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Gelation control of the scleroglucan–zirconium system using oxyacids

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In numerous applications of gels, one sometimes needs to control the gelation process. Here we focus our investigations on a particular means to attain this aim for the scleroglucan–zirconium system. For this purpose some oxyacids have been added to the system. Since the oxyacids involved are known to form complexes of various stability with zirconium, the whole gelation system follows from competition between oxyacid–zirconium and polymer–zirconium complex formation. The zirconium used in this study was in the form of zirconium lactate, and our results show that gelation diminishes in the order of citric, malic, tartaric and lactic acids. This hierarchy was compared to that expected from available equilibrium constants of oxyacid–zirconium complexes.

(Keywords: scleroglucan–zirconium; gelation control; oxyacids)

INTRODUCTION

In a previous paper[1] we dealt with the formation kinetics of polymeric gels that were obtained by means of zirconium addition to scleroglucan solutions. The gelation kinetics were found to be endothermic and to show a classical power-law dependence on polymer concentration C_s (i.e. $\cong C_s^{1.4}$). On the other hand most unusual behaviour was observed, namely the dependence of the gelation kinetics on zirconium concentration. Indeed, our results clearly showed an increase in the gelation kinetics with zirconium concentration, as long as this concentration is below a critical value, and a subsequent fall. This behaviour was explained on the basis of available information about zirconium chemistry. Furthermore, we have also emphasized that the system involved is to be used in an additional oil recovery process by selective modification of the rock reservoir permeability after its in-depth placement. Therefore, this is the reason for our attempt to control the gelation kinetics of such a system. Since some parameters such as temperature are imposed by the nature of the reservoir, only external factors may be changed to attain this aim. Briefly, in aqueous solution zirconium shows complex chemistry. At very low concentration ($\leqslant 5 \times 10^{-4}$ M) and very high acidity ($[H^+] \approx 2\,\text{mol}\,l^{-1}$) zirconium exists in monomeric form[2,3]. Under other conditions, however, it easily undergoes hydration and hydrolysis, and forms polynuclear species such as $Zr_x(L)_n$, where L is a ligand[4,5] like C_2O_4 for example. Scleroglucan is a linear polymer, the basic monomer of which is β-D(+)-dextrose. Its main chain is a succession of $\beta 1 \rightarrow 3$D dextrose units, every third residue being laterally substituted with a $\beta 1 \rightarrow 6$D dextrose.

Scleroglucan crosslinkage by zirconium is a ligand exchange process where some of the original zirconium ligands are replaced by oxygen originating from polymer hydroxyl groups as schematically shown by the following reaction:

$$Zr_x(L)_n + m(P\text{–}OH) + mH_2O$$
$$\rightleftharpoons Zr_x(PO)_m(L)_{n-m} + mL + mH_3O^+$$

Here P–OH represents the reacting polymer unit, and m is a positive whole number. The kinetics of such a reaction depends on the stability of the species involved. So when L is H_2O or OH^-, ligand exchange is a relatively rapid process, whereas it goes much slower for organic ligands. To crosslink polymer chains together, the complexes formed on the right side of the above reaction must obviously be more thermodynamically stable than the initial zirconium complexes. On the other hand, zirconium is known to react with oxyacids to form complexes of different shape and stability[4]. Thus we can reasonably think that, in the presence of various oxyacids, the polymer crosslinking reaction should now compete with the formation of oxyacid–zirconium complexes, which would be of greater thermodynamic stability than the zirconium–polymer complexes. Thus the observed kinetics of gel formation may be influenced in this manner, and the importance of such influence should depend on the nature and relative concentration of the oxyacid. In *Table 1* we have reported the equilibrium constants of zirconium complexes with oxyacids at $[H^+] = 2\,\text{mol}\,l^{-1}$ published earlier by Ryabchikov *et al.*[3].

Zirconium complexes formed with these oxyacids may differ in their shapes and structures as discussed in ref. 3. With trioxyglutaric acid, for example, zirconium forms five ring complexes in which the hydrogen of hydroxyl is not removed during the complexation process, while it is released in the lactic acid case. In any case, we may expect that the addition of an appropriate oxyacid to a polymer solution would result in delaying gel formation

Table 1 Equilibrium constants of Zr complexes[3]

Acids	K_1	K_2
Lactic	190	350
Malic	172	
Tartaric	310	–
Trioxyglutaric	2580	25×10^4
Citric	2600	–

by a factor that would increase as the given oxyacid–zirconium complex stability increases. So in the present study we have examined the influence of the involved oxyacids on the gelation kinetics of the scleroglucan–zirconium system.

