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Sol–gel formation of zirconia: preparation, structure and rheology of sols

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Different sol–gel methods for the preparation of ZrO_2 were investigated. Depending on the chemical composition of the initial solutions, various results such as gel–precipitation, the formation of stable sols or amorphous gels were obtained. Sols prepared by different methods are composed of different structural units and exhibit quite different rheological behaviour such as shear thickening, Newtonian flow, shear thinning and thixotropic flow. By variation of the chemical composition of the sol, an optimized rheological behaviour can be achieved for a given purpose.

1. Introduction

At present, sol–gel techniques are used mainly for the formation of ceramic or glass coatings on various substrates, especially glass [1–3]. Moreover, low formation temperatures and hence small crystallite size enable the production of powders with high sinterability. In many cases lower sintering temperatures are possible leading to a ceramic product with a small mean grain size and hence high mechanical strength. Although there is much research into sol–gel preparations of various glasses and ceramics, the fundamentals are very complicated and only in the case of the SiO_2 formation comparatively well understood [4, 5]. For other sol–gel systems such as those of ZrO_2, TiO_2 or Al_2O_3, there is still a lack of data concerning the gelation process.

Generally the initial solution is composed of metal alkoxides, inorganic salts or salts of organic acids, solvent and sometimes various additives. The chemical composition greatly influences the structure of sols and gels. Thus many other properties also strongly depend on the chemical composition, e.g. rheological behaviour of sols, sol–gel transformation, drying and shrinkage behaviour of gels, calcination behaviour of the dried gels, and sintering behaviour.

This paper reports a study of different sol–gel methods for the preparation of ZrO_2 ceramics, and investigates the influence of chemical composition on the structure, the sol–gel transition and the rheological behaviour.

2. Sol–gel methods for the preparation of ZrO_2

In the literature, various methods for the preparation of ZrO_2-based ceramics have been described. The starting materials most often used were zirconium carboxides, such as $Zr(O\text{-}nC_3H_7)_4$ [6–11], $Zr(O\text{-}iC_3H_7)_4$ [12, 13] or $Zr(O\text{-}nC_4H_9)_4$ [14, 15], but inorganic salts such as $ZrOCl_2 \cdot 8H_2O$ [16–19] or $ZrO(NO_3)_2$ [20] and salts of organic acids, such as zirconium acetate [21–24], were also investigated. Generally alcohols or hydrocarbons [8, 12] were used as solvents. The first reaction step of the sol–gel process, hydrolysis, can be described by the simplified chemical equation:

$$Zr(OR)_4 \xrightarrow[-\,ROH]{H_2O} Zr(OH)_2(OR)_2 \xrightarrow[-\,ROH]{H_2O} Zr(OH)_4 \quad (1)$$

The second step is polycondensation, which might run parallel to the hydrolysis step, depending on the composition of the solution and the reaction conditions.

$$Zr(OH)_2(OR)_2 \xrightarrow{-\,H_2O} ZrO(OR)_2 \quad (2)$$

$$Zr(OH)_4 \xrightarrow{-\,H_2O} ZrO_2 \quad (3)$$

Because both hydrolysis and condensation occur in several steps, the number of chemical reactions is very large and Equations 1–3 provide an extremely simplified description. Depending on the composition of the solution, formation of an homogeneous sol or spontaneous gel precipitation can be observed when water is added to the zirconium alkoxide. Many organic compounds have been described in the literature to prevent the precipitation. Many of them may occur as bidental ligands. Guizard *et al.* [7] described the influence of 1,2-dihydroxyethane (glycol); Debsikdar [6] used acetylacetonate for the stabilization of sols and the addition of acetic acid to titanium ethoxides has been investigated by Livage and co-workers [25, 26].

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Chemical reactions in the presence of bidental ligands may differ from Equations 1–3.

3. Experimental procedure

The different sols were prepared from zirconium acetate (aqueous solution 22 wt %), $Zr(O\text{–}nC_3H_7)_4$ and with the aid of organic chemicals (acetic acid, acetylacetone and isopropanol).

The products were characterized by Fourier transform-infrared (FT–IR) spectroscopy (Mattson Polaris), rheological measurements (Contraves, rheomat 115) and thermal analysis (Netzsch, STA 409).

Sols in the system $Zr(O\text{–}nC_3H_7)_4/CH_3COOH/H_2O$ were prepared in the following manner. A mixture of $Zr(O\text{–}nC_3H_7)_4$ and CH_3COOH was added to a mixture of H_2O and iC_3H_7OH, and homogenized by intensive stirring. Sols were prepared using the method described by Debsikdar [6]: mixing a solution of $Zr(O\text{–}nC_3H_7)_4$ in acetylacetone with an $H_2O/iC_3H_7OH/HNO_3$ solution. The zirconium acetate solution was concentrated by evaporation of the solvent as described by Marshall *et al.* [22]. Gelation times of sols with different compositions were measured using the method described by Sakka and Kamiya [27].

