Condensation and gelation of inorganic ZrO_2–Al_2O_3 sols

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The Partial Charge Model has been applied to analyse quantitatively experimental data on the process of hydrolysis and condensation, leading to gelation of Al^{3+} and Zr^{4+} cations in acidic concentrated inorganic sols. Both Al^{3+} and Zr^{4+} can condense to high polymeric species, but Zr^{4+} requires a higher ratio of hydrolysis than aluminium to initiate polymerization. Oxolation may occur in both aluminium and zirconium precursors. The role of anions in the polymerization process may also be calculated by this model and is assessed. In mixed Al–Zr gel systems, ^{27}Al nuclear magnetic resonance shows that Al^{3+} does not participate in the initial polymerization, but instead decomposes to low polymer species upon mixing. Ageing has little effect on the polymerization of Al^{3+}. Calorimetry shows that the polymerization of Zr^{4+}, initiated by aluminium, accelerates at the beginning and gradually slows down after passing through a rate maximum. For mixtures of aluminium and zirconium precursors, temperature, composition (Al/Zr ratio) and concentration can significantly affect the rate of polymerization, as estimated from the rate of heat evolution.

1. Introduction
Zirconia-toughened ceramics have attracted wide attention because of their unique mechanical properties. However, difficulties can arise in processing conventional ceramic powder precursors; sol–gel precursors are a possible alternative route. Sol–gel processing offers the possibility of making ultrahomogeneous structures at the molecular level and has been widely used in the synthesis of glass and ceramics [1–4]. Many papers have been published on ZrO_2–Al_2O_3 sol–gel methods, but most published methods require organometallic precursors, such as the alkoxides of aluminium and zirconium [2–4], but these are expensive and, moreover, it is not easy to eliminate carbon residues arising from the organic ligands after firing [5]. Inorganic precursors may reduce these disadvantages and are relatively inexpensive and widely available [6, 7]. However, it is characteristic of sol–gel methods that the quality of the product is influenced by all stages of precursor manipulation, including events occurring during the sol–gel transformation, and that this stage of the process is largely empirical.

Basically, the sol–gel process implies the synthesis of an inorganic network by chemical reaction in solution at low temperature. The mechanism of sol–gel transformation has been studied by various methods. The reaction mechanisms have been most extensively studied for silica, but rather less so for other metal oxide precursors. The aqueous chemistry of inorganic salts is quite complicated because of hydrolysis reactions and the experimental difficulties of characterizing aqueous species. Simple ions, e.g. Al^{3+}, Zr^{4+}, do not exist in significant concentrations in the crucial range for gelation; instead complex new ionic species or precipitates develop, depending on pH and concentration. Therefore, it is essential to develop a clearer understanding of solution speciation and of the mechanisms whereby condensation can occur. Theory can assist: Livage and co-workers have developed a Partial Charge Model [8, 9], which provides insight into inorganic polymerization pathways and enables us to predict the nature of stable cation species by calculating the magnitude of partial charge transfer between oxo-, hydroxo-, or aquo-ligand and cations.

In the present investigation, the Partial Charge Model has been applied, used to calculate the partial charge transfer between selected aluminium and zirconium cation species and associated ligands, and thereafter, to predict the speciations of cations and the pathways to polymerization of mixtures of Al_2O_3 and ZrO_2 sols and to correlate experimental data. The nature of Al^{3+} species in precursors and speciation changes occurring during sol–gel transformations have also been determined by ^{27}Al nuclear magnetic resonance (NMR). The kinetic processes of gelation and accompanying enthalpy changes have been determined by isothermal conduction calorimetry.

2. Experimental procedure
Different inorganic precursors containing basic Al^{3+} and Zr^{4+} salts were prepared. The main precursor was ZrO_2 sol, which, upon analysis, corresponded to $Zr(OH)_{2.95}(NO_3)_{1.05}$ (3.65 M in zirconium) [10]. Two kinds of Al^{3+} precursors were used: the main precursor was $Al_2(OH)_5Cl$ (6.17 M in aluminium, Albright and Wilson Ltd, and referred to as Al_2O_3 sol); but other precursors used to study the role of anions include partially denitrated $Al(OH)_x(NO_3)_{3-x}$

(2.10 M in aluminium) made from $Al(NO_3)_3$ with controlled basicity, x; values of x range from 1.1–2.1.

^{27}Al NMR chemical shifts were determined relative to a 0.1 M solution of $Al(NO_3)_3$. The principal aluminium species in this solution is $Al(H_2O)_6^{3+}$ [11–13]. The spectra were obtained on a Bruker spectrometer, operating at 65.2 MHz under static conditions. The pulse time was 11.4 μs with 1 s delay.

