Influence of surfactants on the structure of titanium oxide gels: experiments and simulations

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Abstract

We report here on experimental and numerical studies of the influence of surfactants on mineral gel synthesis. The modification of the gel structure when the ratios water-precursor and water-surfactant vary is brought to the fore by fractal dimension measures. A property of polydispersity of the initial hydrolysis is proposed to explain these results, and is successfully tested through numerical experiments of three dimensional chemically limited aggregation.
I. INTRODUCTION

The irreversible aggregation of molecules in a solution, leading to the formation of a three-dimensional (3D) network or gel, has been the focus of a wide range of studies, from the more theoretical to the more application-oriented ones [1], [7]. The structure of the gel is a well-known case of fractal mass distribution [1].

The polymerization of a mineral monomer in an organic solvent is an example of this sol-gel process. More specifically, a very studied class of monomers is the metal alcoxides one, which elements consist of a metal atom (as silicon(Si) or titanium (Ti)) surrounded by alcoxy (alcohol) groups. In an organic solvent (decane, cyclohexane) and in the presence of water, they readily react in a two-step process leading to the fractal polymer.

In the first step, hydrolysis, the interaction of monomers with water leads to the substitution of some alcoxy groups with short -OH (hydroxy) radicals (the number of groups modified depending at least of the total amount of water available):

\[ Ti(OR)_4 + nH_2O \rightarrow (HO)_nTi(OR)_{4-n} + (4 - n)ROH. \]

Then the hydrolyzed monomers stick together through -OH HO- (oxolation) or -OH RO- (alcoxolation) reactions, to form the inorganic backbone of the fractal polymer (this step is the polycondensation):

\[ -Ti-OH + HO-Ti- \rightarrow H_2O + -Ti-O-Ti-. \]

Due to the presence of four potentially active sites, one obtains a branched polymer and the gelation of the structure.

However, for some very reactive alkoxide precursors (as in our case tetraisopropyl orthotitanate \([Ti(O^iPr)_4])\), the reaction is so fast, even for very small amounts of water, that the precipitation of the solution can be avoided only by introducing amphiphile molecules which control the sol-gel transition by interacting with water or hydroxyl radicals. Only this trapping effect obtained from the introduction of the surfactant allows the formation of the gel by slowing down the hydrolysis, as has been recently investigated [2] [3] [4].
Rather surprisingly, considering the stability of the characteristic fractal dimension of the gel with variations of many parameters, the amphiphilic molecules not only control the kinetics of the reaction, but induce structural variations in the final polymer. In the case where a gel could be synthetized, we have studied experimentally the influence on the process of the water-surfactant and water-precursor ratios. More specifically, we report here of the possibility of understanding some of the observed variations of the gel structure from the following hypothesis: in reactions with very small amounts of water, not all the sites on the monomers will be hydrolyzed and the distribution among the monomers of the hydroxyl (-OH) radicals created in the hydrolysis on the precursor monomers could depend, for a given amount of water, on the \( [H_2O]/[Surf.] \) ratio. Numerical experiments which have been done to test this idea are described in this paper, and explain some evolutions of the fractal dimension of the final gel.

II. EXPERIMENTAL RESULTS

The gels have been synthetized in two different solvents (cyclohexane and decane) from a \( Ti(OiPr)_4 \) monomer. For each solvent, two solutions were prepared, the first (S1) containing the surfactant (Triton X-35) and the water, and the second (S2) the precursor; S1 was then tipped into S2. The characteristic parameters of the solution were the \( Ti(OiPr) \) molality, always fixed to 0.1 \( mol.kg^{-1} \), and the molar ratios:

\[
n = \frac{[H_2O]}{[Surf.]}; \quad h = \frac{[H_2O]}{[Ti(OiPr)_4]}.
\]

These diluted sols exhibit long gelation times and produce gels with a large fractality range \[4\]. The polymeric gelation could be obtained for \( h \) between 2 and 3, and \( n \) between 1 and 2. The structural characteristic of the final gel we were interested in was the fractal dimension, which was measured using ultra small angle x-ray scattering \[5\]. One can see in fig. \[1\] the evolution with \( h \) of the fractal dimension, for two values of \( n \).
As previously said, the kinetic of the sol-gel process can be decomposed in two steps: hydrolysis of the isopropoxy group, and polycondensation of the hydroxyl radicals. Let’s go into some details. On the basis of the partial-charge model [6], alcoxolation (condensation between \(OH\) and \(OR\) groups) should be the favored condensation reaction between partially hydrolyzed, coordinatively saturated titanate precursors. As underlined by Brinker and Scherer [7], the same trend is predicted for silicate but \(^{29}\)Si NMR investigations [8] have shown that oxolation (condensation between \(OH\) groups) is the favored reaction of condensation between partially hydrolyzed silicon alkoxides. Perhaps solvent interactions that are not accounted for by the partial-charge model influence the quality of the leaving group [7]. In our case, the assumption that oxolation is the favored reaction can also be justified taking into account the stronger lyophobicity of the hydroxyl groups in the inverse micellar medium.