4. The $Zr(O\text{–}nC_3H_7)_4/CH_3COOH/H_2O$ system

The concentrations of $Zr(O\text{–}nC_3H_7)_4 \cdot CH_3COOH$ and H_2O were varied over a wide range in such a manner that the total concentration of the three compounds together was always $3\ \text{mol}\,l^{-1}$. Depending on the concentrations, very different products were obtained (see Fig. 1). In two regions in the $Zr(O\text{–}nC_3H_7)_4/CH_3COOH/H_2O$ diagram precipitation could be observed. At low acetic acid concentrations ($[Zr(O\text{–}nC_3H_7)_4]/[CH_3COOH] \geqslant 1$) spontaneous gel precipitation occurs (see Fig. 1, type 1), while at high acetic acid concentrations a very slow precipitation could be observed (see Fig. 1 type 3). In the range of acetic acid concentrations $[H_2O]/[Zr(O\text{–}nC_3H_7)_4] \leqslant 1$ and $0.5 \leqslant [Zr(O\text{–}nC_3H_7)_4]/[CH_3COOH] \leqslant 1$, a totally stable, highly viscous sol was obtained showing no tendency to form a gel (see Fig. 1, type 4). At higher concentrations ($[H_2O]/[Zr(O\text{–}nC_3H_7)_4] > 1$), a sol, which turns to a homogeneous gel after some minutes or days, is formed (see Fig. 1, type 2). In regions of very low $Zr(O\text{–}nC_3H_7)_4$ concentration (< 10%), no gel formation occurs, but the viscosity of the solution increases with time (see Fig. 1, type 5).

Sanchez *et al.* [28] investigated a sol–gel route with different titanium alkoxides as starting materials. Depending on the type of alkoxide, various products were obtained due to different hydrolysis and polycondensation rates. In this paper, the organic rest of the alkoxides was kept constant, but nevertheless, a wide variation of products was obtained. This highlights the fact that both reaction rates and the polymeric products are strongly influenced by the concentrations of the initial solutions.

Gelation times of type 2 sols are shown in Fig. 2. They increase with increasing CH_3COOH content due to its stabilizing influence, and decrease with increasing H_2O content. However, it should be noted that in these experiments, as already mentioned, the total concentration of H_2O, CH_3COOH and $Zr(O\text{–}nC_3H_7)_4$ was constant and therefore the $Zr(O\text{–}nC_3H_7)_4$ concentration was not always the same.

To study the influence of H_2O and CH_3COOH further, the $Zr(O\text{–}nC_3H_7)_4$ concentration was kept constant in another series of experiments, the results of which are shown in Figs 3 and 4. Fig. 3 shows the gelation time, varying over more than six orders of magnitude as the acetic acid content is increased. The maximum slope is obtained at a molar ratio $[CH_3COOH]/[Zr(O\text{–}nC_3H_7)_4]$ of about 3:1. Fig. 4 demonstrates the influence of the water content.

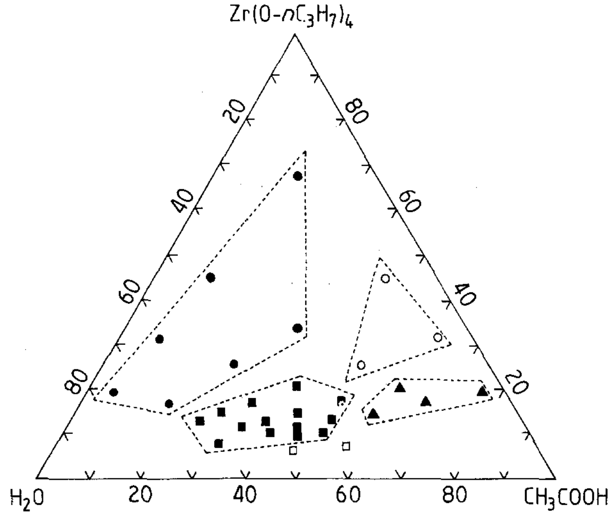


Figure 1 The system $Zr(O\text{–}nC_3H_7)_4/CH_3COOH/H_2O$: (●) type 1, spontaneous precipitation; (■) type 2, stable gel; (▲) type 3, slow precipitation; (○) type 4, gel formation; (□) type 5, no gelation.

