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Ion specificity and viscosity of rutile dispersions

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Abstract The isoelectric point (IEP) of rutile is shifted to higher pH values in the presence of greater than 10^{-4} mol dm $^{-3}$ Ba $^{2+}$, Ca $^{2+}$ and Mg $^{2+}$, and when a critical concentration (5×10^{-4} mol dm $^{-3}$ for Ba $^{2+}$ and 1×10^{-3} mol dm $^{-3}$ for Ca $^{2+}$) is exceeded there is no IEP at all and the ζ potential is always positive. A common intersection point for the ζ -potential curves of the different concentrations of salt is found, but for the various salts the point is shifted from $\zeta = 0$ mV for Mg $^{2+}$ up to $\zeta = 20$ mV for Ba $^{2+}$. Between the IEP and the charge-reversal point a rheologically unstable region is discovered. The shear stress of rutile dispersions (2.5 g rutile + 4 g electrolyte solution) at shear rates of 116 s $^{-1}$ shows the same pH dependence irrespective of the concentration of alkaline-earth metal cations up to 10^{-2} mol dm $^{-3}$. The shear stress is less than 1 Pa below pH 3.8 and in the pH range 5–12 it assumes a value between 50 and 80 Pa at 116 s $^{-1}$ with some scatter; however,

no systematic trend with concentration of alkaline-earth metal cations and a rather insignificant decrease with pH at pristine conditions are observed. The acidic branch of the yield stress (pH) and low shear rate viscosity (pH) curves is insensitive to the presence of alkaline-earth metal cations, and the same behaviour is found for the ζ potential. The alkaline-earth metal cations induce an increase in viscosity in the basic region and a shift in the pH of maximum viscosity to high pH values. It was also discovered that the effect different alkaline-earth metal cations have on the rheological properties at the same concentration is different from the effect induced by indifferent electrolytes. When the ζ potential increases the viscosity at high pH is increased in a series which follows the increase in size of the cation.

Key words Rutile – Zeta potential – Viscosity – Yield stress – Isoelectric point

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Introduction

Dispersions containing about 30% of submicron titania particles by weight show a spectacular change in viscosity as a function of pH. Far from the isoelectric point (IEP) their consistency resembles milk but in the vicinity of the IEP it is more like shoe polish. Thus, the viscosity of such dispersions can change by several

orders of magnitude on addition of one drop of dilute acid or base.

In the absence of strongly adsorbing ions, the rheological properties of the dispersion at low ionic strength may be related to the pristine IEP which is at pH = 5.8–6.2 for rutile and anatase [1–3]. On addition of strongly (chelating) adsorbing anions the IEP of oxides can be shifted to lower pH values, and the point

of maximum viscosity is shifted accordingly [4]. On the other hand, anions like chlorides can also produce a shift in the positive direction for silica [5].

The adsorption of alkaline and alkaline-earth metal cations also affects the electrokinetic properties of oxides. A range of monovalent cations reverses the charge at sufficiently high ionic strength ($0.5\text{--}1.0\text{ mol dm}^{-3}$) [6]. The presence of only $1\text{ mmol dm}^{-3}\text{ Da}^{2+}$ in solution causes a reversal of the sign of the ζ potential of rutile, so that the potential is positive over the entire available pH range [7]. At the same concentration Ca^{2+} causes a sign reversal at $\text{pH} = 7.2$ and magnesium at $\text{pH} = 8.5$. This results in an IEP slightly above the pristine value and a charge-reversal point (CRP) at elevated values. The goal of the present study is to check if this well-known complex electrokinetic behavior is reflected in the rheological properties. The presence of alkaline-earth metal cations at different concentrations in natural and tap water makes their effect on the rheological properties of concentrated dispersions also very important from a practical point of view.

Experimental

The AR grade rutile from Aldrich was washed according to the procedure described in Ref [8]. The specific surface area (ASAP 2010 Micrometrics, Norcross, Ga.) is $2.84\text{ m}^2\text{ g}^{-1}$. The average particle diameter is about $1\text{ }\mu\text{m}$. The Na, Mg, Ca and Ba nitrate salts were of AR grade from Aldrich and were used as obtained.

The ζ potential and particle size were determined using an Acoustosizer from Matec. Titrations were carried out with 10% rutile by weight. The difference between acid and base titrations (hysteresis) was rather insignificant. No attempt to subtract the background from the measured signal was made. This is justified by a comparative study in which the ζ potential agreed with the value obtained by electrophoresis using a range of different instruments. Moreover the O'Brien and Smoluchowski models differed only at extreme pH values. In this paper the O'Brien model is used.