An NMR study of the isopropanol amount in the solution [4] led us to the conclusion of an almost instantaneous hydrolysis compared with the gelation time. Therefore one can hope to study separately the effects of the surfactant presence on the two reaction steps, at least if no important ”second hydrolysis” occurs, due to the water created during the condensation.

Our modelization assumption concerns primarily the way the surfactants could control the hydrolysis. In the solution, the water is trapped on the hydrophilic heads of the amphiphils (with a limit of four molecules of \(H_2O\) on every surfactant), which organize themselves in inverse micellar aggregates in the hydrophobic solvent. Quasielastic light scattering measurements [2] give us a hydrodynamic radius for these structures between 3 nm for \(n = 1\) and 4 nm for \(n = 2\), the surfactant itself having an average extension of 1.5 nm. One can estimate from these radii that the number of pseudo-micelles for one alkoxide is 3.5 times larger for \(n = 1\) than for \(n = 2\). In order to be hydrolysed, the precursor molecules must penetrate into these aggregates. This was the motivation for introducing our ”hydrolysis polydispersity” hypothesis: the number of hydroxyl radicals created on the alkoxide will vary between 1 and 4, with a distribution dependent on \(n\), due to the variation with this parameter of the available water in the micellar structure.
III. THE MODEL AND THE SIMULATION

Let us describe the numerical experiments performed in order to test this assumption. In our three-dimensional algorithm, every particle has six potentially active sites (cubic symmetry). Taking into account the titanium tetravalence, we hydrolyze at most four of these sites, always situated in the same randomly selected plane. The hydrolysis ratio parameter \( h \) is represented by a scalar \( q \) varying between 0.5 and 0.75 for \( h \) between 2 and 3: for \( N \) particle samples, the hydrolysis stops when \( 4Nq \) sites have been hydrolyzed. The implicit hypothesis in taking \( q = h/4 \) is that all the water contained in the solution has been used in the hydrolysis (a conclusion we inferred from our NMR studies). It is far more difficult to introduce \( n \) in the algorithm, for many hypotheses on the molecular behavior are involved in the prediction of its influence on the hydrolysis. We have chosen a parameter \( p \) in \([0, 1]\) to govern directly the polydispersity in hydrolysis of the sample. The idea is as follows: during every round a monomer is randomly chosen and a random number \( z \) generated. Depending on whether \( z > p \), \( p^2 < z < p \), \( p^3 < z < p^2 \), or \( z < p^3 \), 1, 2, 3, or 4 sites are simultaneously hydrolyzed. Then a second particle is selected, among the ones which have not yet been hydrolyzed during this round. When every particle has been selected exactly once for hydrolysis in the round, a next round opens, and so on until the \( 4Nq \) water molecules available have been used.

The algorithmic interest of this procedure is to make the hydrolysis polydispersity vary strongly with \( p \), which increases all eventual polydispersity effects. This does not happen, for example, if at every step the hydrolyzed particle is put again in the sample from which the next one is selected. But what about the physical point of view? Concerning the power law in \( p \) for the choice of the number of hydroxyl radicals created, an independence of the different hydrolyses happening with the same probability when the precursor is in the micellar structure is implicit. It may appear more arbitrary to hydrolyse every particle exactly once.
in ever round. As previously remarked, this is essentially in order to make the hydrolysis polydispersity vary more strongly in the algorithm.

Concerning the aggregation dynamics, we have chosen a chemically-limited model [9], [10] which suppresses all effects due to the diffusion. More precisely, we start from a diffusion-limited model [9], in which the gel fractality results from the brownian motion of the particles which stick together with a probability $c$ when happening to occupy nearest-neighbour lattice sites. Making then $c$ going to 0, we end at the chemical model mentioned above: the particle random path length before aggregation goes to infinity, with the consequence that all the free sites on the aggregate have an equal probability of stick to it, except for steric hindrance. Of course the fractal dimensions obtained are superior to the diffusion-limited model ones.