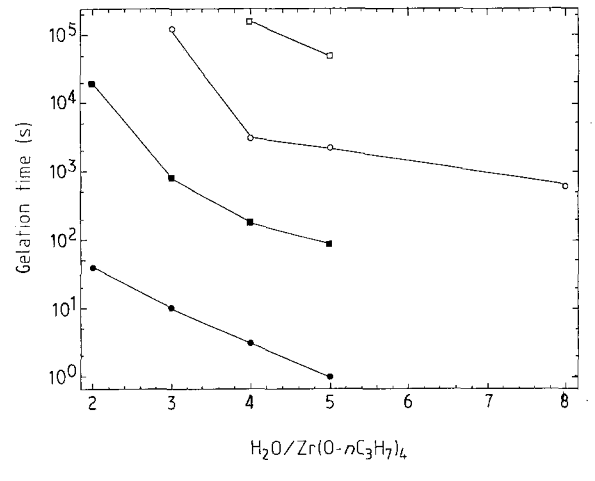


Figure 2 Gelation times of type 2 sols (see Fig. 1) as a function of $[H_2O]$. $[Zr(O\text{–}nC_3H_7)_4] + [CH_3COOH] + [H_2O] = 3\ \text{mol}\,l^{-1}$. $CH_3COOH/Zr(O\text{–}nC_3H_7)_4$: (●) 2, (■) 3, (○) 4, (□) 5.

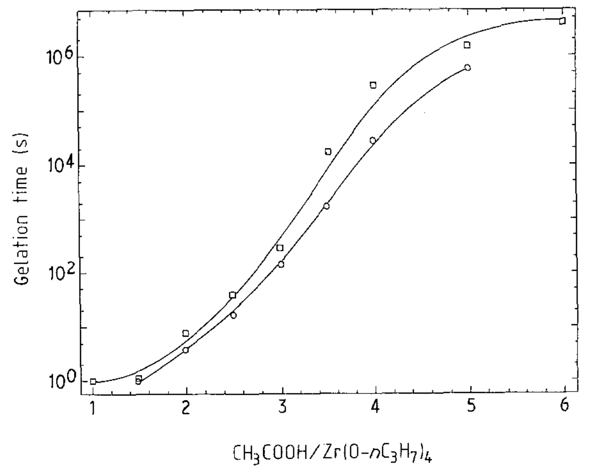


Figure 3 Gelation times of type 2 sols (see Fig. 1) as a function of [CH_3COOH]. [$Zr(O\text{-}nC_3H_7)_4$] = constant. $H_2O/Zr(O\text{-}nC_3H_7)_4$: (□) 3, (○) 4.

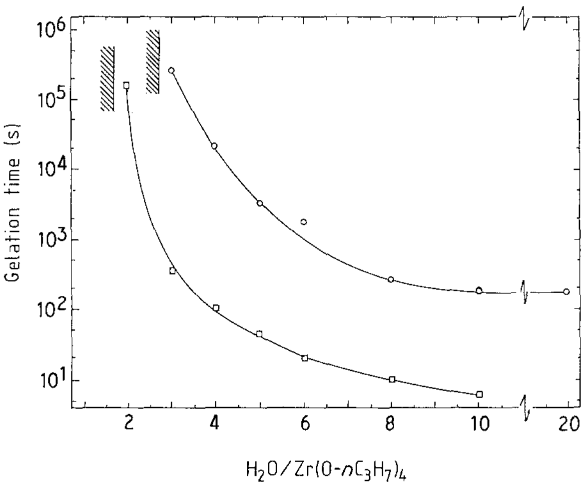


Figure 4 Gelation times of type 2 sols (see Fig. 1) as a function of [H_2O]. [$Zr(O\text{-}nC_3H_7)_4$] = constant. $CH_3COOH/Zr(O\text{-}nC_3H_7)_4$: (□) 3, (○) 4.

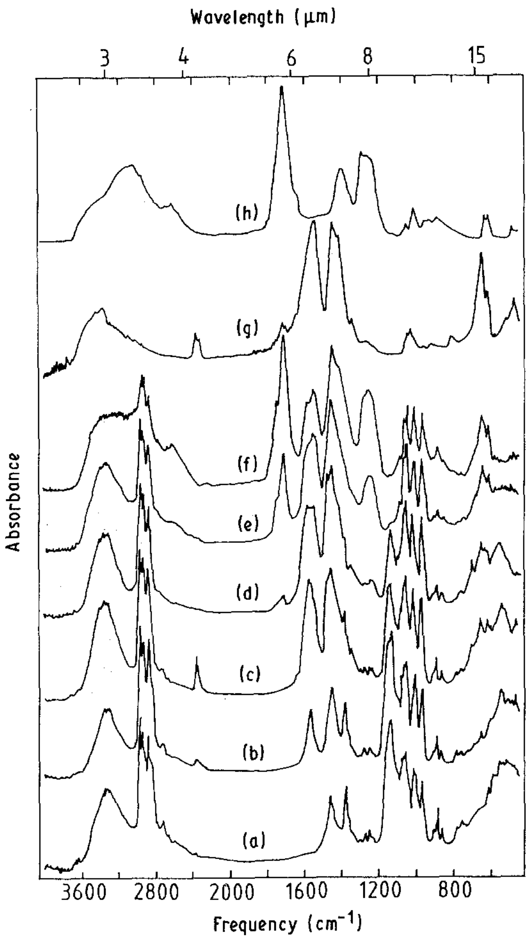


Figure 5 FT-IR spectra of (a) pure $Zr(O\text{-}nC_3H_7)_4$, (b) [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] = 4:1, (c) [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] = 1:1, (e) [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] = 1:2, (d) [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] = 1:4, (f) [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] = 1:8, (g) dried (f), (h) acetic acid.