A Bohlin VOR rheometer was used with the C14 cup-piston system and a $12.4\text{ g} \times \text{cm}$ torsion bar. This system gives high accuracy at low shear rates but is still able to produce quite high shear rate values when the viscosity is moderate. The shear rate was scanned from 0.0461 to 1160 s^{-1} and back at $25\text{ }^\circ\text{C}$. However, when the high shear rate viscosity was too high the scan was automatically stopped at a lower shear rate and the direction was reversed.

Each portion of the slurry was prepared separately using about 4 g Na, Mg, Ca or Ba nitrate solutions and 2.50 g rutile. The pH was adjusted with NaOH solution ($0.2\text{--}10\text{ mol dm}^{-3}$). The sum of the mass of the solution used to adjust the pH and the electrolyte was 4.00 g . The sample was magnetically stirred for at least 1 h in an air-tight polycarbonate bottle. Then the pH was measured, and the sample was put into the rheometer. No special effort was made to protect the system from atmospheric CO_2 . A Denver Instruments AP 15 pH meter with an FET electrode was used to measure the pH of the slurry.

The rheometer gives primary results in the form of shear-stress (shear-rate) functions. Their course is rather complicated and cannot be described by an equation involving a few well-defined parameters. Three shear-rate values were arbitrarily selected to characterize the rheological properties of the dispersions. We used directly measured values (no curve smoothing).

A typical run far from the IEP is shown in Fig. 1. The shear stress at a shear rate of 116 s^{-1} was chosen to characterize the rheological behavior at high shear rates (the values at even higher shear rates are omitted).

A typical run close to the IEP, using a logarithm shear-rate scale, is shown in Fig. 2. The local maximum on the shear-stress (shear-rate) curve is defined as the yield stress. This local maximum appears around a shear rate of 0.5 s^{-1} . This choice is preferred over the extrapolated values to zero shear rates (Bingham, Casson) since the maximum clearly represents a threshold shear-stress value of the aggregates.

The viscosity of concentrated rutile dispersions is a function of the shear rate, even far from the IEP. The curves shown in Figs. 1 and 2 were obtained at an increasing shear rate. The difference between the curves obtained at increasing and decreasing shear rate is not very significant, but some hysteresis is observed (Fig. 3). In the present paper we chose the viscosity obtained from the decreasing shear-rate curve at 1.16 s^{-1} shear rate as representative for low shear rates (this is our arbitrary choice) and it will be referred to as "viscosity".

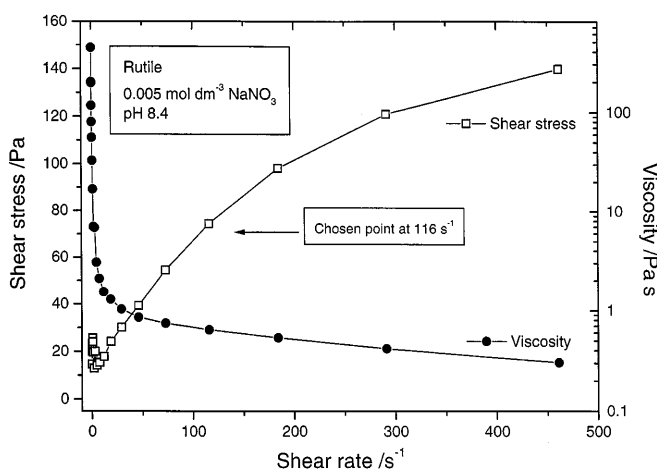


Fig. 1 Typical shear-stress versus shear-rate curve (increasing shear rate) of 2.5 g rutile + 4 g electrolyte solution dispersion far from the isoelectric point (IEP)

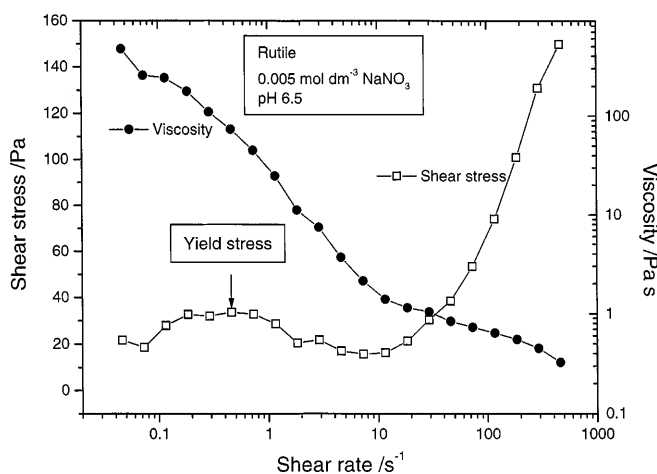


Fig. 2 Typical shear-stress versus shear-rate curve (increasing shear rate) of 2.5 g rutile + 4 g electrolyte solution dispersion close to the IEP