Thermal events associated with sol–gel transformation were traced on a JAF conduction calorimeter. This calorimeter was originally designed for measuring isothermal heats of hydration of cement, so it has a very stable baseline which enables slow heat evolutions, up to ~72 h, to be measured. It is thus very suited to following sol–gel transformations which typically require some minutes or hours for comple-

3.1.1. Hydrolysis and condensation of Al^{3+} and Zr^{4+}

Under conditions of decreasing acidity, the reaction

$$[MO_nH_{2n}]^{z+} + sH_2O$$
$$= [MO_nH_{2n-s}]^{(z-s)+} + sH_3O^+ \quad (3)$$
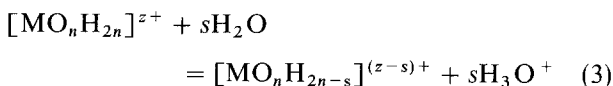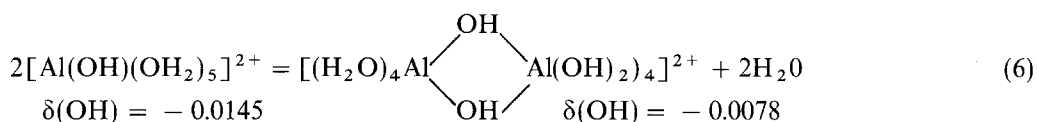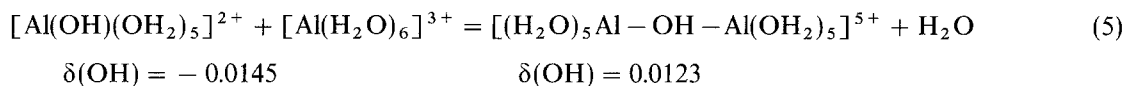
will continue until $\delta(OH) = 0$, leading to charge conservation [9]

$$s = 1.45Z - 0.45n - 1.07(2.71 - x_M^0)/X_M^{0\,1/2} \quad (4)$$

where x_M^0 is the electronegativity of the neutral atom M. In the present case, both Al(III) and Zr(IV) have two species in equilibrium: see Table I.

The condensations of both Al(III) and Zr(IV) commence with olation; they first form a hydroxo bridge, M–OH–M [12]. For Al(III), dimerization may take the form

$$[Al(OH)(OH_2)_5]^{2+} + [Al(H_2O)_6]^{3+} = [(H_2O)_5Al - OH - Al(OH_2)_5]^{5+} + H_2O \quad (5)$$
$$\delta(OH) = -0.0145 \qquad \qquad \delta(OH) = 0.0123$$

$$2[Al(OH)(OH_2)_5]^{2+} = [(H_2O)_4Al \underset{OH}{\overset{OH}{<}} Al(OH)_2)_4]^{2+} + 2H_2O \quad (6)$$
$$\delta(OH) = -0.0145 \qquad \qquad \delta(OH) = -0.0078$$

tion. In this method, one sol is placed in the calorimeter cell and the second sol is added also thermally equilibrated by injection. The duration between readings of the heat evolution over the first 20 min were 3 s, subsequently increased to 2 min.

3. Results and discussion
3.1. Application of the partial charge model to the ZrO_2–Al_2O_3 sol–gel system

When two atoms combine, a partial electron transfer occurs so that each atom acquires a positive or negative partial charge, δ_i. The process of charge transfer will stop when the electronegativities of all constituent atoms become equal to the mean electronegativity, $\bar{X}$. The partial charge, δ_i, can be deduced from the relationships [8, 9]

$$\delta_i = (\bar{X} - X_i^0)/k\bar{X}_i^{0\,1/2} \quad (1)$$

and

$$\bar{X} = (p_iX_i^{0\,1/2} + kz)/(p_i/X_i^{0\,1/2}) \quad (2)$$

where $\bar{X}$ is mean electronegativity of all constitutent atoms as defined in Equation 2; p_i corresponds to the stoichiometry of ith atom in the compound and z is the total charge of the ionic species; X_i^0 is the electronegativity of the neutral atom and k is a constant which depends on the electronegativity scale ($k = 1.36$ for the Pauling scale). This partial charge model (PCM) can predict the relative stabilities of different forms of a given cation in aqueous solution.
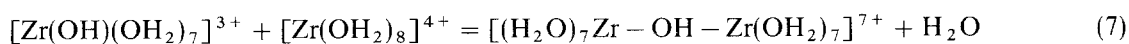
TABLE I Data for the most acidic forms of Al(III) and Zr(IV)