The gelation time varies with the water content over more than four orders of magnitude. However, it should be noted that at a ratio [CH_3COOH]/[$Zr(O\text{-}nC_3H_7)_4$] = 4:1, high water concentrations have almost no influence on the gelation time. The bars shown in Fig. 4 show the region over which a sol forming a homogeneous gel (Fig. 1, type 2), transforms to one which slowly forms a precipitate (Fig. 1, type 3).

Because the addition of acetic acid obviously has great influence on the whole sol–gel process, FT–IR spectra were collected and are shown in Fig. 5, together with spectra of pure $Zr(O\text{-}nC_3H_7)_4$ ana CH_3COOH for comparison. In spectra of pure $Zr(O\text{-}nC_3H_7)_4$, as well as the broad O–H line at 3300 cm^{-1}, some C–H lines in the region from 2850 to 2970 cm^{-1}, due to stretching vibrations, can be seen. Also observed are lines at 1380 and 1460 cm^{-1} due to C–H deformation vibrations, and in the region of 800–1200 cm^{-1} characteristic lines due to the zirconium–oxygen–carbon deformation. In the FT–IR spectra of acetic acid some characteristic lines can also be observed: the C=O stretching vibration at 1710 cm^{-1}, the O–H deformation at 1415 cm^{-1} and the C–O stretching vibration at 1250–1300 cm^{-1}. The FT–IR spectrum of a mixture with the molar ratio [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] = 4:1 shows an additional line at 1561 cm^{-1}, which can neither be observed in the $Zr(O\text{-}nC_3H_7)_4$ spectrum nor in the CH_3COOH spectrum, and the occurrence of a line at 1453 cm^{-1}, which is, however, superimposed by the line at 1460 cm^{-1}. At increasing molar ratios of [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] up to a value of 1:1, a further increase in the intensity of the lines at 1561 and 1453 cm^{-1} can be observed. By comparison with data in the literature [29, 30], the occurrence of these two peaks with a splitting of 108 cm^{-1} can be attributed to the bidental ligand CH_3COO^-, chelating the zirconium atoms. The decrease in the intensity of the infrared line at 1150 cm^{-1}, corresponding to the Zr–O–R bonds is another indication that RO^- is substituted by CH_3COO^-. If the molar ratio [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] is further increased, a broadening of the lines at 1561 and 1453 cm^{-1} can be seen, which, according to previous works [29, 30], might be caused by the occurrence of CH_3COO^- as bridging ligand. At molar ratios of [$Zr(O\text{-}nC_3H_7)_4$]/[CH_3COOH] of 1:2, 1:4 and 1:8, additional lines at 1715 and 1263 cm^{-1} can be observed which correspond to acetic acid, or possibly to the monodental ligand CH_3COO^-.

To investigate further the reaction of $Zr(O\text{-}nC_3H_7)_4$ with CH_3COOH simple calorimetric measurements were made. By rapid stirring, a solution of $Zr(O\text{-}nC_3H_7)_4$ (70 wt % in isopropanol) was mixed with CH_3COOH (molar ratio 1:1). After about 20 min, the same amount of CH_3COOH was added again, and so on. During this procedure the temperature was measured continuously. Equations 7–10 describe chemical reactions which may possibly occur

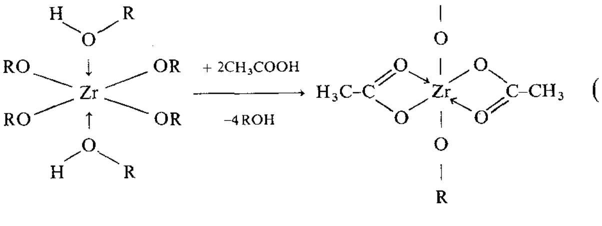
$$Zr(O\text{-}nC_3H_7)_4 \xrightarrow[-nC_3H_7OH]{CH_3COOH} Zr(O\text{-}nC_3H_7)_3(CH_3COO) \quad (7)$$

$$Zr(O\text{-}nC_3H_7)_3(CH_3COO) \xrightarrow[-nC_3H_7OH]{CH_3COOH} Zr(O\text{-}nC_3H_7)_2(CH_3COO)_2 \quad (8)$$

$$Zr(O\text{-}nC_3H_7)_2(CH_3COO)_2 \xrightarrow[-nC_3H_7OH]{CH_3COOH} Zr(O\text{-}nC_3H_7)(CH_3COO)_3 \quad (9)$$

$$Zr(O\text{-}nC_3H_7)(CH_3COO)_3 \xrightarrow[-nC_3H_7OH]{CH_3COOH} Zr(CH_3COO)_4 \quad (10)$$

