approach of particles and thus entry into the large, attractive, van der Waals' potential well. Work is being carried out to establish more clearly the action of the Ba^{2+} ions.

6 Conclusions

The intrinsic instability of $BaTiO_3$ in contact with water and the tendency for Ba^{2+} ions to be released into solution has to be taken into account in any consideration of the behaviour of $BaTiO_3$ powder aqueous suspensions. The presence of CO_2 naturally dissolved in the water will further contribute to $BaTiO_3$ instability and a tendency to form barium carbonate. Rheological studies should therefore ideally be carried out using controlled pressures of CO_2. Under normal atmosphere conditions ζ-potential values obtained by measurements using very fine $BaTiO_3$ particles are likely to be influenced at higher pHs by the irreversible loss of surface Ba^{2+} and the formation of a TiO_2-like surface.

The slightly BaO-deficient powder examined here had an apparent iep in the region of pH 6, but could be satisfactorily deflocculated at pH 4. Yield stress and viscosity rose significantly at pH > 8, but the addition of low concentrations of Ba^{2+} ion

at higher pHs tended to suppress this effect, and can therefore possibly be regarded as beneficial. Further work is needed to establish the precise bases for these effects, and for the action in particular of the Ba^{2+} ions.

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