M	z	n	X_M^0	$2n - p$	Couple
Zr	4	8	1.29	11.41	$[Zr(OH)(OH_2)_7]^{3+}/[Zr(OH_2)_8]^{4+}$
Al	3	6	1.50	15.14	$[Al(OH)(OH_2)_5]^{2+}/[Al(H_2O)_6]^{3+}$

The numerical value of δ for the product indicates whether reaction can continue stepwise. In these examples, polymerization is predicted not to continue indefinitely to form a solid phase. This is mainly due to the fact that the nucleophilic strength of the hydroxo group changes during the condensation process. For Reaction 5, $\delta(OH) = -0.0145$ in the monomer (favourable) and 0.0123 in the dimer, so it is not energetically feasible for reaction to proceed beyond this step. But for Reaction 6, $\delta(OH) = -0.0145$ in the monomer and -0.0078 in the dimer; the hydroxo group remains negatively charged and keeps some nucleophilic character. Condensation can proceed further towards a higher polymer $[Al_3(OH)_4(H_2O)_{10}]^{5+}$, whose $\delta(OH) = -0.0064$, which still remains negatively charged. Therefore, condensation may proceed further, eventually yielding a much higher polymer. The monomeric unit $Al(H_2O)_6^{3+}$, and its dimer and trimer, $Al_2(OH)_2(H_2O)_8^{4+}$ and $Al_3(OH)_4(H_2O)_{10}^{5+}$, have been observed and characterized by potentiometry [14]. Experimentally, they are observed to be relative stable polynuclear hydrolysis products and this is supported by calculation. Occasionally, very high polymers occur, such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, which was found by Johansson in the solid state [15], and which was also reported to occur in solution from ^{27}Al NMR studies by Akitt and co-workers [16–19]. The value of $\delta(OH)$ in this Al_{13} polymer is -0.0460, so it is still capable of further polymerization. The existence of still higher polymers is thus predicted, although they have not been reported. The Al_{13} unit, it may be noted, is formed by oxolation and is not stable under conditions of low pH.
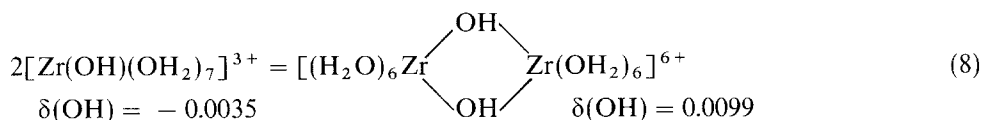
Zr(IV) cannot condense in the same way as Al(III). For example, writing reactions which are mechanistic-

ally the same as for aluminium

$$[Zr(OH)(OH_2)_7]^{3+} + [Zr(OH_2)_8]^{4+} = [(H_2O)_7Zr - OH - Zr(OH_2)_7]^{7+} + H_2O \qquad (7)$$

$$\delta(OH) = -0.0035 \qquad\qquad \delta(OH) = 0.0167$$

$$2[Zr(OH)(OH_2)_7]^{3+} = [(H_2O)_6Zr \overset{\displaystyle OH}{\underset{\displaystyle OH}{<\quad>}} Zr(OH_2)_6]^{6+} \qquad (8)$$

$$\delta(OH) = -0.0035 \qquad\qquad\qquad \delta(OH) = 0.0099$$

The numerical value of $\delta(OH)$ in both resulting condensations, Reactions 7 and 8, is calculated to be positive, so the condensation would not go beyond these steps. Thus, condensation of Zr(IV) should not involve the mechanisms of Reactions 7 and 8. Instead, the initial steps must involve further hydrolysis, for example, to form $[Zr(OH)_2(H_2O)_6]^{2+}$ [20]. Calculation shows that a high ratio of hydrolysis will promote subsequent polymerization. Then
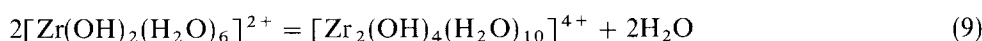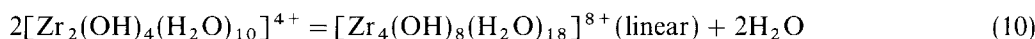
that oxy-hydroxides, i.e. precursors with bridges M–O–M, can be obtained for most Al(III) and Zr(IV) precursors.

