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KINETIC STUDY OF GELATION OF SOLVENTLESS ALKOXIDE–WATER MIXTURES

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A very high-speed rotatory blender was used to enhance the homogenization of TEOS + H_2O mixtures. The effects of several reaction parameters on the gelation rate of these solutions and those submitted to ultrasonic treatment were studied. Comparison of the results points to differing accelerating mechanisms in each case.

1. Introduction

Cavitation is effective in accelerating the hydrolysis of alkoxides making it possible to obtain a homogeneous liquid, which quickly gels, without using a solvent of the alkoxide–water mixture [1].

Solventless hydrolysis appears a way of preparing gels with textural properties which differ significantly from those prepared by the classic procedure in alcoholic dilution. Aerogels of very regular and fine porosity, as well as high density and surface/volume ratio, result from the subsequent hypercritical drying [2] that make them potentially applicable in catalysis and as low-shrinkage matrices for ceramic–ceramic composites.

Essentially, the process which takes place when the mixture is submitted to the action of ultrasounds can be described as follows. Cavitation forms and expands bubbles, up to a maximum radius, during the expansion phase of the ultrasound wave. Then, under the acoustic pressure in the high-pressure phase, the bubbles are compressed to a minimum size at which they adiabatically collapse. Finally, the solute and solvent contained in the bubble react in the vapor phase and the sol foams because of the escape of a part of the alcohol produced by the hydrolysis reaction.

Alkoxide solventless hydrolysis can also be promoted by mechanical ultrarapid stirring of the mixture. Very little is known about the nature of the reactions that occur in these conditions. Nevertheless, one can expect a different catalysis with other rate constants both of the mixture under stirring and after stopping the external action; gels with different textural characteristics should result.

When carrying out a comparative study, gelation time, t_G, is the most important macroscopic parameter. This time is a function of the hydrolysis and polycondensation rate constants of the mixture during and after the external action. These rates depend on the hydrolysis and polycondensation ratios and, hence, on the energy delivered to the system. The amount of silanol groups present in the sol is evaluated through a control of the base that may be added for a certain variation of the gelation time. Finally, information about the polycondensation degree can be obtained by seeding the solution with small silica particles and measuring their influence on gelation time.

2. Experimental

Gels were obtained by hydrolysis of $Si(OEt)_4$, TEOS, with HNO_3 acidified water at $pH = 1.5$. Unless indicated otherwise, the molar ratio $R_w = [H_2O]/[TEOS]$ used in all the experiments was equal to 4.

In the ultrasonics procedure, the two-phase TEOS + H_2O mixtures were subjected to ultrasonic radiation produced by a sonifier (Vibracell. Sonics & Materials, USA), operating at 20 kHz with a titanium transducer of 13 mm diameter driven by an electrostrictive device. Insonation took place in a glass container 40 mm in diameter, kept open to allow vapors to escape. 'Turbogels' were elaborated in the same way but using a rotatory blender (Ultraturrax TP 18/10) operating at 20000 rpm as external agent. During stirring, the temperature increases to 80 ° C, then stabilizes at about 75 ° C; however, the maximum temperature reached during sonication was 73 ° C.

It seems reasonable to assume that, at a constant power delivered to the system, the energy density dissipated per volume unit, U_a, is a function of the external action time, t, and the volume, V, as: $U_a = P_a t_a$, where $t_a = t/V$ and P_a, estimated by calorimetric measurements on a fixed volume of water, was taken equal to 45 and 15 W for 'turbo-' and 'sonogels', respectively.

The homogeneous solutions so obtained were poured into test tubes, and gelation time t_G at 50 ° C was checked. This was defined as the time interval between the end of t_a and the moment when, on tilting the tube, no more fluidity was observed. The influence on this parameter of U_a, and of sol pH adjustment with diluted ammonium hydroxide (6.62×10^{-6} M) (measured as $R_b = [NH_4OH]/[TEOS]$), was tested. The reaction stage reached by the mixtures submitted to a fixed U_a under different experimental conditions (R_w, environment temperature, presence of particles) was evaluated by means of the molar ratio of diluted base R_{bs} which must be added for gelation during the experiment (gelation in situ). The environment temperature was controlled by immerging the container in a thermostated bath.