In our algorithm, the following are associated with every particle at every step: (1) the list of its six sites and their state (hydrolyzed, non-hydrolyzed, or already used in condensation); (2) the reference number of the cluster to which it belongs; (3) its 3D coordinates inside its cluster (i.e. its position relative to the other particles in the same cluster only). So each cluster is on a lattice but the whole process is not, at least not in a box [11].

At every step, two bonds are selected randomly among the $6N$ ones. In order for the aggregation process to take place, they must obey the following conditions: (P1) they both must be hydrolyzed sites; (P2) they must belong to two different particles not being in the same cluster; (P3) moreover, cluster rotation is excluded, so the two bonds must be on two opposites sites on the same symmetry axis of the monomer. Only if these conditions are fulfilled can one then check the steric possibility of the aggregation, due to the presence of other molecules already connected to the selected sites.

Why this model? To neglect the hazards of the diffusion is equivalent to accelerating the aggregation dynamics; this is an important advantage since we wish to explore a two-dimensional parameter space, which requires many drawings. Although the physical polymerization process in our solutions is conceivably controlled in part by the diffusion, its effect is only to globally decrease the fractal dimension of the final aggregate, without modifying
the relative variations due to polydispersity effects. So the same trends must be observed in this model for the dimension in the \( p \) and \( q \) phase space, unless other assumptions are made on the influence of surfactants during the polymerization process, as discussed below.

Being not in a box, it was not possible to introduce a gelation test (like the existence of a percolation cluster) giving to the algorithm a systematic stopping condition. The end of the simulation happens when (1) all the particles are in one cluster (2) \((6N)^2\) successive attempts to select bonds fulfilling the (P1)-(P3) conditions have been unsuccessful (3) \(N^2\) successive sticking attempts have failed due to steric reasons. None of these conditions, even the first, has anything to do with a physical gelation. One can obtain the fraction \(a_N\) of the initial \(N\) particles sample found in the biggest final aggregate; to impose \(a_N = 1\) as a gelation criterion give a phase transition diagram in the \(p, q\) plane with a gelation domain narrowly limited around the \(q = 1\) limit (value corresponding to total hydrolysis). This is clearly not correlated to the physical gelation domain, which contain all the \(h > 2\) part of the phase space. Moreover it is obvious that the physical gelation does not necessitate all the monomers to be polymerized.

After the conclusion of the aggregation process, we compute the fractal dimension of the biggest aggregate created. We obtain it from the double logarithm graph of the two points correlation function calculated with the following algorithm: for every particle the array of distances of the other monomers, by increasing order, is obtained; one then averages over all the arrays (i.e. over all the cluster monomers). With \(c(r)\) the two-points correlation function, and \(D\) the fractal dimension, one has:

\[
n_R(D) = \int_0^R c(r) d^3 r = R^D.
\]

And from the slope of the linear function

\[
log N = f (log R)
\]

the fractal dimension is easily obtained.
IV. DISCUSSION

With this method, we have done numerical experiments to be compared with Fig. 1, $q$ varying from 0.5 to 0.75 and $p$ from 0 to 1. The step for $q$ was $5 \times 10^{-2}$, and $10^{-1}$ for $p$. Due to the very nature of the simulation algorithm, the cluster self-similarity is obtained only on distances of approximately one-quarter of its maximum radius. Hence, to observe the linearity of the correlation function on many orders of magnitude, it should be necessary to work on particle samples of at least $10^4$ elements. On a RISK workstation, the aggregation algorithm could take many hours to complete. Nevertheless, it is remarkable that on 1000 particles samples, sufficient information can be obtained on the fractal dimension, a fact that has been observed in all the $(p, q)$-phase space. This is all the more true if one averages over many samples, a procedure which increases only linearly the execution time. Nevertheless the dimensions are a little smaller (of 0.2 approximately) than the physical ones. Fig. 2 shows the proportion evolutions with $p$ ("polydispersity") of the different species for $q = 0.5$ ($h = 2$) and $q = 0.75$ ($h = 3$). For the same two extremal values of $q$, Fig. 3 shows the fractal dimension evolution with $p$. To compare with the experimental evolutions, one must remember the correspondence $q \rightarrow h$ and $p \rightarrow n$. The $h = 2$ plot of 3 can be compared to the bottom experimental plot. The $p$ variation at constant $h$ corresponds moreover to vertical evolutions between the two plots of 1 (top). So we predict that the two evolutions with $h$ will converge for values of $q$ near 1, and not cross, as in the experimental data.