3.1.3. Role of anions
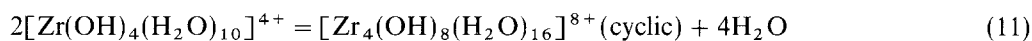The role of the counter anion has thus far been neglected.

$$2[Zr(OH)_2(H_2O)_6]^{2+} = [Zr_2(OH)_4(H_2O)_{10}]^{4+} + 2H_2O \qquad (9)$$

$$\delta(OH) = -0.0319 \qquad\qquad \delta(OH) = -0.0221$$

$\delta(OH)$ is still negative, so $[Zr_2(OH)_4(H_2O)_{10}]^{4+}$ can condense further

$$2[Zr_2(OH)_4(H_2O)_{10}]^{4+} = [Zr_4(OH)_8(H_2O)_{18}]^{8+}(linear) + 2H_2O \qquad (10)$$

$$\delta(OH) = -0.0221 \qquad\qquad \delta(OH) = -0.0160$$

and

$$2[Zr(OH)_4(H_2O)_{10}]^{4+} = [Zr_4(OH)_8(H_2O)_{16}]^{8+}(cyclic) + 4H_2O \qquad (11)$$

$$\delta(OH) = -0.0221 \qquad\qquad \delta(OH) = -0.0088$$

The hydroxo groups remain negatively charged and keep some nucleophilic character in Reactions 10 and 11. So, condensation can proceed further towards higher polymers. Zr(IV) has a great tendency to polymerize by this route with no limiting value of molecular weight evident [20].

3.1.2. Oxolation
Oxolation leads to the formation of oxo bridges, M–O–M, between two metal cations M. The condition for oxo bridge formation is that $\delta(H_2O) > 0$ in the following equilibrium [9]

$$
\begin{array}{c}
H(\delta^+)(\delta^+)H - OH - (\delta^-) \\
| \qquad\qquad | \\
-M-O-M- = - M-O-M- \\
| \\
OH(\delta^-)
\end{array}
\qquad (12)
$$
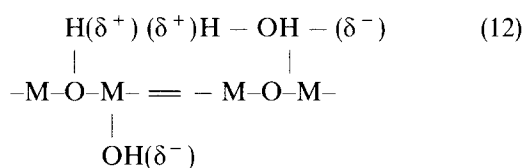
Table II shows the calculated results of $\delta(H_2O)$ for Al(III) and Zr(IV) aquo-hydro ligands. It shows

lected. However, the anion plays a very important role in the control of the hydrolysis and condensation of the inorganic precursor. The gelation time of many gel systems, notably of Al–Zr mixed gels, can be affected by the presence of an acid catalyst [6]. Chemical control of nucleation and growth in aqueous solutions is often achieved by making a correct choice of anion, which is thus important to successful preparation of the final product. The anions may play two roles: chemical or (and) physical. The chemical role of the anion in influencing the pH of the system and its ability to participate in acidic buffers is comparatively well documented in standard textbooks. The physical role is less well documented. The anion can coordinate to the metal atom directly, leading to formation of a new molecular precursor whose chemical reactivity towards hydrolysis and condensation is altered, or the anion may participate as counter ions in an aquated $M(H_2O, OH^-)$ complex, forming an electrical double layer and thereby modifying the ionic strength

TABLE II Stability of some Al(III) and Zr(IV) precursors deduced from Partial Charge Model calculations
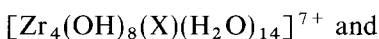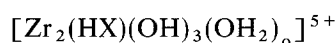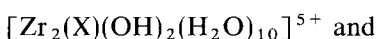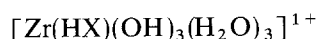
Precursor	$\delta(H_2O)$	Precursor	$\delta(H_2O)$
$[Al_2(OH)_2(H_2O)_8]^{4+}$	0.095	$[Zr_2(OH)_4(H_2O)_{10}]^{4+}$	0.080
$[Al_3(OH)_4(H_2O)_{10}]^{5+}$	0.096	$[Zr_4(OH)_8(H_2O)_{10}]^{8+}$	0.094
$[Al(OH)_3(H_2O)_3]$	0.000[a]	$[Zr(OH)_4(OH_2)_4]$	0.001
$Al(OH)_3$	0.516	$Zr(OH)_4$	0.002

[a]Arbitrarily taken as zero.

of the solution and tendency to coagulate of the n-mer. Of course, some anions will play a dual role.

Associated species $[M(OH)_s X(OH)_2)_{n-s-1}]^{(z-s-1)+}$ may be formed in an aqueous solution in the presence of anions. The stability of M–X against both ionic dissociation and hydrolysis can be determined by means of PCM calculations. The criteria for M–X to be stable are that $x > 0$ and $\delta(HX) < 0$, where x is the charge variation of the anion, X, after its complexation [8, 9].