3. Results and discussion

3.1. Modification of gelation time

The gelation time of homogeneous solutions obtained after different doses of sonication or stirring was tested (fig. 1). Both cases exhibit the exponential decrease described in a previous work [3] concerning gelation time as a function of the supplied sonic energy. Only one regime is observed for 'turbogels', unlike sonogels, for which two well-differentiated regimes appear.

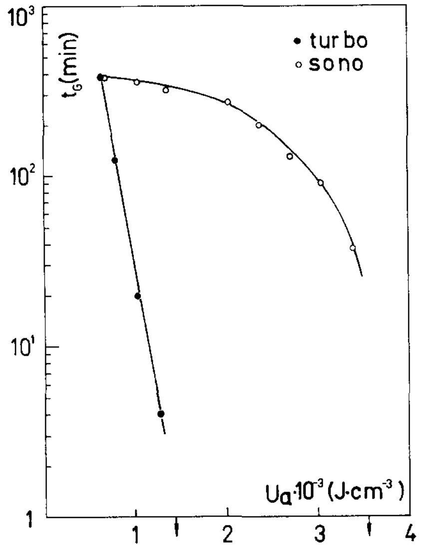

Fig. 1. Gelation time after different doses of sonication or stirring.

This behavior can be explained on the basis of the evolution with time of the polycondensation ratio, $c(t)$. It behaves corresponding to the resulting product of a second order consecutive reaction [4]. The kinetic rate constants depends on the degree of substitution of the monomer. Here, as a first approach to the problem, overall hydrolysis (k_H) and polycondensation (k_C) rate constants are considered as proposed by Orcel and Hench [5]. Thus, these curves could be fitted by a function of the form

$$c(t) = 1 + \frac{1}{\alpha_2 - \alpha_1} \times (\alpha_1 \exp(-\alpha_2 t) - \alpha_2 \exp(-\alpha_1 t)),$$

α_1 and α_2 being directly related to k_H and k_C.

The results indicate that the values of k_H and k_C of the mixture subjected to the action of an external agent such as ultrasound or ultrarapid stirring are one (sono) or two (turbo) orders of magnitude larger than without the application. The curves in fig. 2 could be a description of the

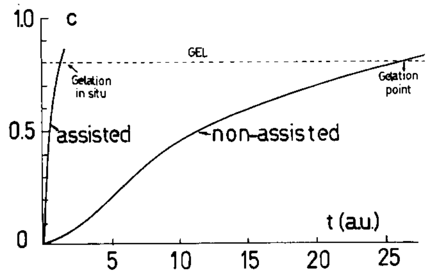

Fig. 2. Modelling of the average condensation degree for an assisted and a non-assisted reaction.

polycondensation ratios with assisted and non-assisted catalysis. Any abrupt change in the kinetic rate constants involves a second-order discontinuity in $t_a = U_a/P_a$, having $c(t_a) = c(t_0)$ as a boundary condition.

The evolution of a system involving, firstly, a sono- or turbocatalysis, and then left on its own, is represented in fig. 3. The gel point is reached for a certain value of c for which no fluidity is observed. It is obvious that an increase in the reactivity of the mixture under an external agent entails a reduction of the in situ gelation energy, U_{as}, as well as an increase in the natural reactivity of the system decreases the gelation time for the bloating threshold energy. Figure 4 shows ln $t_G(U_a)$ function for $c_{gel} = 0.8$ obtained with two different overall kinetic rate constants. In other words, the slope of the curve, d(ln t_G)/dU_a, increases for higher kinetic rate constants of the mixture under the external action, and for lower reactivity of the system left on its own. Thus, the results shown in fig. 1 indicate that k_H and k_C of the solution under stirring are higher than under ultrasound and lower after the application of the external agent.