EXPERIMENTAL

The solvent used was a synthetic seawater ($30\,\mathrm{g\,l^{-1}}$ NaCl + $3\,\mathrm{g\,l^{-1}}\,\mathrm{CaCl_2}$) and the respective polymer and zirconium concentrations were fixed at $C_s = 1000$ ppm and $C_{Zr} = 25$ ppm. C_{Zr} is given here in ZrO_2 equivalent, but the sample used was furnished in the form of zirconium lactate in order to stabilize it. C_s was five times greater than the overlapping polymer concentration C_s^* determined from the phase diagram[6] and below which no gelation should be observed. The desired quantity of the chosen oxyacid was then added to polymer solution and the pH was adjusted to 7 using HCl or NaOH before the addition of zirconium. The gelation kinetics was determined by following the change in the solution elastic modulus in the course of time until gelation was over. This was done by means of a controlled stress rheometer and measurements were performed at a frequency of 1 Hz in the linear regime. Since the elastic modulus variation is related to the created bond density, the gelation kinetics were simply given by the G' *versus* time curve slope, $\mathrm{d}G'/\mathrm{d}t$, determined here a few minutes after the onset of gelation. Indeed, following the theory of elasticity[7], the elastic modulus is proportional to the formed crosslink density ν as shown below:

$$G' - G'_0 = q\nu kT$$

where G'_0 is the elastic modulus of uncrosslinked polymer solution, kT the Boltzmann factor and q a parameter that depends on the functionality. Criticism of and limitations in the use of the relation above have been discussed elsewhere[8]. It appears, however, that $\mathrm{d}G'/\mathrm{d}t$ may be a measure of the rate of created bond density during the gelation process, $\mathrm{d}\nu/\mathrm{d}t$, at fixed temperature. Moreover, this relation may be used to determine the final created bond density, or the gel strength, as gelation was over.

RESULTS AND DISCUSSION

As we emphasized above, the crosslinker used is zirconium lactate. The obtained results are plotted in terms of $\mathrm{d}G'/\mathrm{d}t$ *versus* the relative concentration of added acid to the ZrO_2 concentration, which we shall abbreviate in the remainder of the text as L/Zr ratio. Let us first examine the influence of lactate addition on the gelation kinetics of the system. *Figure 1* shows that the gelation kinetics is insensitive to lactic acid concentration until it reaches a somewhat critical value, after which it decreases slowly. Such behaviour may simply be explained by the fact that the polymer crosslinking reaction is preceded by a dissociation reaction of zirconium lactate. Thus an increase in lactate concentration should result in the displacement of this reaction for the benefit of zirconium lactate formation. Nevertheless, at low added lactate concentrations, the lactate ligands are still less active in attaching zirconium ions. In this way the gelation kinetics is determined by the zirconium–polymer complex formation. At significantly higher lactate concentrations, the competition between the crosslinking reaction and zirconium lactate formation changes over.

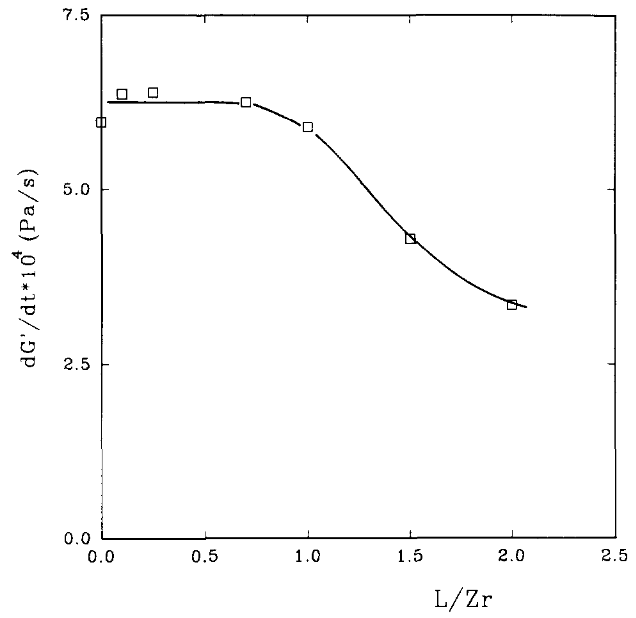

Figure 1 Gelation kinetics $\mathrm{d}G'/\mathrm{d}t$ plotted *versus* the molar fraction of added lactate relative to zirconium at $C_{Zr} = 25$ ppm, $C_s = 1000$ ppm, pH = 7 and $T = 35$°C