Calculations on some typical Al(III) and Zr(IV) precursors

$[Al(X)(OH_2)_4]^{2+}$ and $[Al(OH)(HX)(H_2O)_3]^{2+}$

$[Al(X)(OH)(H_2O)_3]^{1+}$ and

$[Al(HX)(OH)_2(OH_2)_2]^{1+}$

$[Al_2(X)(OH)_2(OH_2)_6]^{3+}$ and

$[Al_2(HX)(OH)_3(H_2O)_5]^{3+}$

$[Zr(X)(H_2O)_6]^{3+}$ and $[Zr(OH)(HX)(OH_2)_5]^{3+}$

$[Zr(X)(OH)_2(OH_2)_4]^{1+}$ and

$[Zr(HX)(OH)_3(H_2O)_3]^{1+}$

$[Zr_2(X)(OH)_2(H_2O)_{10}]^{5+}$ and

$[Zr_2(HX)(OH)_3(OH_2)_9]^{5+}$

$[Zr_4(OH)_8(X)(H_2O)_{14}]^{7+}$ and

$[Zr_4(OH)_9(HX)(H_2O)_{13}]^{7+}$
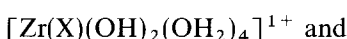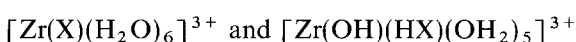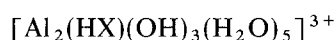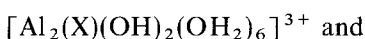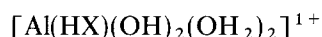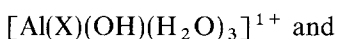
have been made for ClO_4^-, NO_3^-, HSO_4^-, HCO_3^-, CH_3COO^-, Cl^- and F^-. The results show that most anions can coordinate with Al^{3+} and Zr^{4+} in acidic solutions; Cl^- and CH_3COO^- are exceptions. On this basis, it is difficult to understand why CH_3COO^- prolongs the gelation time considerably [6]. Some researchers have studied similar systems, $Zr(OR)_4$ and $Ti(OR)_4$, with acetic acid [5]. They pointed out that the coordination number of titanium increases from 5 to 6 upon addition of acetic acid, because an acetate group bonding to titanium behaves as a bidentate ligand (chelating and bridging); this leads to an increase in the activation energy barrier for polymerization and nucleation [23]. But PCM results on the Al_2O_3–ZrO_2 sol system are not in agreement
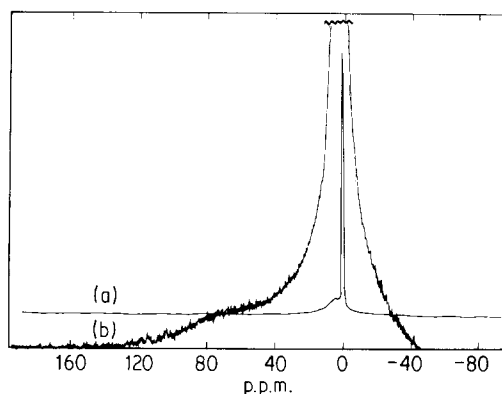

Figure 1 ^{27}Al NMR spectra of Al(III) precursor $Al(OH)_{1.6}(NO_3)_{1.4}$. (a) Original spectra, (b) vertical enhancement of the spectra in (a).

with those given by Mehrotra [5], which show that CH_3COO^- cannot coordinate with Zr^{4+} and Al^{3+} directly: zirconium has a high positive charge, and it is not easy to satisfy its full coordination. Therefore, nucleophilic addition of AcOH, as acetate, is believed to be feasible, giving rise to a temporary transition state with a high coordination. It is supposed that the acetate groups are not immediately removed by hydrolysis and/or condensation. Thus, the functionality of $[Zr(OH)_n \cdot mH_2O \cdot (OAc)_x^-]^{(4-n-x)^+}$ is less than that of $Zr[(OH)_n \cdot mH_2O]^{(4-n)^+}$, and the more (OAc) groups become coordinated to the metal, the lower its functionality will be, with the result that gelation times are increased.

3.2. ^{27}Al NMR study on Al_2O_3 sols and their gelation

^{27}Al NMR provides an excellent means for distinguishing between 4-, 5-, and 6-coordinate aluminium species in solution and can thus play an important role in obtaining information on species in solution during the sol–gel processing stages for alumina. Broadly speaking, the observed range of chemical shifts can be separated into three regions [21]: (a) alkylaluminium compounds with 150 p.p.m. and more shift to the low field; (b) tetrahedrally coordinated aluminium with between 140 and 40 p.p.m. shift; (c) and octahedrally coordinated aluminium, between 40 and -46 p.p.m. shift. Five-coordinated aluminium is said to resonate between the octahedral and tetrahedral regions [21].

