Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of the European Ceramic Society 26 (2006) 1171–1177
www.elsevier.com/locate/jeurceramsoc

Hydrolysis of carboxylic lactones in alumina slurries

Y. Yin[a, 1], Jon G.P. Binner[b, *, 1], M.J. Hey[c], J.R. Mitchell[d]

[a] *Dytech Corporation Ltd., Dronfield, Sheffield, UK*
[b] *Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough LE113TU, UK*
[c] *School of Chemistry, The University of Nottingham, University Park, Nottingham NG72RD, UK*
[d] *School of Biological Sciences, The University of Nottingham, University Park, Nottingham NG72RD, UK*

Received 20 March 2004; received in revised form 22 December 2004; accepted 10 January 2005
Available online 12 March 2005

Abstract

The hydrolysis of three carboxylic lactones, β-butyrolactone, D-gulonic γ-lactone, and (±)-α-hydroxy γ-butyrolactone, has been investigated in water and electrosterically stabilised alumina slurries. The effect of the acidification behaviour on the viscosity of the alumina slurries due to coagulation has also been studied. It has been found that the reaction temperature has a more significant influence than lactone concentration on the hydrolysis and acidification rate and hence on the time before the slurry becomes sufficiently rigid to be self-supporting.

Keywords: Suspensions; Al_2O_3; Coagulation

1. Introduction

In the wet processing of ceramics, the stability and rheology of a colloidal dispersion depend to a great extent on the electrostatic forces acting between the ceramic particles and the medium. In aqueous systems, the charge on the particles can be controlled by the system pH. If the particles all have the same charge they repel each other and a stable dispersion is formed. At the isoelectric point the particles are uncharged and the system becomes flocculated, for alumina this is typically at a pH of between 7 and 9. In between these extremes, the level of charge, and hence degree of dispersion, can be manipulated readily. If the pH change were activated in situ at a controllable rate, the viscosity of the suspension could be increased or decreased to suit a particular process. One example of such viscosity manipulation is in the coagulation casting of ceramics.[1–3] A low viscosity ceramic dispersion is cast into a mould where an in situ pH change occurs causing a rapid increase in viscosity to a point where the cast body is rigid enough to be de-moulded. This offers the ability to produce complex-shaped ceramics fast and economically.

The hydrolysis of carboxylic esters and their cyclic analogues, lactones, has been intensively investigated for many decades, especially in the biochemical and biological context.[4–10] When mixed with water the lactone-ring opens to form a hydroxy-carboxylic acid, e.g. the hydrolysis of β-butyrolactone (BBL) produces β-hydroxybutyric acid

$$\mathrm{BBL} + H_2O \rightarrow CH_3CH(OH)CH_2CO_2H$$

The hydroxy-acid acid partially dissociates and subsequently acidifies the solution; the amount dissociated being dependent upon the characteristics of the acid in question and the original pH of the medium.

The rate of lactone hydrolysis, which can be several orders of magnitude greater than the hydrolysis of the corresponding open-chain esters, is influenced by many factors the most important of which is the ring-size of the lactone.[9,11,12] There is a decrease in reactivity in the series 6- > 4- > 5- > 7-membered rings, which is attributed to an interplay between conforma-

---

[*] Corresponding author.
E-mail address: j.binner@lboro.ac.uk (J.G.P. Binner).

[1] Formerly with the Department of Materials Engineering and Materials Design, The University of Nottingham, UK.

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.01.037

tional and angle strain effects.[10,13] Because the ring structure forces a *cis* conformation around the acyl carbon-alkyl oxygen linkage, there is an abnormally high dipole moment associated with lactones of 4-, 5- and 6-membered rings, making hydrolysis relatively easy.[14]

In addition to the ring structure, side group attachments also affect the hydrolysis reaction rate and its temperature dependence significantly.[11,15] Research performed by our group[15] using both ceramic slurries and simple aqueous solutions has shown that different side groups and their relative attachment positions to the ring can greatly affect the hydrolysis rate even if the ring member is kept constant. In general, alkyl substitution on the ring decreases the hydrolysis rate whilst OH group substitution increases it. By careful selection of the types of lactones, their concentrations, reaction temperatures and other factors, it is therefore feasible to manipulate the hydrolysis process in a controlled manner to achieve desired ion concentration changes in a system.

The existence of catalysts (acid and base) and different nucleophiles in the system also affects the hydrolysis mechanism. Up to eight reaction routes have been suggested and many of them experimentally observed.[12] The large difference between the $k_{\mathrm{H_2O}}$ and $k_{\mathrm{OH^-}}$ for a particular lactone makes the overall hydrolysis reaction rate highly solution pH dependent. With the formation of the corresponding hydroxy acid and its subsequent dissociation, the solution pH gradually decreases. The reaction mechanism therefore continuously shifts from an $\mathrm{OH^-}$ catalysed second order reaction towards the addition-elimination pathway with water as the predominant nucleophile. With the exception of β-lactones, which exhibit appreciable hydrolysis rates below pH 9 over a wide pH range, all other water-catalysed hydrolyses are extremely slow.[14] As to the alkaline hydrolyses, Blackburn et al [13] pointed out that they are all of unimolecular characteristics, that is, of first-order kinetics.