For the first two additions of CH_3COOH, the temperature increase was 12.9 and 10.5 °C, respectively; the next two additions resulted in a temperature increase of 5.3 and 1.5 °C. It should be mentioned that the temperature rose within seconds for the first, second and fourth additions, while during the third addition, the temperature increased only slowly, within 10 min. It can be concluded that the reactions described by Equations 7 and 8 proceeded completely, while that described by Equation 9 did not, and that kinetic effects play an important part. The increase in temperature during the fourth step is related to the mixing enthalpy, and not to the chemical reaction described by Equation 10. This argument agrees well with the FT–IR spectra, where no further substitution of nC_3H_7OH ligands could be observed when the molar ratio $[Zr(O\text{-}nC_3H_7)_4]/[CH_3COOH]$ was lowered to a value of 1:4. Therefore, a compound with the formula $Zr(O\text{-}nC_3H_7)_{4-x}(CH_3COO)_x$ (with: $2 \leqslant x < 3$) can be assumed even when an excess of acetic acid is present. For the addition of 2 mol CH_3COOH to 1 mol $Zr(O\text{-}nC_3H_7)_4$ the following structural changes are suggested:



(11)

Infrared spectra of the hydrolysed mixtures of Zr-*n*-propoxide with acetic acid showed that the bidental acetate ligand was stable against hydrolysis. Therefore, the formation of bridging oxygen bonds only can occur by hydrolysis of Zr–alkoxide bonds. By adjusting the amount of acetic acid, a control of the molecular structure of the polymers should be possible.

The FT–IR spectrum of the dried gel shows: two lines at 1561 and 1453 cm^{-1} corresponding to CH_3COO^- as a bidental ligand; strong absorption at 650 cm^{-1} corresponding to Zr–O bonds; no lines in the region of 800–1200 cm^{-1} corresponding to Zr–O–C bonds of the alkoxides.

Fig. 6 summarizes FT–IR spectra of some dried gels prepared by different procedures. Spectrum a is of a sample prepared by drying an aqueous solution of zirconium acetate; spectrum b has already been shown in Fig. 5 obtained by drying a mixture of $Zr(O\text{-}nC_3H_7)_4$ and CH_3COOH; spectrum c is of a dried homogeneous gel (see Fig. 1, type 2); the spectrum of a dried precipitate is shown in Fig. 6d (see Fig. 1, type 3). No remarkable differences can be seen in all these spectra; therefore, it can be concluded that the structure is always the same, independent of the preparation procedure. TGA measurements of all gels at 1000 °C show a total weight loss in the range of 45–47 wt %. This is in good agreement with a weight loss of 45.2 wt %, calculated for a compound with the formula $ZrO(CH_3COO)_2$. This formula also fits the FT–IR spectra of Fig. 6, where no lines corresponding to zirconium alkoxide bonds could be observed.

5. Rheological behaviour of the sols

In Fig. 7 the programme for measuring the flow curves is shown. A compromise between two different time-dependent parameters influencing the measurements must be made. On changing the shear rate, some time is necessary to reach a new steady state

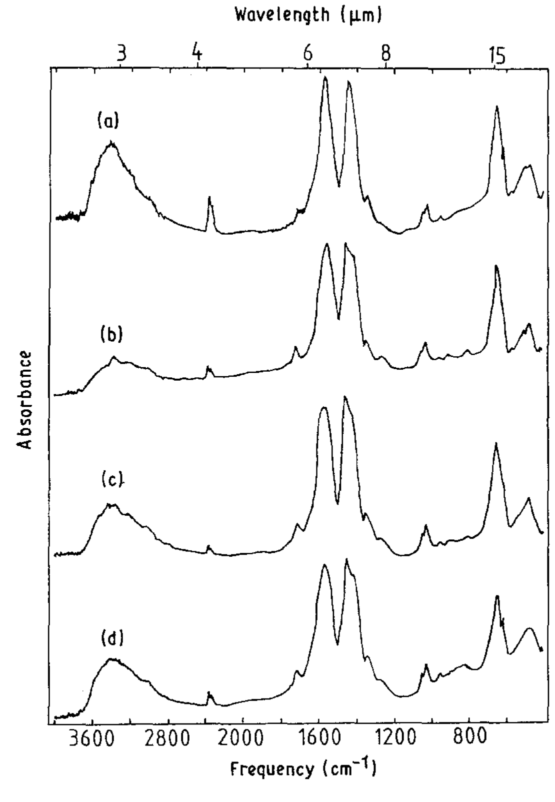


Figure 6 FT–IR spectra of some dried compounds: (a) precipitate (see Fig. 1, type 1); (b) gel (see Fig. 1, type 4); (c) a mixture of $[Zr(O\text{-}nC_3H_7)_4]/[CH_3COOH] = 1:8$; (d) zirconium acetate.