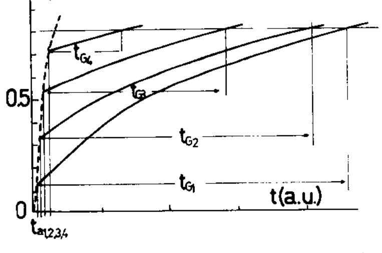

Fig. 3. Evolution of the polycondensation ratio of systems previously subjected to ultrasounds or ultrarapid stirring doses (t_{a1}, t_{a2}, etc.) and then left on their own. t_{G1}, t_{G2}, etc., represent the gelation time for doses 1, 2, ..., respectively.

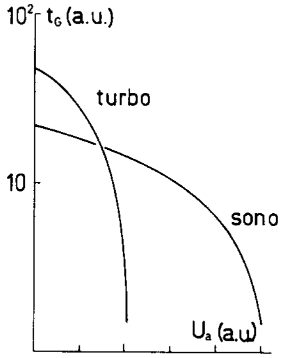

Fig. 4. Behavior of ln t_G as a function of the supplied energy for different overall kinetic rate constants: high α_1 and α_2 during the action of an external agent (ultrasounds or blender) and low α_1 and α_2 after the application and vice versa.

At this point, it should be noted that the alcohol which is produced immediately after the start of hydrolysis helps in the mutual dissolution of TEOS and water. Naturally, mixing at this stage causes an increase of the reaction rate during

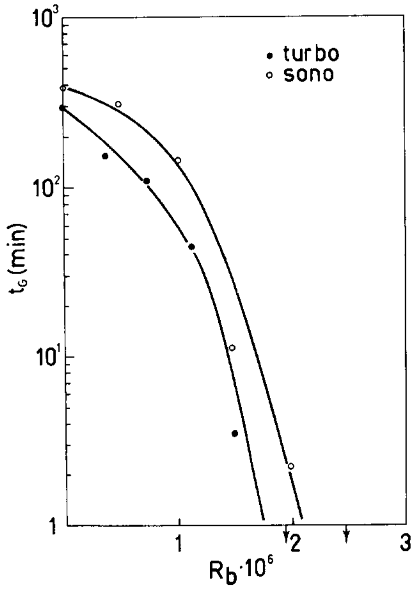

Fig. 5. Gelation time reduction by pH adjustment. The pH increase is more effective for the sonosolution since it is less polycondensed.

the external action and, due to dilution, a decrease of it when the system is left on its own.

For low polycondensation ratio, t_g is not much affected by an increase in the energy dose. When it is such that the inflection point of $c(t)$ curve is surpassed, a very much bigger reduction occurs in gelation time, with the variation of the slope observed in the curves. The high slope of curve $\ln t_G(U_a)$ is related to a more advanced level of polycondensation after stirring.

It is known that the addition of base to the gelifying mixtures favors condensation between silanol groups, inducing a faster gelation. The gelation time reduction by pH adjustment is depicted in fig. 5 for both 'sono-' and 'turbo-' solutions submitted to a constant dose ($U_a = 682$ J/cm^3).

When the base is added, the effect of an external agent will be accompanied by an increase of kinetic rate constants, that is, the condensation rate of the system left on its own is stimulated. As rate constants are higher when intermediate species hold more –OH groups [4], the pH increase will be more effective for the sonosolution, since it is less polycondensed.

This is shown (fig. 6), when eliminating the time between the last two figures. The 'turbosolution' can be taken near the gelation point very much more effectively by increasing the dose supplied than by means of pH adjustment. This confirms that, after bloating, while hydrolysis of TEOS is even catalyzed by ultrasounds, high speed stirring provokes a very strong increase of the polycondensation rate.

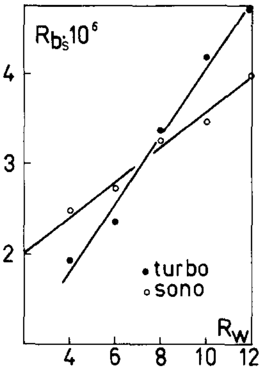

Fig. 7. Influence of the TEOS dilution on the amount of base required for in situ gelation.