The ability to change a system's pH with variable rate and equilibrium acidity has resulted in lactones having many practical applications. In particular, since lactones only consist of hydrogen, oxygen and carbon and hence the danger of contamination by added acid ion groups can be kept to minimum, this acidification method has found wide applications in food processing and medicine-related areas.[16–22] The method has also been applied to engineering processes where continuous or time delayed pH changes in solutions or suspensions are needed to control the release of certain ions at a pre-set rate for either accelerating or retarding the process.[1,2,23–25] Easy removal of the reaction products afterwards (by heating or other methods) and reduction of impurities involved during processing make the method very attractive.

The purpose of the present work was to investigate the possibility of using hydroxylic lactones as an in situ pH, and hence viscosity, modifier for aqueous alumina dispersions. This work has since been patented.[26]

2. Experimental

The hydrolysis behaviour of a number of lactones has been investigated using titration and pH measurements in an aqueous alumina slurry. The latter was prepared by stirring alumina powder into a premixed solution of dispersant and deionised water. A fine, calcined alumina powder with an average grain size of 0.5 μm and a specific surface area of $9.2\,\mathrm{m^2\,g^{-1}}$ (A-16SG, Alcoa, USA) was used whilst the dispersant was a 40 wt.% aqueous solution of ammonium polyacrylate (NHPA) with an average molecular weight of 3500 (Dispex A40, Allied Colloids, UK). Based on previous work,[27] the slurry had an 81 wt.% solids content and the dispersant was added at a level of 1.4 mg NHPA per gram of alumina. After vigorous mechanical mixing, the 300 g slurry was exposed to ultrasonic energy for 1.5 min to break up the remaining agglomerates and then stored in refrigerator for at least 24 h to allow sufficient time for complete dispersion. The slurry prepared in this way had a characteristic pH value of approximately 9.45 at ambient temperature and was easily pourable with an average viscosity of 0.5 Pa s at $109\,\mathrm{s^{-1}}$ shear rate.

Out of over twenty lactones tested in the present investigation, three are presented and discussed in this paper: β-butyrolactone (98%), D-gulonic γ-lactone (99%), and α-hydroxy γ-butyrolactone (technical grade), all supplied by Aldrich, Gillingham, Dorset, UK, and used as received without further purification.

The hydrolysis experiments were performed on 50–100 g batches of the slurry that were equilibrated using an ice bath (0 °C), a refrigerator (7 ± 2 °C) and a water bath (25, 35, 45 and 55 °C; all ± 0.5 °C). To reduce liquid condensation onto the inner surfaces of the beaker and cover film, the water bath was placed in a constant temperature chamber of the same temperature as that of the bath. For comparison, one of the lactones, β-butyrolactone, was also hydrolysed in deionised water at pH 9.45 to determine the effect of the presence of the alumina in the slurry on the hydrolysis kinetics. After at least 30 min thermal equilibration, a pre-determined mass of lactone was introduced into the solution or slurry by mechanical stirring. 1 g aliquots were removed at timed intervals and diluted with deionised water at a mass ratio of 1:20 or 1:10 in order to determine the rate of formation of the acid species by titration with 0.1N volumetric standard hydrochloric acid or sodium hydroxide using phenolphthalein as an indicator. For the pH measurements, the lactone concentrations used in the slurry hydrolyses were 1.5×10^{-5}, 2.5×10^{-5}, 4×10^{-5} and 6×10^{-5} mol per gram of slurry, equivalent to 0.0265 M, 0.06625 M, 0.106 M, and 0.159 M by taking the slurry density as $2.650\,\mathrm{g\,cm^{-3}}$. The dissociated acid concentration was monitored at one minute intervals with a pH meter with 4-digit accuracy and temperature compensation (Jenway 3020, Jencon Scientific Ltd., UK), and the electrodes were calibrated before and after each run. The viscosity of the alumina slurry was determined with a rotational viscometer (Bohlin 88, Bohlin Instruments, UK) at a constant shear rate between