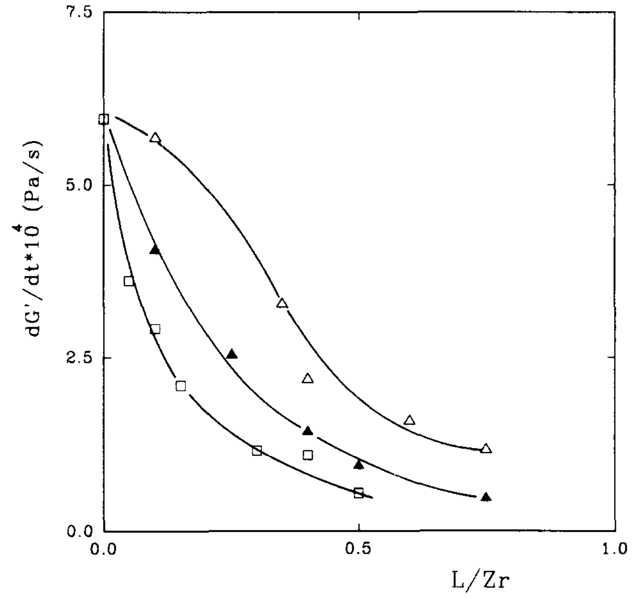

Figure 2 Influence of addition of various oxyacids on gelation kinetics in the same conditions as in *Figure 1*: (□) citric acid, (▲) malic acid and (△) tartaric acid

Following the same procedure, we have investigated the influence of the oxyacids listed in *Table 1* on the gelation kinetics. Since the equilibrium constants of trioxyglutaric and citric acids are close, the influence of trioxyglutaric acid was not considered in the present study. As can be seen on *Figure 2*, the gelation of the scleroglucan–zirconium system is highly restricted by oxyacid addition. This restriction is indeed dependent on the oxyacid nature so the following remarks can be made:

As in the lactic acid case, a critical concentration beyond which the gelation kinetics is affected seems to exist for tartaric acid but was undetectable for the others. Nevertheless, this critical tartrate concentration is much lower than the lactate one. Such behaviour was previously observed by Albonico *et al.*[9] for the polyacrylamide–chromium system in which chromium was in the complexed form. These authors have shown the existence of such a critical concentration when ligands such as glycolate or salicylate were added to the system as a delaying gelation agent.

The main unexpected result is the obtained hierarchy of used acids. Indeed, our results seem inconsistent with the expected oxyacid hierarchy if the equilibrium constants of zirconium complexes with oxyacids listed in *Table 1* are used as criteria. This observed discrepancy may be due to the difference in pH conditions since the involved hierarchy is established in highly acidic medium, i.e. $[H^+] \sim 1\,\mathrm{mol\,l^{-1}}$, while the pH was adjusted to 7 in this work. Nevertheless we think that the main reason is that the order of stability constants can differ from that of equilibrium constants of reactions involving zirconium as discussed in ref. 3.

Finally, we would point out that the final gel strength was affected by oxyacid addition in the same way as the gelation kinetics (data not shown). So, strictly speaking, the addition of oxyacids to the system should not be considered as a delaying gelation procedure.

CONCLUSION

In the present study we have examined the influence of some oxyacids on the gelation of the scleroglucan–zirconium system. We have shown that the addition of such oxyacids should result in restricting gel formation. This restriction depends on oxyacid nature and its relative concentration. When the influence of oxyacids is considered, our results show that the expected hierarchy from the equilibrium constants of oxyacid–zirconium complexes is not preserved since we have to consider stability constants to this purpose. We finally point out that sometimes, for an unknown reason, the strength of formed gels overcomes the desired level. So, in this case, a subsequent injection in the treated rock of an appropriate oxyacid may supply to gelation correction of the scleroglucan–zirconium system.

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