For all the $q$ values, the fractal dimension increases with $p$. This is easily understood from fig. 2. When $p = 0$, the distribution of differently hydrolyzed species shows no polydispersity: it is peaked on a value depending on $q$; for example for $q = 0.5$, all the particles have two hydrolyzed sites, for $q = 0.75$ three hydrolyzed sites. As $p$ increases, the proportion of particles having more hydrolyzed sites than this initial value increases, and forms a greater proportion of the final aggregate (remember that this cluster contains not necessarily all the particles of the sample). At the $p = 1$ limit, only four-hydrolyzed-site particles remain.

The important point is that when $q$ increases, the domain of variation of the fractal dimen-
sion decreases with $p$. At the $q = 1$ limit (complete hydrolysis) of course the polydispersity cannot play any role, and $p$ has no influence on the fractal dimension, since all the possible sites are hydrolyzed. The asymptotic value of the dimension is then the same as for $p = 1$, since as previously said only particles with four hydrolyzed sites remain for this value. Now for the evolution with $q$ of the dimension, as previously mentioned, one of the difficulties of this simulation is the gauging of the $n$ and $p$ scales. However, the increasing of the fractal dimension with $h$ for $n = 1$ can clearly be associated with the same evolution with $q$ for $p = 0$. The ranges of evolution coincide rather well (Fig. 3).

For $n = 2$, taking into account the error bars in the x-ray determination of the gel structure, one could interpret in at least two ways the evolution of the fractal dimension. The first is a convergence of the $n = 1$ and $n = 2$ curves to a common asymptotic value (2.4), around which the $n = 2$ curve would not vary very much. This is in fact the prediction of our simulation for a pure hydrolysis effect. For $p = 1$, the dimension is constantly equal to the asymptotic limit 2.35. Taking for $n = 2$ values of $p$ near 1 would give a slight increase of the dimension with $h$.

However, the experimental evolution of the fractal dimension with $h$ for large values of $n$ seemed to point out another interpretation, and could definitively not be explained by our model. For $n = 2$, due to one experimental point, the fractal dimension decreased with $h$, and crossed the increasing $n = 1$ curve. No mechanism based on the initial hydrolysis could account for this trend, since, given any kind of initial distribution of hydroxyl radicals, the fractal dimension must always increase with the hydrolysis rate, or at least stay constant if it appears that the hydrolysis has no effect on the structure of the gel. In any case, for $h \to 4$, the dimension must for any value of $n$ converge to the same limit, corresponding to the total hydrolysis case, for which the distribution of the radicals has no role to play. The lack of experimental points in this region of the $n, h$ phase diagram led us to perform a second set of measures at $n = 2$ and $2.5 < h < 3$. With more values, the fractal dimension appears in this range remarkably constant (see fig. 4), and coherent with the predicted asymptotic value 2.35. We concluded that the $n = 2, h = 3$ value of fig. 1 was not reproducible. The
evolution in the \((h, n)\) phase space predicted by the model seems to be confirmed.

V. CONCLUSION

We have succeeded in understanding through simulation the fractal dimension evolution for all the regions of the \((h, n)\) phase diagram, with a hydrolysis polydispersity hypothesis in the first stage of the reaction. The dimension increases with \(h\) and \(n\) in a well understood way. Therefore it appears that the influence of the surfactants molecules on the sol-gel process could be limited to the first step of the gelification. Interactions occurring later, in particular with the hydroxyl radicals, seem to be without effect on the structural properties of the gel.

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FIGURES

FIG. 1. Experiments: fractal dimension variation with $h$ for $n = 1$ and $n = 2$ (bottom); same variation with $n$ for $h = 2$ (top).

FIG. 2. Polydispersity variation with $p$ for $q = 0.75$ (top) and $q = 0.5$ (bottom).

FIG. 3. Simulation: fractal dimension variation with $p$ for $h = 2$ and $h = 3$.

FIG. 4. Experiment: evolution of the dimension for $n = 2$, $2.5 < h < 3$. 
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The graph shows the fractal dimension as a function of the water/surfactant ratio \( n \) and the hydrolysis rate \( h \).

For different values of \( n \), the fractal dimension varies with \( h \).

- For \( n = 1 \), the fractal dimension increases with \( h \) from 1.8 to 2.8.
- For \( n = 2 \), the fractal dimension increases from 1.8 to 2.8 as \( h \) increases from 2 to 3.

The graph indicates a non-linear relationship between the fractal dimension, water/surfactant ratio, and hydrolysis rate.
The graph illustrates the relationship between the fractal dimension and polydispersity $p$, with two different cases labeled as $h=2$ and $h=3$. The fractal dimension increases as $p$ increases for both cases, indicating a more complex structure with higher polydispersity.