The ^{27}Al NMR spectra for a series of precursors, $Al(OH)_x(NO_3)_{3-x}$, with different basicities, x, are almost the same, although their gelation times with ZrO_2 sol are quite different [6]. Fig. 1a shows data for a sol with $x = 1.6$ and 2.1 M in aluminium. The sharp peak around 0 p.p.m. indicates that aluminium is in an octahedral environment which is attributed to $Al(H_2O)_6^{3+}$ [12, 13]; the very narrow line width of the signals shows that aluminium is in a highly symmetric environment. The broad, weak peak on the left side of the sharp peak is assigned to the dimeric aluminium species $Al_2(OH)_2(H_2)_8^{4+}$, and the presence of colloidal aquated aluminium [12, 13]. After enlargement of these spectra, another very weak peak around 75 p.p.m. can be seen (Fig. 1b); it is attributed to tetrahedrally coordinated aluminium atoms in the cationic species $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ [15–19]. The concentration of the Al_{13} polymeric unit in these sols is very low.

However, the ^{27}Al NMR spectrum of $Al_2(OH)_5Cl$ is very different from the sample above: see Fig. 2e. One sharp resonance at 2.7 p.p.m. is still assigned to octahedrally coordinated aluminium cations. The wide and quite strong peak around 80 p.p.m. is also due to the polyoxycation Al_{13}. Another strong but wide peak at 13.7 p.p.m. indicates that this sol contains a large number of polynuclear species: dimeric, trimeric as well as colloidal aquated aluminium. The pH of $Al_2(OH)_5Cl$ solution (or sol) is 3.5, which is much higher than that of other precursors described here, whose pH is typically 2–3 [6]. So, the higher the
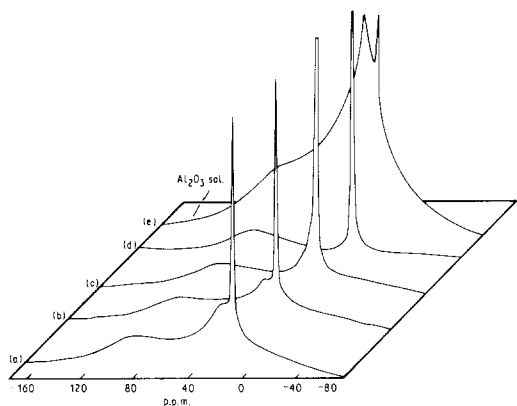
Figure 2 ^{27}Al NMR spectra during the gelation and ageing with composition ZrO_2 sol : $Al_2(OH)_5Cl = 3:1$ (by volume). (a) $t = 5$ min, (b) $t = 14$ min, (c) ageing at $20°C$ for 2 weeks, RH = 100%, (d) the sample in (c) autoclaved at $130°C$ for 19 days, (e) precursor $Al(OH)_5Cl$.

pH of Al^{3+} solution, the greater will be the concentration of polynuclear species. The ^{27}Al NMR results are basically in agreement with an analysis of the speciation made using the PCM.

Fig. 2 shows the ^{27}Al NMR spectra during sol–gel processing and at different ageing times. This polymer had the initial formulation ZrO_2 sol: $Al_2(OH)_5Cl = 3:1$ (by volume). Comparing Fig. 2a and d with Fig. 2e, one can conclude that (1) the concentration of polynuclear species, including dimers and trimers, but especially of Al_{13}, is reduced as a consequence of mixing and (2) the concentration of aluminium polynuclear species does not change very much during subsequent ageing. The main species in this mixture is octahedral $Al(H_2O)_6^{3+}$. But, after autoclaving at $130°C$ for 19 days, the concentration of polynuclear species, especially of Al_{13}, is slightly increased. This arises because the pH decreases sharply upon mixing aluminium reagent with ZrO_2 sol; the latter has a very low pH, approximately zero. The results show that Al^{3+} polynuclear species are reversibly decomposed at low pH and that simple hydrated $Al(III)$ does not copolymerize with $Zr(IV)$ during the sol–gel transformation. The pH of mixture increases gradually during ageing, but does not rise above 2, which is still much lower than that of the precursor aluminium solution of $Al_2(OH)_5Cl$ and too low for significant aluminium condensation to occur.

3.3. Kinetics of gelation

Extensive literature exists on modelling gelation processes, leading to prediction of the kinetics of growth and of the fractal structures of the resulting clusters [25]. On the other hand, many techniques have been used to extract information on each step of the process. The experimental methods most frequently used to explore the kinetics of gelation are viscometry and NMR spectroscopy, including ^{1}H NMR and, in silicate systems, ^{29}Si NMR. But no single technique can give the whole picture of gelation. Gelation is an exothermal reaction, so it can be easily studied by thermochemical methods, preferably using an isother-

mal calorimeter. These afford another perspective on the gelation process. In the following discussion, we assume that the heat of reaction per zirconium unit remains approximately constant per n-mer, which is probably true because n is already greater than 4 in the as-supplied concentrated ZrO_2 sol [20]. Figs. 3–5 show isothermal calorimetric data, from which it is concluded that:

1. Polymerization achieves a maximum rate in a very short time, within a few minutes, the rate decreasing sharply thereafter. After about 15 min, the rate of polymerization is slow, but polymerization continues after the gelation point is reached;

2. Temperature affects polymerization rates significantly (see Fig. 3). It determines the maximum rate of reaction, the time required to achieve this rate as well as the total heat evolution within a fixed time. The higher the temperature, the higher will be the maximum rate of reaction and the shorter the time required to achieve this maximum rate.