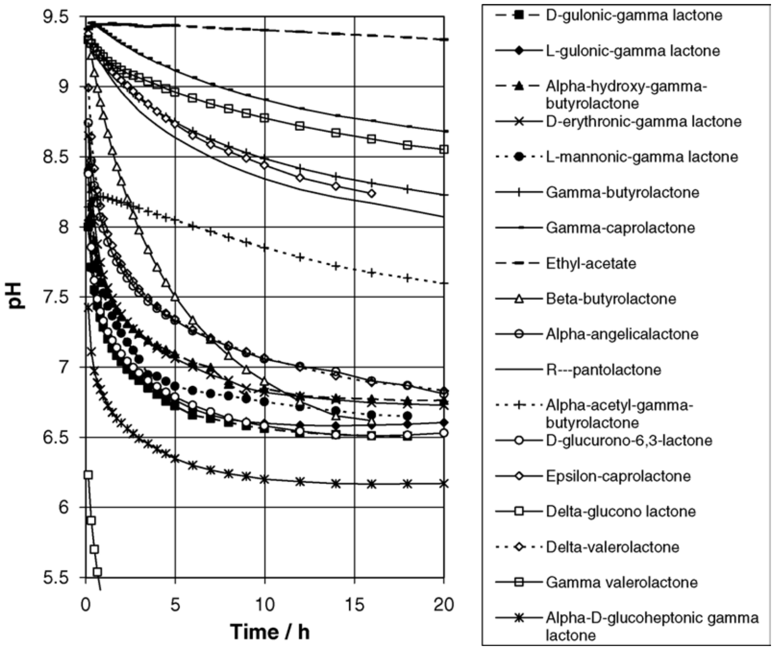

Fig. 1. hydrolysis of various lactones in 81 wt.% alumina slurry at 25 °C. Lactone concentration 4×10^{-5} mol g^{-1} of slurry.

105 and 110 s^{-1}, mimicking the operations of a typical ceramic casting process. An experimentally determined value, pH 7.5, was used as the coagulation point at which the alumina slurry became self-supporting and the piece, without any loss of water, could be safely removed from the non-porous casting mould.

3. Results and discussion

Fig. 1 illustrates the pH changes resulting from the hydrolysis of all the lactones examined in the current study by the alumina slurry. It may be observed that there is a great deal of variation in hydrolysis rate. This is known to be a result of both the size of the ring structure and also the presence of different side attachments. An in-depth examination of the role of the side-attachments is being presented elsewhere.[15]

Fig. 2 shows the kinetics of the hydrolysis of β-butyrolactone in alumina slurry (a) and deionised water (b) at different temperatures. The plots of $\ln[a - c]$ (where a: initial concentration and c: concentration reacted) against time t demonstrate linear behaviour indicating that the hydrolysis reactions have first-order kinetics. This first-order reaction mechanism has been well documented and for β-lactones alkyl-oxygen fission has been shown to be the dominant mechanism, at least in water.[4,28,29]

When other conditions were kept constant, a comparison between the reaction rate constants in deionised water and the alumina slurry, reveals that the hydrolysis rate in the slurry was 2 (at 55 °C) to 12 (at 0 °C) times faster than that in the water. This increase of reaction rate may be explained by the presence of strong nucleophiles and polar species in the slurry system. In weak acid or neutral aqueous solutions the preponderant nucleophile present is water, a poor nucleophile, which reacts slowly to form an intermediate. However, in the alumina slurry many stronger nucleophiles will have been present, such as ammonia, charged acrylate chains and the alumina particle surfaces in addition to the water and hydroxide ions. The alumina particles, in particular, also have inherent impurities such as Na_2O present.

The effect of temperature on the two systems is illustrated by the Arrhenius plot in Fig. 3, which shows the observed reaction rates, k, as a function of temperature. An activation energy for β-butyrolactone hydrolysis in deionised water of 87 ± 5 kJ mol^{-1} was obtained across the temperature range 0–55 °C. This value agrees very well with that obtained for the neutral hydrolysis of β-propiolactone, 82 kJ mol^{-1},[29] and also falls within most of the activation energies obtained from various esters, typically between 65 and 130 kJ mol^{-1}.[4] This high activation energy shows that the water hydrolysis has a strong temperature dependence. Significant reaction rate change can thus be achieved with just a moderate temperature adjustment.

With respect to hydrolysis in the alumina slurry, a smaller activation energy of 59 ± 5 kJ mol^{-1} was obtained. This lower value is probably a result of a surface catalysed hydrolysis process taking place on the particle surfaces. However, it is still significant enough to cause the hydrolysis time to vary from less than one hour at 55 °C to virtually infinite at 0 °C.

Fig. 4 shows the effect of lactone concentration (a) and temperature (b) on the rate of pH change for β-butyrolactone. It may be seen that in both cases there is an initial rapid pH de-