3.2. Influence of reaction conditions

Figure 7 shows that, at an increasing dilution of TEOS, R_{bs} takes higher values, rising more quickly for the turbosolutions. Experimentally, it can be observed that the higher R_w, the larger the delay in foaming time and the lower the temperature rise.

The effect of the environment temperature is also stronger in turbogels, for which there is no reaction at 30 ° C, and gelation in situ occurs before the end of stirring time at 70 ° C (fig. 8). In this case, the environment temperature has an

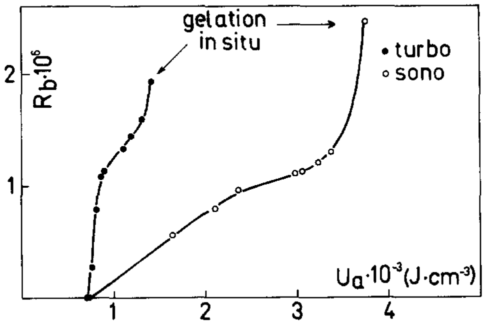

Fig. 6. Calculated equivalence between pH adjustment for a supplied dose of energy and U_a. Note that taking the turbosolution near the gelation point is done very much more effectively by increasing the dose supplied than by means of pH adjustment.

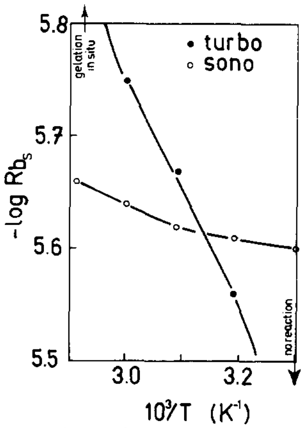

Fig. 8. Influence of reaction temperature on the amount of base required for in situ gelation.

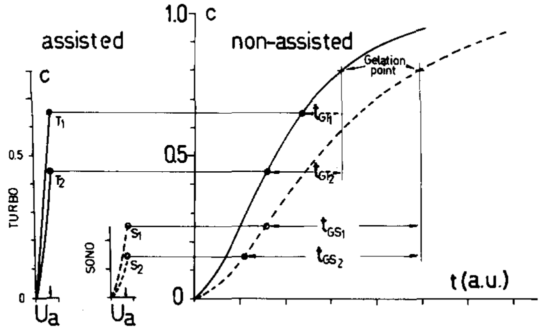

Fig. 9. Modelling of the influence of a kinetic rate constant change on the gelation time of a turbo- and a sonosolution for two different temperatures. The former one is more sensitive due to the higher polycondensation ratio reached during the assisted reaction for which the inflection point has been surpassed.

opposite effect on the foaming temperature and time. If polycondensation is accelerated after foaming, any effect which anticipates it will favor a more advanced reaction stage. A temperature increase causes an increase in the rate constants. In fig. 9 a modelling of the influence of a kinetic rate constant change on the gelation time of a turbo- and a sonosolution is shown. The former is more sensitive due to the higher polycondensation ratio reached during the assisted reaction for which the inflection point has been surpassed. The greater the constants, the greater dc/dU_a; therefore the reaction conditions are more sensitive for high-speed stirring action.

The presence of fine silica particles in both kinds of solutions was also investigated. While no noticeable changes were observed for sonogels, gelation in situ was always observed in turbogels after foaming for several concentrations, as can be expected for a solution with a higher condensation ratio.

4. Conclusion

Ultrarapid stirring appears effective to promote TEOS hydrolysis producing a homogeneous liquid which quickly gels.

The results of the gelation time seem to indicate that the rotatory blender action induces higher overall rate constants than ultrasounds given rise to highly polycondensed solution, the reactivity of which is lower than that of the sonosolution.

The turbocatalysis is more sensitive to the change of temperature, dilution and 'seeding' and, hence, its effects are less regular and less easy to control than those of sonocatalysis.

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