Effects of the Type of Alcoholic Solvent on the Formation of SiO₂ Wet Gels in Sol–Gel Process

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SiO₂系湿潤ゲル形成におけるアルコール系溶媒の効果

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The effect of the type of alcoholic solvent on the formation of SiO₂ gels in the sol–gel process has been studied by observing the gelation time in a tightly closed system. A large difference in the rate of gelation was found among fifteen kinds of alcohols used as the solvent. The gelation time decreased with increasing boiling point of the alcohol. The gelation time could be correlated with electrical properties, such as the dielectric constant and the solubility parameter of the solvent. The hydrolytated species of tetraalkoxysilane are solvated by alcohol and the degree of this solvation differs among alcohols. A model of the alcohol solvation process is suggested.

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1. Introduction

The preparation of gels, glasses and ceramics by means of the sol–gel method starts with the gelation of the sol, which is affected by numerous factors, such as the type of solvent, the catalyst, the amount of water and the reaction temperature. It is known that various shapes, such as powder, fiber, coating film and bulk body can be made by controlling these factors. 1–4

The effects of the catalyst and the water content on the formation of silica gel in the sol–gel process have been investigated by numerous researchers. 5–10 It was found that the hydrolysis and condensation reactions in the gelation of the solution depend on those factors. For example, Iler 11 explained that the condensation reaction of colloidal silica particles in aqueous solutions above pH 2 is base-catalyzed and below pH 2 is acid-catalyzed. On the other hand, there have only been a few studies on the effect of solvent on the gelation time. 11–13 It has been reported that the difference in gelation time is mainly ascribed to the difference in the rate of solvent vaporization. 12 Brinker 8 has shown that gelation time is inversely proportional to condensation rate:

\[ \text{Gelation time} \propto (\text{condensation rate})^{-1} \] (1)

Experimental results by Iler 10 and Pope and Mackenzie 12 support Eq. (1). There has been no systematic study, however, on the effect of the type of solvent on the gelation time, i.e., condensation rate.

It is scientifically and technologically significant to clarify the gelation mechanism, particularly the effect of an alcoholic solvent for the preparation of fibers and coating films.

In this study, we focused on the effect of the type of alcoholic solvent on the gelation of the alkoxide solution. The experiments have been conducted in a tightly closed system to prevent vaporization of the solvent.

2. Experimental

In examining the gelation of tetraalkoxysilane (Si(OR)₄), fifteen different alcohols supplied by Kanto Chemical Co. were used. The properties of the alcohols used as solvents are shown in Table 1. For lower acidic conditions (approximately pH 2), the starting solutions were prepared by mixing Si(OEt)₄, alcohol and water in the volume ratio of 1 : 0.48 : 0.35, or in the molar ratio of Si(OEt)₄ : methanol : water : catalyst (HCl) = 1 : 2 : 4.5 : 0.018. Two different procedures were used for preparing the starting solutions as shown in Fig. 1. Method–I is a procedure used by numerous researchers, in which the solvent is mixed in the starting solution. In Method–II, the solvent was added after the hydrolysis reaction took place in the solution consisting of Si(OEt)₄, H₂O and catalyst (HCl), in order to avoid the ligand exchange between alcohol and alkoxide. 11

\[ \text{Si(OR)₄} + x'\text{OH} \leftrightarrow \text{Si(OR)₄} \rightarrow (\text{OR'}^+) + x\text{ROH} \] (2)

Gelation was also examined for some combinations of silicon
alkoxide and alcohol. When higher acidic conditions below pH 2 were employed, these are specifically indicated in the figure captions.

The clear solutions or sols were poured into polypropylene beakers, which were tightly covered with plastic wraps, and were kept standing at room temperature (approximately 20°C) for gelation. The gelation point was defined as the time at which the sol in a container would not move upon tilting the container, as reported by Iler.\textsuperscript{10}

3. Results and discussion

Figure 2 shows the relation between the gelation time of the solutions and the boiling point of the solvent at pH > 2 (hereafter, referred to as base-catalyzed condition) for Method-I and Method-II. It is seen that the gelation time depends on the boiling point, i.e., the gelation time is shorter for alcohols of higher boiling point in both methods.

Figure 3 shows the gelation time for the combination of Si(OR)\textsubscript{4} and ROH. The gelation time for the combination of Si(OR)\textsubscript{3} and ROH is similar to that for the combination of Si(OR)\textsubscript{4} and ROH. For example, the combination of Si(OMe)\textsubscript{4} and EtOH and that of Si(OEt)\textsubscript{4} and MeOH had a similar gelation time. In other words, this may indicate that the ligand exchange, if it occurs, does not have any significant effect on the gelation behavior.

Figure 2 shows that the gelation time of the Si(OEt)\textsubscript{4} solution depends on the boiling point of the solvent. The influence of the boiling point is related to the concentration of the solution. It has been reported that the difference in gelation time is mainly ascribed to the difference in the rate of solvent vaporization.\textsuperscript{12}

Figure 4 shows the weight loss of sols as a function of time in the gelation process, in which the gelation time is shown by arrow. The gelation time for the open system is shorter than that for a tightly closed system. In the open system, as the solvent and water are vaporized from the sols, the silicate oligomeric species are concentrated, which makes the gelation time short. A particularly large difference is seen for methanol. It should be noted, however, that even in the open system, the gelation time of the sol with 1-pentanol is shorter than that with methanol, indicating that the vaporization rate of the solvent is not the determining parameter for the gelation time.