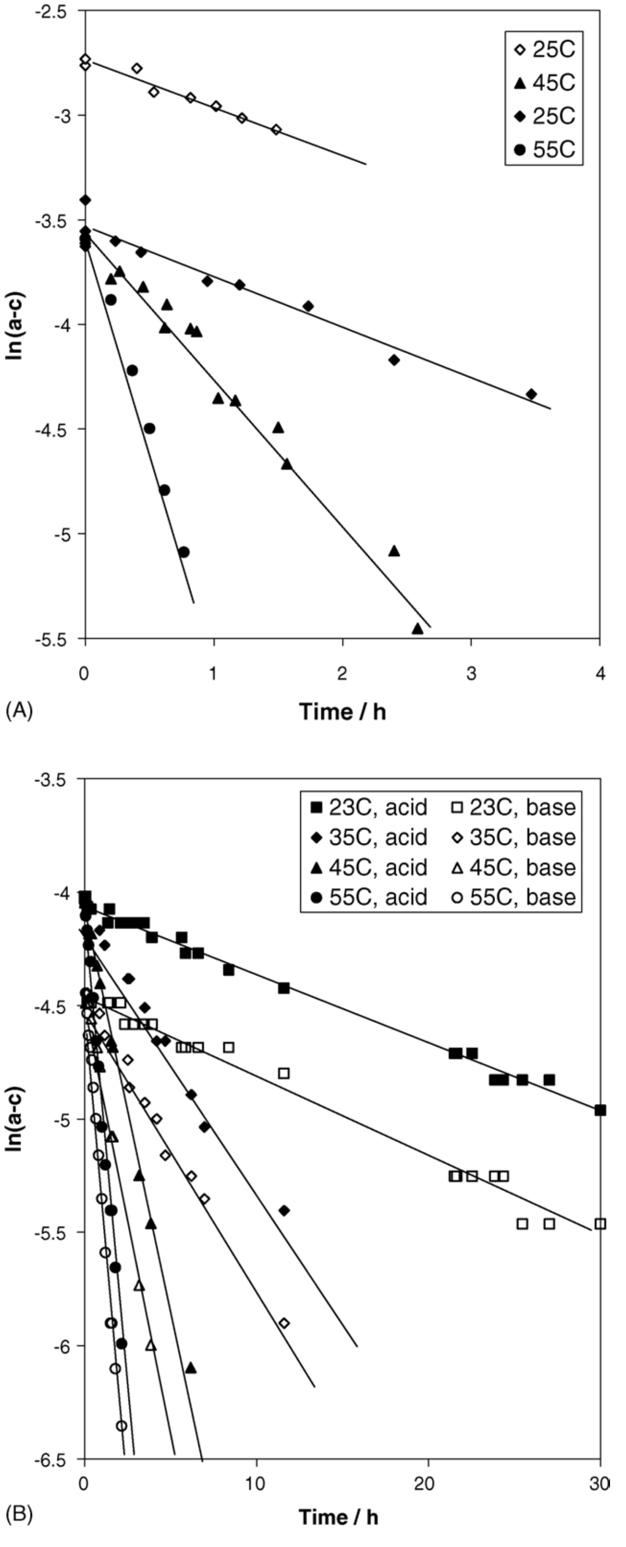

Fig. 2. Kinetics of β-butyrolactone hydrolysis in alumina slurry (A) and deionised water (B). The initial lactone concentration in (A) was 1.5×10^{-5} mol per gram of slurry. 0.005N HCl or NaOH were added to the water in (B) to act as catalysts.

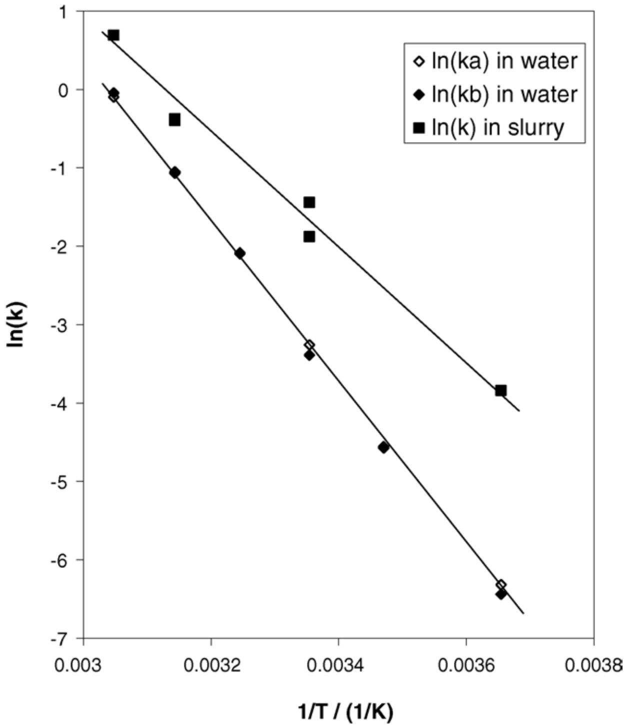

Fig. 3. Arrhenius plot of the effect of temperature on the hydrolysis of β-butyrolactone in water and alumina slurry.

crease followed by a more gradual change as the system heads towards equilibrium. If a parabolic relationship between pH change, ΔpH, and time, *t*, is assumed:

$$\Delta \mathrm{pH} = -A\sqrt{t}$$

then when all the data gathered is considered, the constant *A* is found to be more sensitive to temperature than initial lactone concentration.

Acidification rates, i.e. $d[H^+]/dt$, are plotted against time in Fig. 5 for different initial concentrations of β-butyrolactone. It can be seen that the acidification rates reach a maximum at about 300 min after initiation of reaction, increasing slightly with increasing lactone concentration. This suggests that the hydrolysis process is dependent on the solvent pH. It must be remembered that the latter is continuously shifting as the hydrolysis proceeds. Hence, the proportion of acid- and base-catalysed reactions, relative to hydrolysis by the weak nucleophile H_2O, changes accordingly. This gradual change of reaction mechanism is found to be particularly common with β-lactones.[4,27]

Since the β-hydroxybutyric acid formed is a weak acid, the proportion of the acid dissociated depends on the pH according to the Henderson–Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}[\text{carboxylate}]/[\text{carboxylic acid}]$$

where $\mathrm{p}K_a$ is the negative logarithm of the acid dissociation constant. From the combined results of titration and pH experiments, $\mathrm{p}K_a$ for the β-hydroxybutyric acid in de-ionised water was found to be 4.68 at 25 °C, comparable to the value