Results and discussion

Surface charge density

The surface-charging curves of rutile for two different concentrations of NaNO_3 , representing an indifferent electrolyte, are shown in Fig. 4. This was potentiometrically determined by recording the amount of NaOH consumed to produce the given pH. The point of zero charge (PZC), ($\sigma_0 = 0$), is at $\text{pH} = 6.2$ and this value is slightly higher than the pristine value reported in the literature [3, 9]. The surface-charging-curves can be interpreted in terms of the 1-pK-Stern model [10] with Stern capacity of 1.9 C m^{-2} and 6 sites nm^{-2} . The

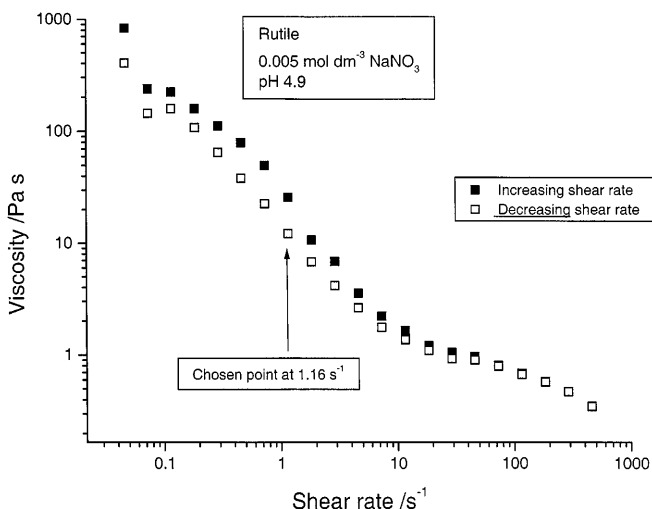


Fig. 3 Typical shear-stress versus shear-rate curves (increasing and decreasing shear rate) of 2.5 g rutile + 4 g electrolyte solution dispersion far from the IEP

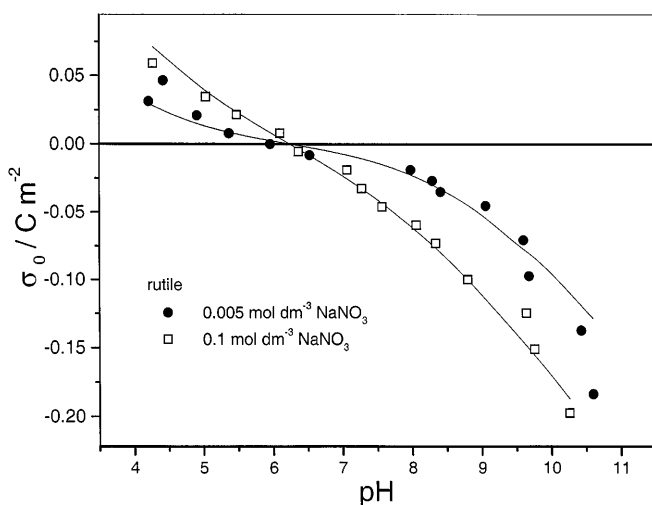


Fig. 4 Surface charging of anatase for 0.005 and 0.1 mol dm^{-3} NaNO_3 . Symbols: experimental data; lines: calculated values

surface-charge curves plotted as a function of pH are indicated in Fig. 4. The set of parameters found in the fit is not unique and many different combinations of Stern capacity and density of surface sites reasonably match the experimental results.

ζ potential

The IEP at low NaNO_3 concentrations at $\text{pH} 6.2$ matches the PZC. The effect of the Mg^{2+} , Ca^{2+} and Ba^{2+} cations at concentrations lower than $10^{-2} \text{ mol dm}^{-3}$ on the acidic branch of the electrokinetic curves is relatively small (Figs. 5–7). In the basic region some depression of the negative ζ potential was observed but without a shift in the IEP at a concentration of alkaline-earth metal cations as low as $10^{-4} \text{ mol dm}^{-3}$. At $3 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Ba}(\text{NO}_3)_2$ the shift in the IEP of rutile is substantial and it is more pronounced for Ba^{2+} than for Ca^{2+} or Mg^{2+} at a given concentration. When a critical concentration of about $5 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Ba}(\text{NO}_3)_2$ is exceeded there is no IEP and the ζ potential is always positive with a shallow minimum near the pristine IEP. For anatase the IEP was found up to $\text{Ba}(\text{NO}_3)_2$ concentrations of $3 \times 10^{-3} \text{ mol dm}^{-3}$ (Table 1) indicating that the crystal structure or conditioning may influence the adsorption of Ba^{2+} [2]. The absolute value of the ζ potential at the minimum gradually increases and shifts to lower pH when the Ba^{2+} concentration increases and at $10^{-2} \text{ mol dm}^{-3}$ Ba^{2+} the ζ potential is almost pH-independent (Fig. 7). A common intersection point (CIP) of all ζ potential curves on the positive potential side at around $\zeta = 20 \text{ mV}$ is also found. A CIP of ζ -potential curves