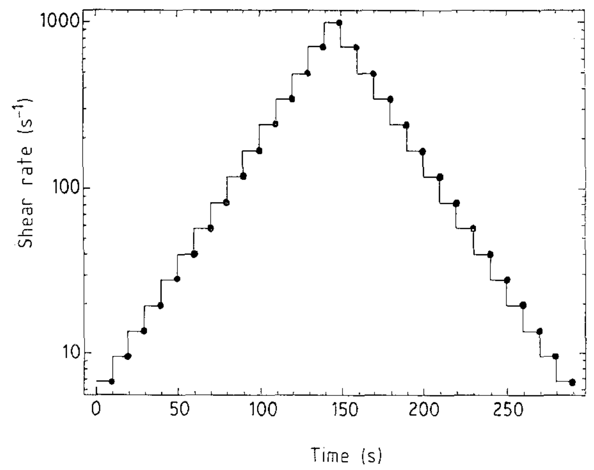


Figure 7 Programme for measuring the flow curves of sols: the dots mark the time at which the shear stress was measured.

with a constant shear stress. This effect cannot be neglected because, especially near the gelation point, the sols show thixotropic flow behaviour (see Fig. 8). Times up to 10 min are often observed, until the shear stress reaches a constant value. On the other hand, the recording of every flow curve should be finished as quickly as possible, because the rheology of the sol changes with time. To obtain comparable data, all rheological measurements were made using the same programme, shown in Fig. 7. The rotary speed of the cylinder, and hence the shear rate, was changed every 10 s. The corresponding shear stress was measured immediately before changing the shear rate (see dots in Fig. 7).

In Fig. 8 different flow curves of sols, which later turn to homogeneous gels, are shown. The composition of the sol was $[Zr(O\text{-}nC_3H_7)_4]:[CH_3COOH]:[H_2O] = 1:4:4$. After the preparation of the sol, shear thickening, and subsequently Newtonian flow, shear thinning and thixotropic behaviour can be observed. Except for the shear thickening at the beginning of the measurement, these changes in rheology have already been observed in TEOS-based sols [31–33].

A remarkable feature in flow behaviour of this sol can be seen on the curve after 6 h, corresponding to the gelation point. When the shear rate is lowered to a very slow deformation, the corresponding shear stress increases again. It can be assumed that after destruction of the gel network at higher shear rates, a reconstruction at low shear rates occurs.

Fig. 9 supports this assumption. Here, a second flow curve was recorded 10 min after completing the measurement near the gelation point. Within this relatively short time, at strength of the gel increased from 10 Pa to 15 Pa. The shift between these two curves is related to further destruction of the gel network by repeated shearing of the gel.

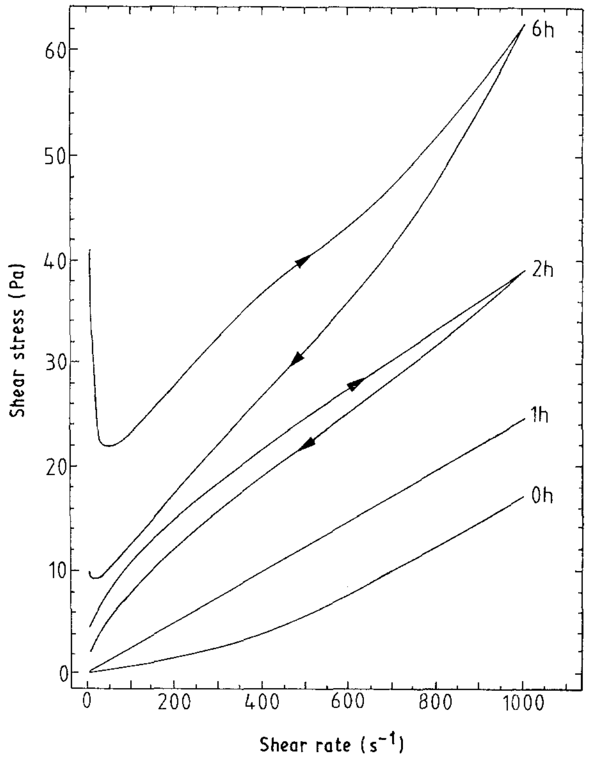


Figure 8 Flow curves (shear rate D versus shear stress τ) for a sol in the system $[Zr(O\text{-}nC_3H_7)_4]:[CH_3COOH]:[H_2O] = 1:4:4$; gelation time ≈ 6 h.