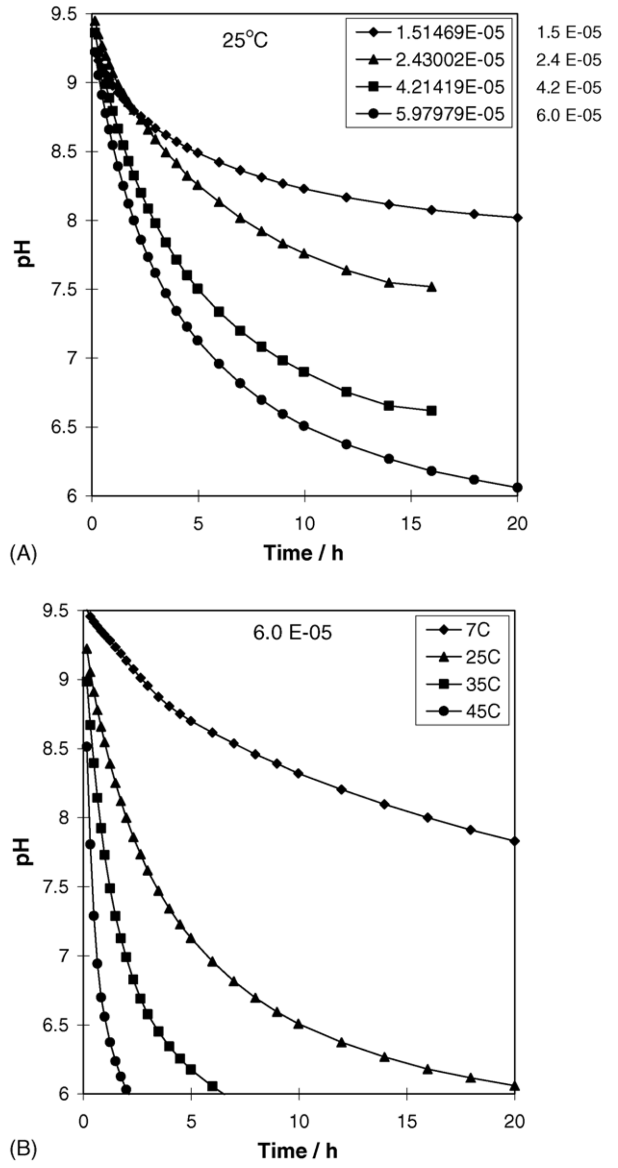

Fig. 4. Hydrolysis of β-butyrolactone in alumina slurry: (A) lactone concentrations are in mol per gram of slurry. Reaction temperature: 25 °C; (B) lactone concentration: 6.0 × 10^{-5} mol per gram of slurry.

for butyric acid at the same temperature (pK_a = 4.82). The dissociation of the hydroxy-acid would therefore be expected to vary from effectively 100% at pH 9 to around 95% at pH 6. At its peak in the reaction process, the RCOOH formation was measured to be around 200 times faster than the formation rate of [H^+]. On the other hand, in the alumina slurry the RCOOH formation was 2500–3000 times faster than the rate of [H^+] formation. This suggests that the equivalent K_a in the ceramic slurry is one to two orders of magnitude smaller. However this conclusion must be regarded with care since there was always a mismatch between titration and pH values, even when β-hydroxybutyric acid was added directly into the system. It is quite probable that the hydroxy-acids adsorbed onto the alumina particles [30] and it is also possible that they underwent further reactions to form salts or complexes.[31]

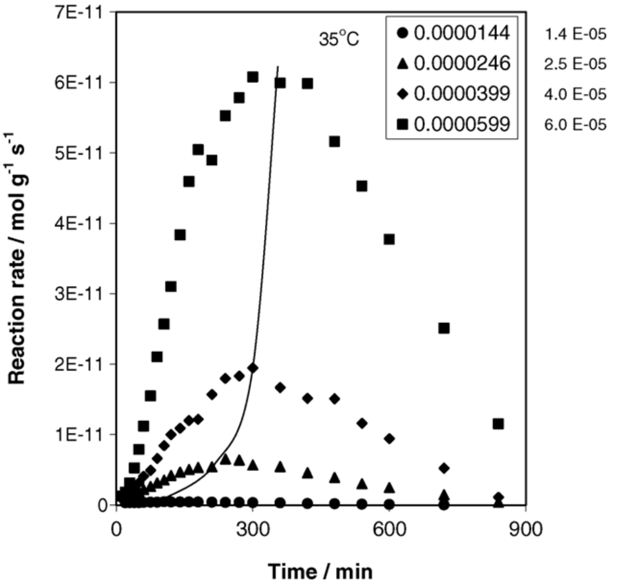

Fig. 5. Time dependence of the rate of β-butyrolactone hydrolysis in slurry. Experiment temperature 35 °C. Legend shows initial lactone concentrations in mol per gram of slurry.