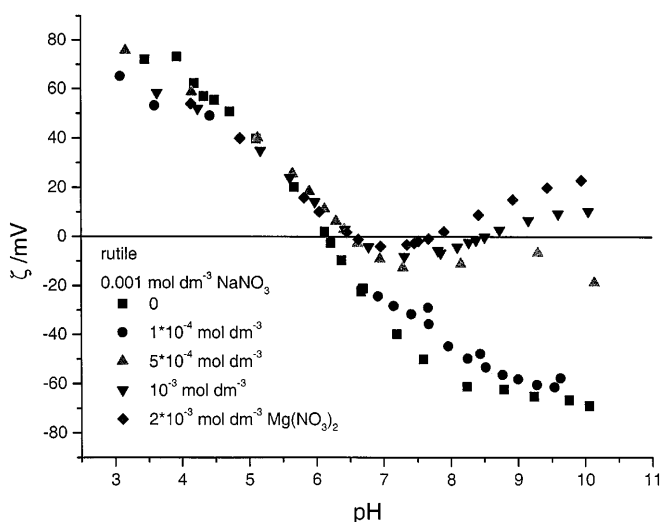


Fig. 5 Effect of magnesium on the ζ potential of rutile

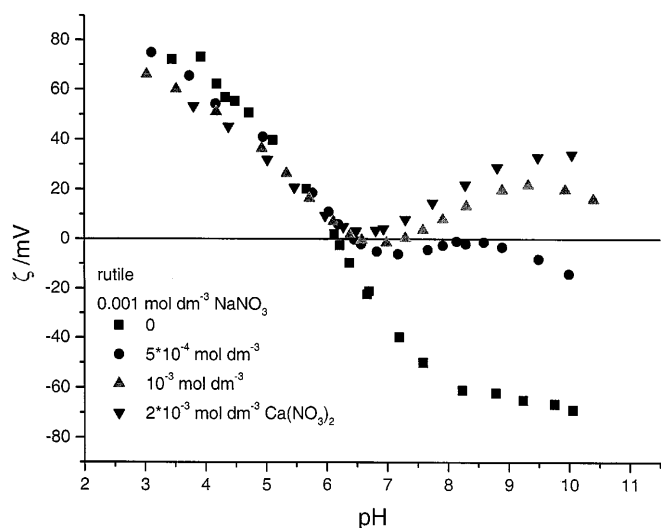


Fig. 6 Effect of calcium on the ζ potential of rutile

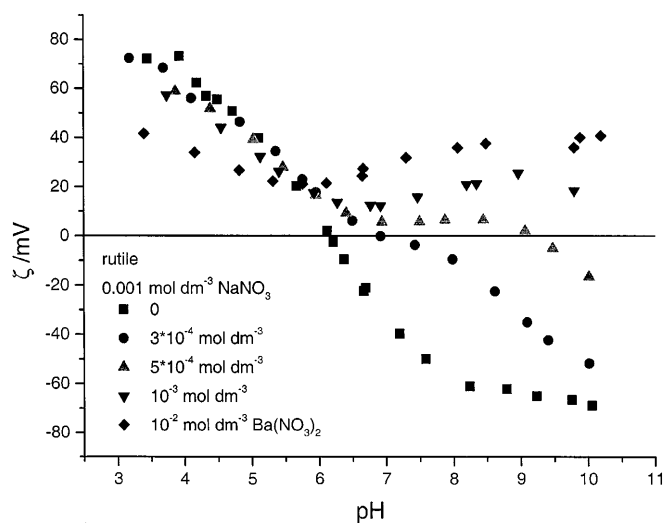


Fig. 7 Effect of barium on the ζ potential of rutile

Table 1 The ζ potential and the pH values of the common intersection point (CIP), the isoelectric point (IEP), the charge-reversal point (CRP) and the maximum viscosity for different salt concentrations. Values in parentheses are extrapolated values and show uncertainty