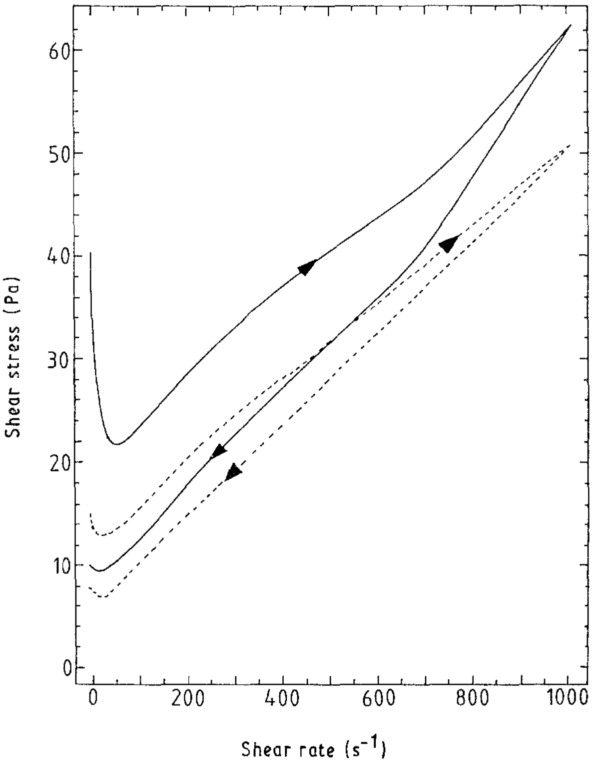


Figure 9 Repeated measurement of a flow curve in the system $Zr(O\text{-}nC_3H_7)_4\text{–}CH_3COOH\text{–}H_2O$ after short time. (——) 6 h, (- - -) repeated after 10 min.

A quite different behaviour can be seen in the case of a zirconium acetate solution (Fig. 10). Here, shear thickening and Newtonian flow can be observed, but no shear thinning or thixotropic flow. Up to high viscosities the sol exhibits Newtonian behaviour, and the formation of fibres by dipping a glass rod in the sol, or extruding the sol through a nozzle, is easily possible as reported earlier [22–24]. The Newtonian flow behaviour of sols which can be drawn to fibres has also been measured in the case of TEOS-based sols [31–33]. The FT–IR spectra of dried gels prepared by the alkoxide route and prepared from zirconium acetate are identical; the structural units in both

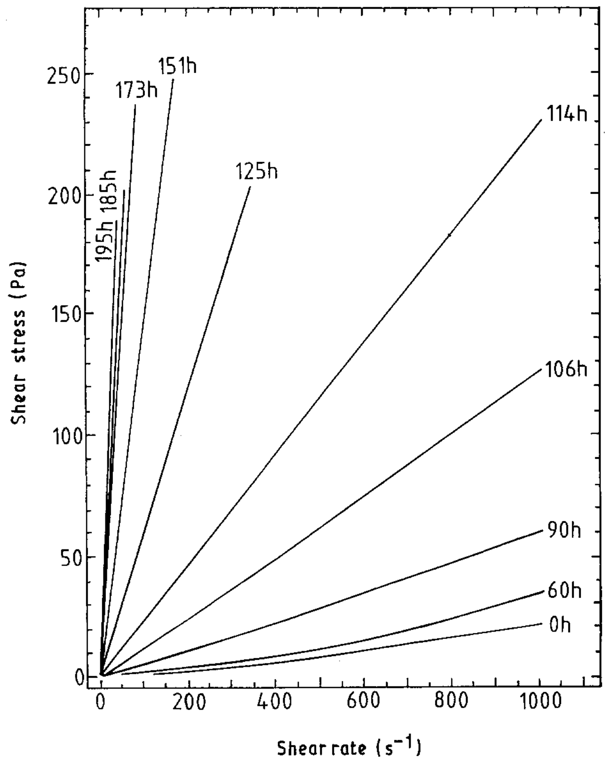


Figure 10 Flow curve for a zirconium acetate solution (gelation time ≈ 195 h).

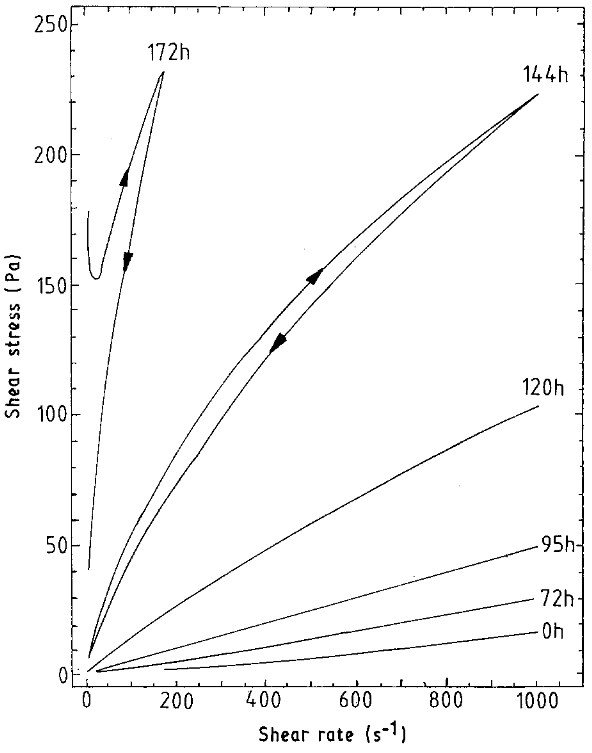


Figure 11 Flow curves for the sol prepared by the method described by Debsikdar [6] (gelation time ≈ 172 h).