At 81 wt.% solids loading, the alumina slurry under investigation had a very large viscosity swing from 0.5 Pa s at pH 9.5 to over 20 Pa s (the upper limit for the viscometer used) in the pH range between 4 and 9. The casting experiments showed that when the system pH reached 7.5 the gelled slurry was rigid enough to be self-supporting and could be removed from the mould without deformation. Work at a lower solids loading of 70 wt.% revealed the approximate shape of the curve, Fig. 6. Fig. 7 shows the hydrolysis time, defined as the time to reach pH 7.5 after the addition of the lactone, as a function of temperature and concentration. The data support Fig. 4 in showing that temperature has a stronger influence on hydrolysis than lactone concentration.

Figs. 8 and 9 show the results obtained from the hydrolysis of D-gulonic γ-lactone and α-hydroxy-γ-butyrolactone at

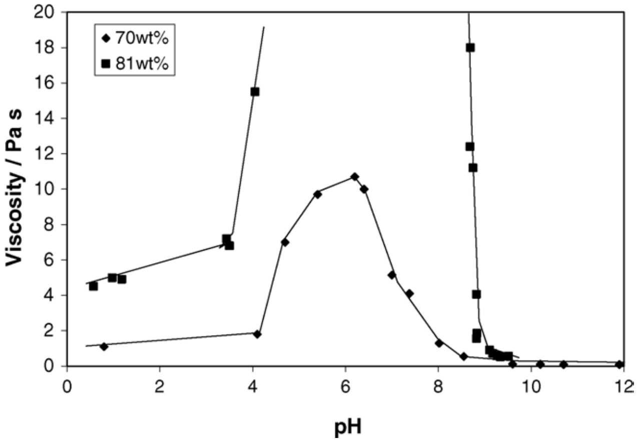

Fig. 6. The relationship between the slurry viscosity and pH. Both slurries are dispersed with the ammonium polyacrylate dispersant.

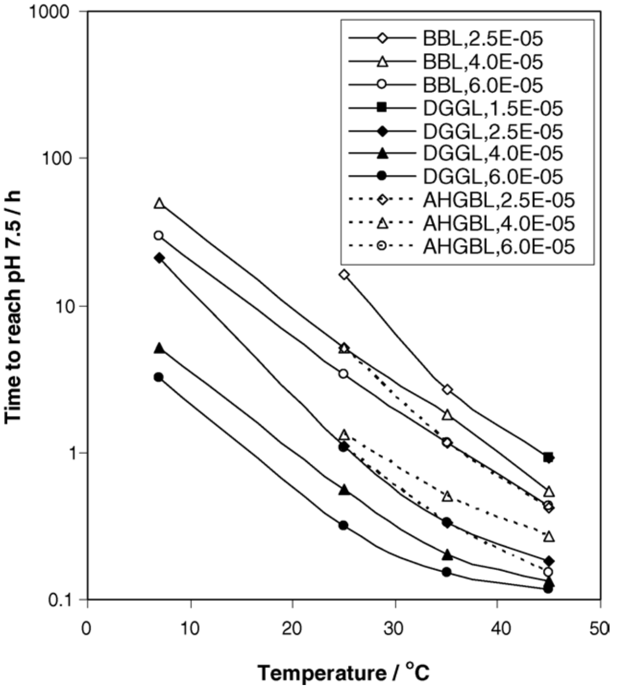

Fig. 7. The influences of reaction temperature and lactone concentration on hydrolysis time for the system to reach pH 7.5. BBL: β-butyrolactone; DGGL: D-gulonic-γ lactone; AHGBL: α-hydroxy-γ-butyrolactone.

35 °C. Comparison with Fig. 5 shows that a totally different shape of curve was obtained in both cases (the ‘bell-shaped’ curve of Fig. 5 was only seen with 4-membered ring lactones). Assuming that the same type of series reaction with a reversible step was occurring, then it suggests that there was a significant difference in the relative values of k, k_{-1} and k_2. The shape of the curves suggests that k_{-1} was much smaller and that the reaction pathway was tending towards a consecutive first-order reaction.

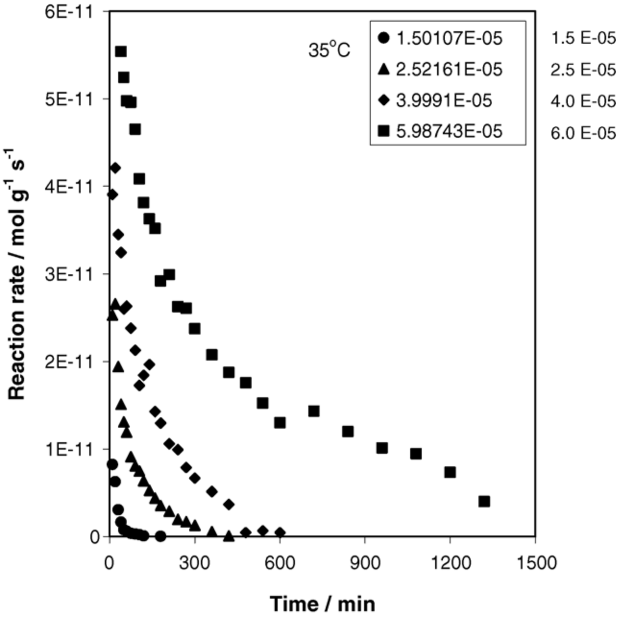

Fig. 8. The influence of D-gulonic-γ lactone concentration on hydrolysis rate in the alumina slurry. Experiment temperature 35 °C.