3. In the ZrO_2 sol–$Al_2(OH)_5Cl(Al_2O_3$ sol) system, see Fig. 4, the higher the content of Al_2O_3 the higher will be the maximum reaction rate and the shorter the time required to achieve this maximum value. As pointed out previously, Al^{3+} ions do not polymerize in the course of the sol–gel transformation, but they condition a higher pH regime in which hydrolysis and polymerization of Zr^{4+} occurs more
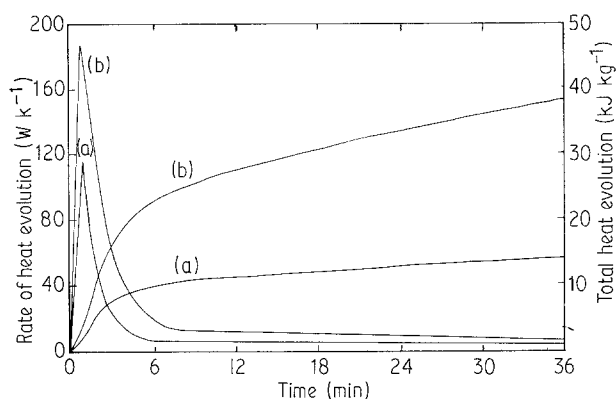

Figure 3 Isothermal calorimetry of the gelation process at different temperatures, same composition as sample in Fig. 4b. (a) $T = 3$ °C, (b) $T = 21$ °C.
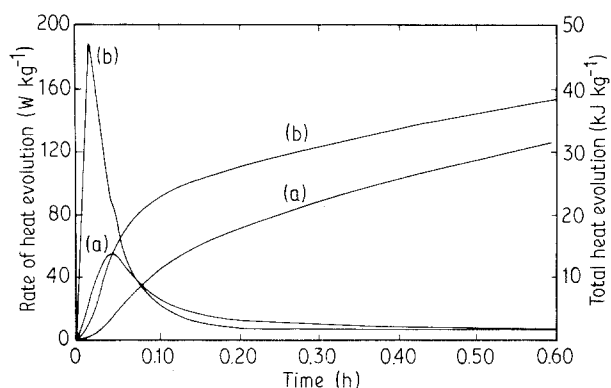

Figure 4 Isothermal calorimetry of the gelation process with different compositions at 21 °C. (a) ZrO_2 sol: Al_2O_3 sol $= 3:1$ (by volume), (b) ZrO_2 sol: Al_2O_3 sol $= 1:2$ (by volume).
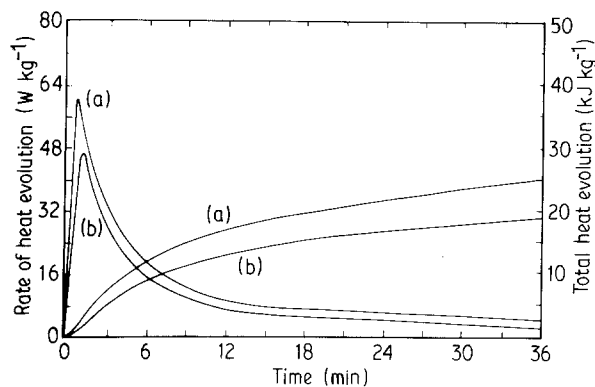
Figure 5 Isothermal calorimetry of the gelation process with different Al(III) precursors at 21 °C. (a) ZrO_2 sol:$Al(OH)_{2.1}(NO_3)_{0.9}$ = 3:1 (by volume), (b) ZrO_2 sol:$Al(OH)_{1.1}(NO_3)_{1.9}$ = 3:1 (by volume).

rapidly. The cumulative heat evolution is determined by the Zr^{4+} content, but a high content of Al_2O_3 sol can make the reaction rate peak earlier, because the rate of polymerization is pH-dependent;

4. In the ZrO_2 sol–$Al(OH)_x(NO_3)_{3-x}$ system, the higher the basicity value, x, the higher will be the maximum rate of reaction and the total heat evolution occurring in a limited time (see Fig. 5).