Salt	C_{Salt} /mol dm ⁻³	ζ potential(CIP) /mV	pH(CIP)	pH(IEP)	pH(CRP)	pH(max. visc.)
NaNO ₃	<0.1	0	6.2	6.2	–	6.6
Mg(NO ₃) ₂	1×10^{-4}	0	6.6	6.6	–	–
	5×10^{-4}	0	6.6	6.6	–	–
	1×10^{-3}	0	6.6	6.6	8.5	7.0 (5.4)
	2×10^{-3}	0	6.6	6.6	7.7	–
Ca(NO ₃) ₂	5×10^{-4}	6.1	6.2	6.5	8.2	–
	1×10^{-3}	6.1	6.2	6.6	7.2	5.8
	2×10^{-3}	6.1	6.2	–	–	–
Ba(NO ₃) ₂	1×10^{-4}	–	–	–	–	(5.8)
	3×10^{-4}	19.5	5.8	6.9	–	6.4
	5×10^{-4}	19.5	5.8	9.2	–	7.0
	1×10^{-3}	19.5	5.8	–	–	6.9
	1×10^{-2}	19.5	5.8	–	–	6.9

is also found for indifferent electrolytes at low ionic strengths oxides [1, 6, 11].

On the other hand, for certain Mg²⁺ and Ca²⁺ concentrations rutile has one IEP and CRP. For Ca²⁺ a CIP is found just above the $\zeta = 0$ line (≈ 6 mV), but for Mg²⁺ the CIP coincides with the IEP. The height position of the CIP seems to increase with the size of the alkaline-earth metal cation.

The extracted IEPs, the CRPs and the CIPs are collected in Table 1. Interestingly, the positions of these critical pH found in the present study for 10^{-3} mol dm⁻³ Mg²⁺ almost exactly match the ones found in Ref. [7] for the same Mg²⁺ concentration. It seems that the solid-to-liquid ratio does not significantly affect the course of electrokinetic curves at a given Mg²⁺ concentration. The electrokinetic curve reported in Ref. [7] for 10^{-3} mol dm⁻³ Ca²⁺ corresponds to our curve obtained at 2×10^{-3} mol dm⁻³ Ca²⁺. Considering the difference in the solid-to-liquid ratio by many orders of magnitude between this study and that reported in Ref. [7] the difference in concentration of a factor of 2 is relatively insignificant. Our electrokinetic results for Ba²⁺ are also in good agreement with those reported in Ref. [7]. Such a result is not obvious, for example, the course of electrokinetic curves of oxides at a given initial concentration of heavy-metal cations [12] is in general very sensitive to the solid-to-liquid ratio. The difference may be explained by the solvation of the ions. The hydration is much more stable for the Mg²⁺ and Ca²⁺ ions compared with the Ba²⁺ ion [13]. The specific adsorption of Ba²⁺ is thus facilitated over Ca²⁺ and Mg²⁺, producing a larger effect on the surface potential.

The relationship between ζ^2 and viscosity

A linear relationship between ζ^2 and yield stress (which is linearly correlated with viscosity) derived in Ref. [14] has been observed in the absence of alkaline-earth metal cations in acidic solutions up to relatively high ionic

strengths [1, 2]. Although the scatter is large the linear relationship seems to hold for dilute solutions of divalent cations, but the results obtained at high concentrations of Ba^{2+} , Ca^{2+} and Mg^{2+} seem to contradict this rule. Figure 8 shows the $10^{-3} \text{ mol dm}^{-3}$ solution of Mg^{2+} . The low pH corresponds to a high ζ^2 and the trend is the same as obtained at pristine conditions. At pH greater than 6 the ζ^2 of rutile in the presence of $10^{-3} \text{ mol dm}^{-3} \text{ Mg}^{2+}$ is always small (Fig. 5) but for these low ζ^2 values both high and low viscosities may be obtained.

Viscosity as a function of pH

The presence of alkaline-earth metal cations leads to an increase in yield stress and viscosity. An opposite effect was reported in Ref. [4], namely, the presence of strongly adsorbing (chelating) anions depressed the yield stress of zirconia dispersions. The maximum of the viscosity(pH) curves approximately corresponds to the IEP (Fig. 9a). The difference between the IEP and the maximum of viscosity or yield stress often exceeds one pH unit, but the qualitative trend is correct: the alkaline-earth metal cations always cause a shift of these maxima to high pH values. At the same time the value of the maximum always increases with ionic strength as shown in Fig. 9b. The pH values of the maximum viscosity are collected in Table 1. The trend for Ba^{2+} is that at low ionic strength the IEP value is equal to or lower than the maximum (viscosity), but at higher ionic strength the opposite is true. The shift of the maximum viscosity is due to the leveling off of the ζ -pH curve after the IEP and the subsequent appearance of the CRP. The

rheological parameters (η , τ) in this range may be considered unstable. This feature is clearly shown for $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Mg}^{2+}$ in Fig. 10, the viscosity (pH) curve having a range which coincides with the IEP. Rather unstable viscosity values are found within a concentration range prior to the CRP. The corresponding yield stress (pH) curve has even more scattered values but otherwise shows the same trend as the viscosity (pH) curve.