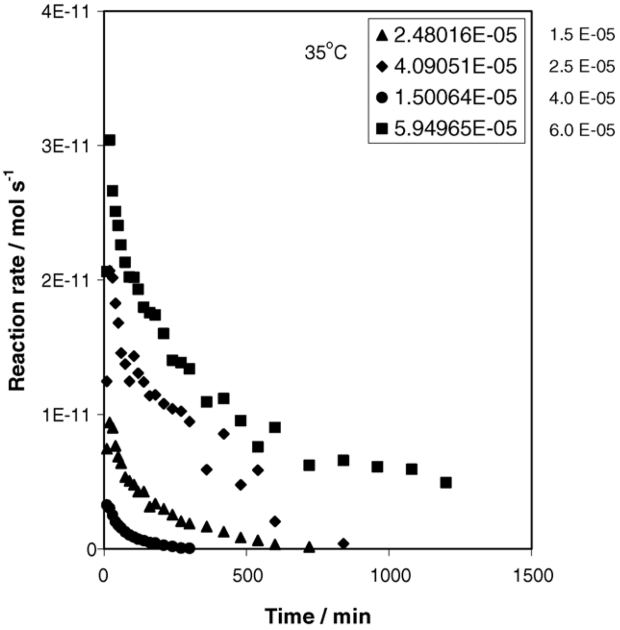

Fig. 9. The hydrolysis of α-hydroxy-γ-butyrolactone in alumina slurry. Legend shows the initial lactone concentration and the experiment temperature is 35 °C.

It is interesting that Figs. 8 and 9 show similar behaviour, the differences being attributed to the number of hydroxyl ion substitutions of hydrogen ions on the lactone ring structure.[12] Both α-hydroxy-γ-butyrolactone and D-gulonic-γ lactone are five membered-ring lactones with the former having one and the latter four OH substitutions. When in certain conformations the OH side groups can hydrogen bond with the incoming water molecule and effectively trap the water close to the carbonyl carbon and hence hydrolyse more easily.[8,12] The influence of these OH traps, however, was found to be only effective in the alkaline catalysed region. No apparent difference in water catalysed hydrolysis was observed within the experimental accuracy limit.

4. Conclusions

The hydrolysis of β-butyrolactone in both water and alumina slurries showed first-order reaction kinetics and the reaction rate in the alumina slurries was about an order of magnitude higher than in the water. Temperature showed a significant influence on the reaction rate with the activation energy being $87.5 \pm 5\,\mathrm{kJ\,mol^{-1}}$ in water and $59 \pm 5\,\mathrm{kJ\,mol^{-1}}$ in the alumina slurries. The catalysis process was, however, found to be pH dependent.

Hydrolysis of both D-gulonic-γ lactone and α-hydroxy-γ-butyrolactone showed similar behaviour to each other but very different to that of the β-butyrolactone. The difference in the reaction rate was primarily attributed to the difference in side group attachments.

As the pH of the alumina suspension approached the isoelectric point the viscosity increased significantly until the material was self-supporting. This allowed the process to be used to produce green bodies that could be removed after casting for as little as ∼10 min in a mould.