Figure 5 shows the relation between the gelation time and the dielectric constant of the solvent. It is seen that the gelation time is shorter for alcohols of lower dielectric constants, although relatively large scattering of the data points is found. Then, we discuss the effect of the dielectric constant of the solvent. When an ion in a vacuum is moved into a solvent, the ion is stabilized by the solvation. The dielectric constant of a solvent is a measure of the ability of the solvent to stabilize an ion. In the colloidal silica-water system, water-miscible organic liquids have a similar destabilizing effect on alkali-stabilized sols as electrolytes, presumably because the dielectric constant of the medium is reduced.\textsuperscript{16} This suggests that the dielectric constant may be related to

Fig. 1. Flowchart for gel preparation.

Fig. 2. Relation of gelation time and boiling point of solvents under base-catalyzed condition by Method-I (\(\bullet\)) and Method-II (\(\circ\)).

Fig. 3. Gelation time of combination of silicon alkoxide and alcohol solvent (Si(OR)\textsubscript{4} : Solvent : H\textsubscript{2}O : HCl = 1 : 4 : 10 : 0.03 in molar ratio).
Fig. 4. Gelation time (shown by arrow) and time dependence of weight of sols in closed and open systems.

gelation. The results shown in Fig. 5 would partly support this conclusion.

The base-catalyzed condensation reaction proceeds as illustrated in Fig. 6(8,11) and this reaction is the rate-determining step.11 Generally, stabilization of hydrolysate species by solvation decreases the condensation rate in the $\text{SiO}_2$ reaction. Protic solvents, which form a hydrogen bond with nucleophilic deprotonated silanols, are expected to retard base-catalyzed condensation. Unfortunately, little data is available to unambiguously determine the effect of solvent type on the condensation rate.6) Alcohols which were used as solvents in this work are protic solvents, and thus, they would form a hydrogen bond to nucleophilic deprotonated silanols, i.e., alcohol solvation. Lower alcohols have a higher hydrogen-donating ability, and it is expected that the gelation time is longer than that of higher alcohols, as indicated in Fig. 5. It is expected that an alcohol retards base-catalyzed condensation.

A scheme of alcohol solvation in a base-catalyzed reaction is suggested as shown in Fig. 7. It is assumed that the attacking species, $\text{SiO}^-$, is stabilized by alcohol solvation when the condensation reaction occurs under a base-catalyzed condition, and this decreases the condensation rate. The degree of the solvation is different for different alcohols, and increases with increasing dielectric constant. Therefore, alcoholic solvents of higher dielectric constants, which would result in stronger solvation, are considered to increase the gelation time under the base-catalyzed condition.

A good correlation is seen in Fig. 5, however, only for primary alcohols. It is assumed that the degree of solvation is similar when the alcoholic solvents have the same values of dielectric constant. Secondary and tertiary alcohols are bulkier than primary alcohols and thus the rate-determining reaction shown in Fig. 6 is inhibited by steric hindrance for the secondary and tertiary alcohols. This explains why the gelation time of secondary and tertiary alcohols is longer than that of primary alcohols.

Then, we examined the acid-catalyzed condensation reaction. Figure 8 shows the relation between the gelation time and the dielectric constant of the solvent for solutions prepared by Method-I under the acid-catalyzed condition. In this figure, the results for the solutions leading to the $10\text{P}_2\text{O}_5 \cdot 90\text{SiO}_2$ composite gels are shown. The acid-catalyzed condition is realized, since H$_3$PO$_4$ was used as a starting material. It is evident from Fig. 8 that the gelation time becomes longer with the increase of dielectric constant of the solvent. Comparing Fig. 5 and Fig. 8, it is seen that the tendency of the change of the gelation time with the dielectric constant of the solvent is similar for base- and acid-catalyzed conditions.

The acid-catalyzed condensation reaction proceeds as illustrated in Fig. 9.11 Alcohols are capable of solvating an anion and a cation. Figure 10 shows the solvation scheme under the acid-catalyzed condition. It is assumed that the attacking species, $\text{Si}^-\text{HO}^- \cdot \text{R}$, is stabilized by alcohol solvation in acid catalysis condensation.

It has been shown that the polarity of the solvent is one of

\[
\text{Si}^-\text{O}^- + \text{Si}^-\text{OR} \\
\text{slow}
\]

\[
\text{Si}^-\text{O}^-\text{Si}^- + \text{RO}^-
\]

\(\text{R} : \text{Alkyl Group or H}\)

Fig. 6. Base-catalyzed condensation reaction mechanism.

Fig. 7. Base-catalyzed solvation model.
the important factors affecting gelation. The solubility parameter of the solvent is also a measure of polarization. This parameter is related to the boiling point of the solvent because it is defined as the square root of cohesive energy density, which is calculated from the boiling point of the solvent. Therefore, it is considered that the gelation time depends on the boiling point of the solvent.

It appears that the gelation time depends on not only the dielectric constant and boiling point of solvents but also on other properties, such as refractive index, dipole moment, viscosity, surface tension, molecular size, and type of functional group. Therefore, when other solvents, such as formamide, dimethylformamide and glycerol are used, all these various factors should be considered.

4. Conclusions

Fifteen alcohols were used as solvents for the preparation of silica wet gels by the sol–gel method, and the rate of gelation of the solution in a tightly closed system was measured. The following results were obtained.

1. The gelation time decreased with the increase of boiling point of the alcohol.

2. The gelation time increased with increasing the dielectric constant of the alcohol under base- and acid-catalyzed conditions. This was explained by a model of the alcohol solvation in which hydrolysedated species of tetraalkoxysilane are solvated by alcohol and the degree of this solvation represented by the dielectric constant or polarity of solvent affects the gelation time.

3. Steric hindrance of solvating alcohol affected the rate of condensation.

4. The gelation time was not affected by the ligand exchange reaction.

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References