For concentrations over $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ca}^{2+}$ and Ba^{2+} the viscosity curves are superimposed for acidic dispersions. At high pH viscosity, values follows a parallel, slightly descending trend as shown in Fig. 11, being close to the viscosity dependence of the $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ NaNO}_3$ system. The curves show that addition of a divalent salt increases the viscosity,

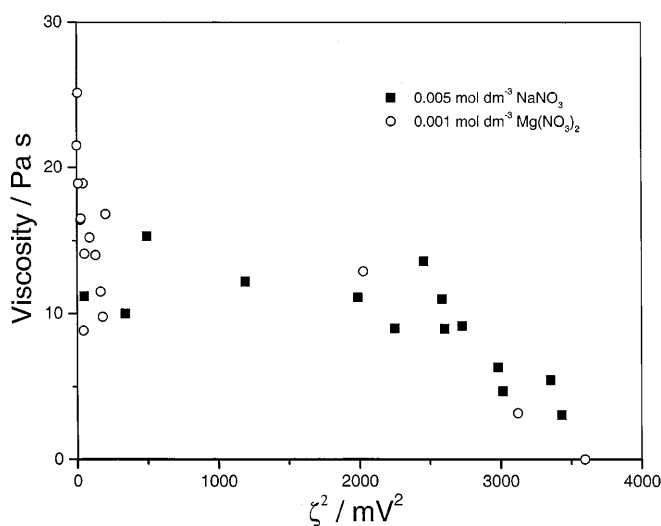


Fig. 8 The relationship between ζ^2 and viscosity of rutile dispersions in the presence of various electrolytes

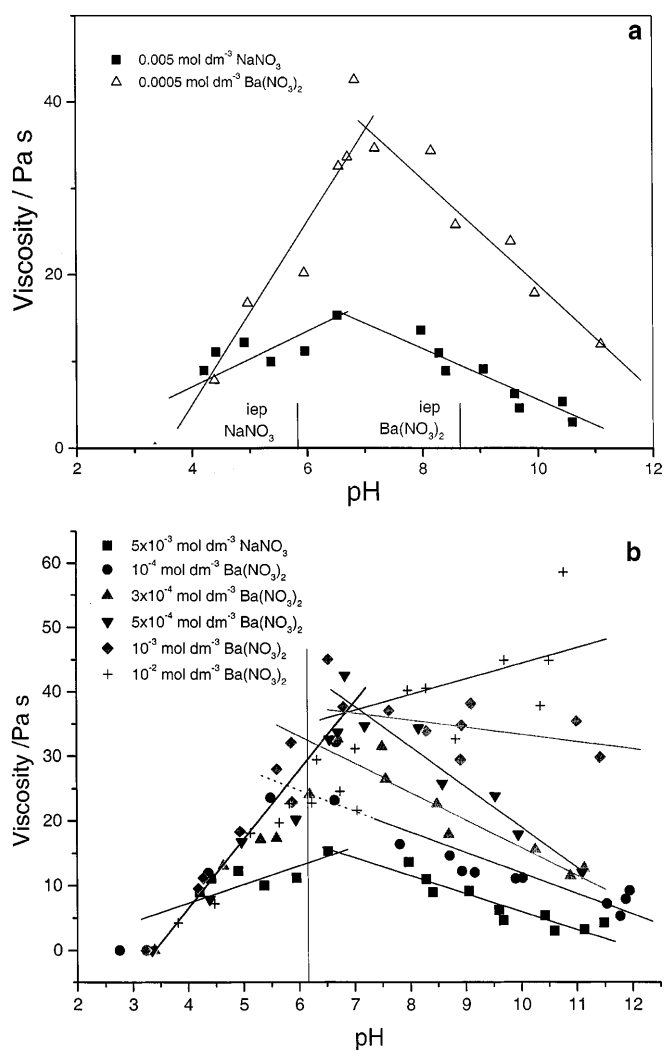


Fig. 9 a Viscosity of rutile dispersions as a function of pH in the presence of $0.005 \text{ mol dm}^{-3} \text{ NaNO}_3$ and $0.0005 \text{ mol dm}^{-3} \text{ Ba(NO}_3)_2$. **b** Viscosity of rutile dispersions as a function of pH for various $\text{Ba(NO}_3)_2$ concentrations