gels are the same. The different rheological behaviour, therefore, is due to different interactions with the solvent. This could be shown using the following experiments: in the first, zirconium acetate was mixed with isopropanol and HNO_3; afterwards the rheological behaviour was the same as of a gel prepared by the alkoxide route. In the second experiment, dried alkoxide derived gel was dissolved in water and afterwards showed the same rheological behaviour as a zirconium acetate solution. The interaction of the polymeric chains with water as solvent should be much stronger than with isopropanol – possibly the chain lengths in water are smaller because CH_3COO– ligands can be exchanged more easily with water than with isopropanol.

A third example of the flow behaviour of a sol is shown in Fig. 11. It was prepared as described by Debsikdar [6]. The amount of acetylacetone (0.8 mol acetylacetone per mol $Zr(O\text{–}nC_3H_7)_4$), used to modify the alkoxide precursor, enables the later formation of a three-dimensional network. As in the case of Zr–*n*-propoxide with acetic acid, the whole spectrum from shear thickening to thixotropic flow can be seen. However, there are remarkable differences between these two sols. In this case, the curve tends to a zero shear stress if the shear rate is lowered.

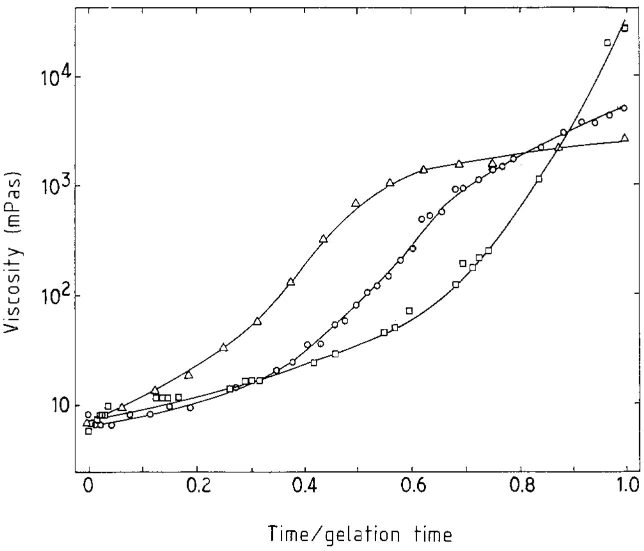


Figure 12 Comparison of viscosity against time for the three different systems (shear rate, $D = 80\,s^{-1}$). (△) $Zr(O\text{–}nC_3H_7)_4$–CH_3COOH–H_2O, (○) Zirconium acetate, (□) $Zr(O\text{–}nC_3H_7)_4$–acetylacetone–H_2O.

Fig. 12 shows a comparison of the viscosities and their time dependences of the three types of sols investigated. The different behaviour of all three examples can clearly be seen. The sol modified by addition of acetic acid reaches a threshold, due to the occurrence of linear polymer chains which become entangled to form a gel. If a shear stress is applied, this network can be destroyed mechanically, but will be reconstructed when the forces are removed. When alcohol as solvent is replaced by water, as in the second example, a Newtonian flow can be observed up to high viscosities. A steady increase in the viscosity can be seen with decreasing amount of solvent. In contrast to the two other examples, the gel formation is not related to chemical reactions such as hydrolysis or polycondensation. In the highly viscous state, the concentration of the polymeric zirconium compound reaches a critical point and forms a glassy gel. The sol prepared as described by Debsikdar [6] shows the behaviour typical of alkoxide-derived sols [31–33]. The viscosity increases slowly with time but on reaching the gelation time increases sharply.

6. Conclusion

Three different sols investigated showed very different structure and rheological behaviour. Zirconium acetate solutions with water as solvent, form linear polymeric chains showing Newtonian behaviour up to very high viscosities. Zirconium-*n*-propoxide solutions modified by the addition of acetic acid, produced various results such as gel precipitation, the formation of stable sols or homogeneous gels. Sols prepared by this method are composed of the same structural units as zirconium acetate, but exhibit quite different rheological behaviour. Here, shear thickening, Newtonian flow, shear thinning and thixotropic flow can be observed.

The sol with acetylacetone as stabilizer enables the formation of a three-dimensional network and, as in the case of a stabilization with acetic acid, the entire range from shear thickening to thixotropic flow can be observed. By variation of the chemical composition of the sol, an optimized rheological behaviour can be achieved for a given purpose.

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