The results of conductivity measurements made on the same compositions are in good agreement with calorimetry; see Fig. 6. Conductivity decreases sharply at the beginning of reaction, but the rate of change slows because the content of mobile ions decreases and the viscosity of sol increases during polymerization.

Normally, gelation can be divided into three stages. In the first, the reaction (polymerization) is controlled by diffusion: one sol is diffusing into another after initial mixing. Once diffusion is finished and the mixture is homogeneous, the first stage will merge imperceptibly with the second stage. In this second stage, reaction is controlled mainly by the rate of polymerization. In the Al_2O_3–ZrO_2 sol–gel system, it is only controlled by the rate of polymerization of Zr^{4+} because, as shown, aluminium remains in a low state of polymerization. Therefore, the kinetics of polymerization can be treated by the Arrhenius relation: the constant of reaction is

$$k = k_0 \exp(-E/RT) \qquad (13)$$

where k_0 is constant, R is the ideal gas constant, T is temperature and E is activation energy. This is an accelerating stage, because polymerization is an exothermic process and reaction is accelerated as temperature increases. The temperature-dependence of gelation time, t_{gel}, can be deduced from Equation 13, leading to

$$\ln(t_{gel}) = A + E_g/RT \qquad (14)$$

where E_g is an activation energy for gelation. The composition of mixtures (Zr/Al ratio) can affect the gelation time markedly (see Table III). The higher the content of Al_2O_3 sol, the shorter the gelation time will be. Thus, higher pH accelerates the polymerization Zr^{4+}. But the activation energy calculated from
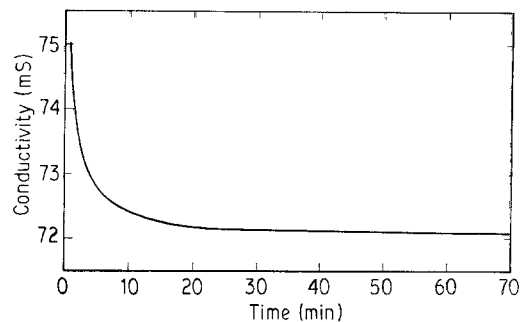

Figure 6 Conductivity changes during sol–gel transformation ($T = 20$ °C). Composition ZrO_2 sol:Al_2O_3 sol = 3:1 (by volume).

TABLE III Composition of mixtures and the gelation parameters (20 °C)

	Composition[a]				
	1 : 3	1 : 1	3 : 1	6 : 1	10 : 1
t_{gel}(min)	5.3	8.5	11.3	17.3	32.3
E_g(kcal mol^{-1})	18.4	17.9	17.4	18.8	18.2

[a]Ratio of ZrO_2 sol to Al_2O_3 sol by volume: see text for sol composition.

Equation 14 does not change when the compositions are different; Table III compares different values from which it can be seen that activation energy almost remains constant at 18.1 ± 0.7 Kcal mol^{-1}.

This low activation energy implies that gelation will occur rapidly and also, may occur at all temperatures at which an aqueous phase persists. Actually, this "activation energy" cannot be ascribed to any particular reaction, because gelation depends in a complicated way on the rates of hydrolysis, polymerization and diffusion of clusters.

In the third stage, the reaction rate again becomes diffusion controlled. Now, however, the diffusion process involves two components: one is the diffusion of reaction product (higher molecular weight zirconium polymer) and the other is the unreacted units (lower molecular weight polymer). Polymerization should slow gradually because of two factors: the concentration of potentially reactive low-molecular weight units becomes progressively less, and the diffusion coefficients of unreacted and reacted units decrease as gelation proceeds due to the increasing viscosity of the sol. The gelation kinetics demonstrated by calorimetry are consistent with this general description of the process.

4. Conclusions

Theory and experiment show that both Al^{3+} and Zr^{4+} precursors can condense to high polymers, but Zr^{4+} needs to achieve a higher ratio of hydrolysis before its condensation can proceed spontaneously. Oxolation may occur in cationic precursors. Most of the anions considered can coordinate to aluminium or zirconium atoms; Cl^- and CH_3COO^- are exceptions. Application of the partial charge model theory is very successful in correlating and interpreting data.

^{27}Al NMR shows that Al^{3+} does not copolymerize with zirconium but instead, higher molecular weight polymers of aluminium decompose to lower molecular weight units. Al^{3+} precursors do, however, supply the rise in pH necessary for Zr^{4+} polymerization. Isothermal calorimetry results show that gelation reactions accelerate initially, but gradually slow down after achieving a maximum rate. The higher the temperature, and/or the higher the content of Al^{3+} precursor, and/or the higher the basicity of Al^{3+} precursors, the higher will be the maximum rate of reaction and the greater the total heat evolved up to the gel point.

Acknowledgements

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