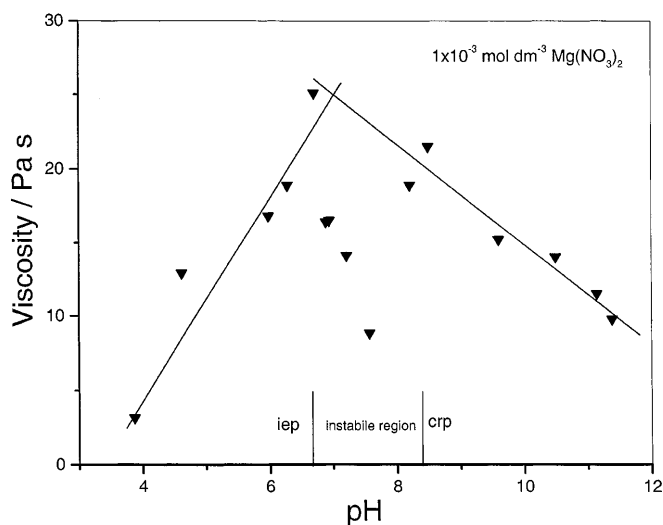


Fig. 10 Viscosity of rutile dispersions as a function of pH in the presence of $0.001 \text{ mol dm}^{-3} \text{ Mg(NO}_3)_2$

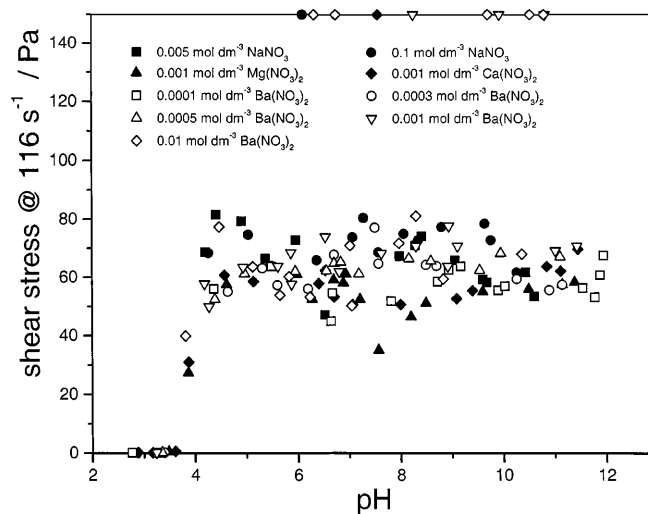


Fig. 12 The shear stress of rutile dispersions at a shear rate of 116 s^{-1} as a function of pH in the presence of various electrolytes

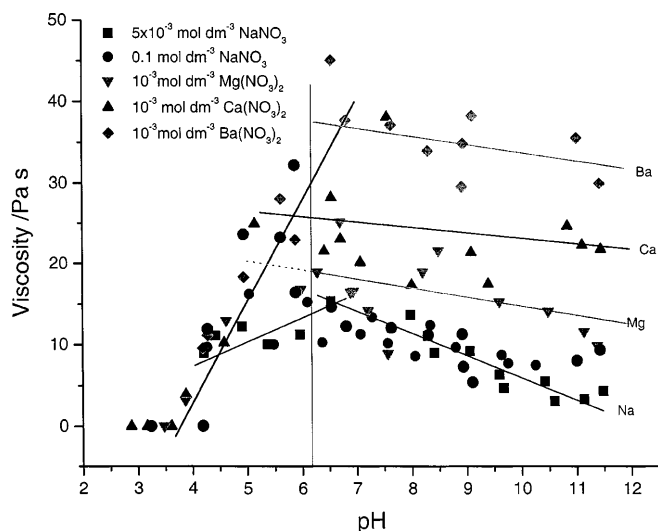


Fig. 11 Viscosity of rutile dispersions as a function of pH for $10^{-3} \text{ mol dm}^{-3} \text{ Mg, Ca and Ba(NO}_3)_2$ with $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ representing an indifferent 1:1 electrolyte

but to different levels for the different 2:1 salts. When comparing the ζ potentials and the viscosity at around $\text{pH} = 10$ for the salts at $1 \times 10^{-3} \text{ mol dm}^{-3}$ it was discovered that the higher the ζ potential was, the higher the viscosity was. The ζ potentials of Ba^{2+} , Ca^{2+} and Mg^{2+} at $\text{pH} = 10$ were 20, 15 and 10 mV, respectively. This also follows the same ion series as the CIP position on the ζ -potential curves. The ζ potential and the viscosity increase at $\text{pH} = 10$ with increasing size of the alkaline-earth metal ions.