References

1. Graule, T. J., Baader, F. H. and Gauckler, L. J., Casting uniform ceramics with direct coagulation. *Chemtech.*, 1995, **25**, 31–37.
2. Graule, T. J., Gauckler, L. J. and Baader, F. H., Direct coagulation casting—a new green shaping technique, Pt.1 Processing principles. *Ind. Ceram.*, 1996, **16**, 31–35.
3. Graule, T. J. and Gauckler, J. L., Process for producing Ceramic Green Bodies, EU Patent EP0605694 (1994) and US Patent US5667548 (1997).
4. Benkovic, S. J., Kirby, A. J. and Talbot, R. J. E., Comprehensive chemical kinetics. In *Ester Formation and Hydrolysis and Related Reactions*, *vol. 10*, ed. C. H. Bamford and C. F. H. Tipper. Elsevier, Amsterdam, 1972.
5. Wiberg, K. B., Waldron, R. F., Schulte, G. and Saunders, M., Lactones. 1. X-ray crystallographic studies of nonanolactone and tridecanolactone: nature of CH···O nonbonded interactions. *J. Am. Chem. Soc.*, 1991, **113**, 971–977.
6. Wiberg, K. B. and Waldron, R. F., Lactones. 2. Enthalpies of hydrolysis, reduction and formation of the C4-C13 monocyclic lactones. Strain energies and conformations. *J. Am. Chem. Soc.*, 1991, **113**, 7697–7705.
7. Huisgen, R. and Ott, H., Die konfiguration der carbonestergruppe und die sondereigenschaften der lactone. *Tetrahedron*, 1959, **6**, 253–267.
8. Jencks, W. P. and Carriuolo, J., Reactivity of nucleophilic reagents toward esters. *J. Am. Chem. Soc.*, 1960, **82**, 1778–1786.
9. Kaiser, E. T. and Kezdy, F. J., Hydrolysis of cyclic esters. In *Progress in Bioorganic Chemistry*, *4*, ed. E. T. Kaiser and F. J. Kezdy. Wiley Interscience, NY, 1976, pp. 239–267.
10. Boyd, G. V., The chemistry of lactones and lactams. In *The Chemistry of Acid Derivatives, Supplement B, Part 1*, ed. S. Patai. John Willey and Sons, Chichester, 1979, pp. 491–531, Chapter 10.
11. Streitwieser, A., Heathcock, C. H. and Kosower, E. M, *Introduction to Organic Chemistry* (*4th ed.*). Macmillan Publishing Company, NY, 1992.
12. March, J., *Advanced organic chemistry, reactions, mechanisms and structure* (*3rd ed.*). John Wiley and Sons, NY, 1985.
13. Blackburn, G. M. and Dodds, H. L. H., Strain effects in acyl transfer reactions. Part III, hydroxide and buffer-catalysed hydrolysis of small and medium ring lactones. *J. Chem. Soc. Perkin Trans. II*, 1974, pp. 377–382.
14. Albert, A., *Heterocyclic Chemistry an Introduction* (*2nd ed.*). The Athlone Press, London, 1968, pp. 16–19.
15. McDermott, A. and Binner, J. G. P., In-situ acidification of electrosterically dispersed alumina suspensions: effect of coagulant structure. *J. Eur. Ceram. Soc.*, submitted for publication.
16. Kohyama, K., Yoshida, M. and Nishinari, K., Rheological study on gelation of soybean-11S protein by glucono-delta-lactone. *J. Agric. Food Sci.*, 1992, **40**, 740–744.
17. Malin, M., Hiljanenvainio, M., Karjalainen, T. and Seppala, J., Biodegradable lactone copolymers. 2. Hydrolytic study of epsilon-caprolactone and lactide copolymers. *J. Appl. Polym. Sci.*, 1996, **59**, 1289–1298.
18. Wibullucksanakul, S., Hashimoto, K. and Okada, M., Swelling behavior and controlled-release of new hydrolyzable poly(ether urethane) gels derived from saccharide and L-lysine derivatives and poly(ethylene glycol). *Macromol. Chem. Phys.*, 1996, **197**, 1865–1876.
19. Lucey, J. A., van Vliet, T., Grolle, K., Geurts, T. and Walstra, P., Properties of acid casein gels made by acidification with glucono-delta-lactone. 1. Rheological properties. *Int. Dairy J.*, 1997, **7**, 381–388.
20. Eleya, M. M. O., Banon, S. D. and Hardy, J., A comparative study of pH and temperature effects on the acidic coagulation of milks from cows, goats and sheep. *J. Dairy Sci.*, 1995, **78**, 2675–2682.
21. Mouquet, C., Aymard, C., Guilbert, S., Cuvelier, G. and Launay, B., Influence of initial pH on gelation kinetics of texturized passion fruit pulp. *Food Sci. and Tech.—Lebensmittel-Wissenschaft and Technologie*, 1997, **30**, 129–134.
22. Fly, J. A., Clarke, P. T., DuParquet, H., Toyne, S. and Ausustin, M. A., Use of glucono-delta-lactone in the manufacture of yogurt. *Austr. J. Dairy Tech.*, 1997, **52**, 20–23.
23. Sugama, T., Carciello, N. R. and Gray, G., Alkali carbonation of calcium aluminate cements: influence of set-retarding admixtures under hydrothermal conditions. *J. Mater. Sci.*, 1992, **27**, 4016–4909.
24. UK Patent, GB2111041-A, Reactivatable Set-Inhibited Cemenitious Compositions, 29/06/83.
25. Ingold, C. K., *Structure and Mechanism in Organic Chemistry* (*2nd ed.*). Cornell University Press, NY, 1969, Also see summary in Ref. [9], pp. 334–338.
26. International patent: WO 96/04219. Coagulation to make dense ceramics. Sambrook, R. M., Binner, J. G. P., Davies, J., and McDermott, A. J., 1996 and European patent: EP 0773913. Making dense ceramics by coagulation. Sambrook, R. M., Binner, J. G. P., Davies, J. and McDermott, A. J., 2001.
27. McDermott, A., Direct Coagulation of Ceramics, PhD thesis, The University of Nottingham, 2000.
28. Olson, A. R. and Miller, R. J., The mechanism of the aqueous hydrolysis of β-butyrolactone. *J. Am. Chem. Soc.*, 1938, **60**, 2687–2692.
29. Long, F. A. and Purchase, M., The kinetics of hydrolysis of β-propiolactone in acid, neutral and basic solutions. *J. Am. Chem. Soc.*, 1950, **72**, 3267–3273.
30. Hidber, P. C., Graule, T. J. and Gauckler, L. J., Influence of the dispersant structure on properties of electrostatically stabilised aqueous alumina suspensions. *J. Eur. Ceram. Soc.*, 1997, **17**(2/3), 239–249.
31. Connors, K. A., *Chemical Kinetics, the Study of Reaction Rates in Solution*. VCH Publishers, Inc., NY, 1990.