The coincidence between the electrokinetic potential and low-shear-rate viscosity is far from ideal, but the

maximum of viscosity approximately matches the IEP, at least at pristine conditions and at low concentrations of alkaline-earth metal cations.

In contrast, the shear stress at high shear rate does not show a maximum at the IEP (Fig. 12). The points on the upper axis only indicate that between the IEP and the CRP the scatter in the data became considerable due to the instability of the dispersions. The shear stress at these pH values may or may not be very high. The points on the lower axis ($\text{pH} < 4$) indicate that the shear stress is certainly less than 1 Pa for given salt concentrations and pH values. The shear stress of rutile dispersions at a shear rate of 116 s^{-1} shows the same pH dependence irrespective of the presence of alkaline-earth metal cations up to $10^{-2} \text{ mol dm}^{-3}$. The shear stress is less than 1 Pa below $\text{pH} 3.8$. In the pH range 5–12 it assumes an almost constant value of 50–80 Pa at 116 s^{-1} with some scatter and an insignificant decrease with pH. In general there is no systematic trend with concentration of alkaline-earth metal cations, but the instability is shown as a larger scatter in the shear stress within the critical pH limits (IEP and CRP).

The increase in the shear stress from less than 1 Pa to the maximum value is observed over the pH range 3.8–4.4, which is well below the pristine IEP, and which is insensitive to the type of divalent salt. This pH range corresponds to a ζ potential of about +60 mV for all the systems for which a shear stress less than 1 Pa was observed.

Conclusion

The results of this study show a CIP for the ζ -potential curves of divalent cations. The position of the CIP on

the ζ -potential axis is related to the size of the alkaline-earth metal cation. The difference between the size of the cations also affects the ζ potential on the alkaline side, giving a higher ζ potential for the larger cation. This phenomenon can also be verified by rheology; the larger the alkaline-earth metal cations, the higher the viscosity at high pH.

The rheology results show a significant difference between low- and high-shear-rate behavior of concentrated rutile dispersions. Both are sensitive to surface charging, but the pH dependencies are completely different. For a low shear rate, of the order of 1 s^{-1} , the maximum of viscosity approximately corresponds to the IEP at low ionic strengths.

Low-viscosity regions exist on both sides of the IEP for intermediate and low ionic strengths, up to $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ba}(\text{NO}_3)_2$, and this is also true for

indifferent electrolytes even at two decades higher concentration.

For ionic strengths greater than $10^{-3} \text{ mol dm}^{-3} \text{ Ba}^{2+}$ and Ca^{2+} the high pH viscosity reaches a plateau, corresponding to a constant ζ potential. In contrast to acidic dispersions, which show an electrolyte-independent behavior, a higher ζ potential gives a higher but equally dependent viscosity in the high pH region. For a high shear rate, of the order of 100 s^{-1} , a low viscosity is observed only at pH values far below the IEP.

The absence of the effect of alkaline-earth metal cations on the high-shear-rate rheology, in spite of their severe effect on the ζ potential, indicates that a simple relationship between the absolute value of electrokinetic potential and high-shear-rate viscosity does not exist. They are, however, related to each other.

References

- Gustafsson J, Mikkola P, Jokinen M, Rosenholm JB Physical Chemistry Chemical Physics (submitted)
- Kosmulski M, Gustafsson J, Rosenholm JB (1999) *J Colloid Interface Sci* 209:200
- Kosmulski M (1997) *Langmuir* 13:6315
- Leong YK, Scales PJ, Healy TW, Boger DV, Buscall R (1993) *J Chem Soc Faraday Trans* 89:2473
- Kosmulski M J (1998) *Colloid Interface Sci* 208:543
- Kosmulski M, Rosenholm JB (1996) *J Phys Chem* 100:11681
- Jang HM, Fuerstenau DW (1986) *Colloids Surf* 21:235
- Kosmulski M, Matijevic E (1992) *Colloids Surf* 64:57
- Lyklema J (1995) *Fundamentals of interface and colloid science*, vol II. Academic Press, London
- Kosmulski M *Colloids Surf* (1995) 95:81
- Rosenholm JB, Manelius F, Strandén J, Kosmulski M, Fagerholm H, Byman-Fagerholm H, Petterson ABA (1998) In: Smart R St C, Nowotny J (eds) *Ceramic interfaces – properties and applications*. IOM Communications, London, pp 433–460
- Kosmulski M, Eriksson P, Gustafsson J, Rosenholm JB *Langmuir* (submitted)
- Lyklema J (1993) *Fundamentals of interface and colloid science*, vol I. Academic Press, London, pp 5.1–5.114
- Hunter RJ, Nicol SK (1968) *J Colloid Interface Sci* 28:250