

## Critical factors in sol-gel transition of silicon metal alkoxide solutions

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## Silicon metal alkoxide 용액의 sol-gel 전이에서 중요 인자

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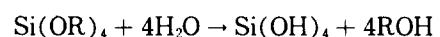
**Abstract** The important factors of reaction conditions in sol-gel transition of silicon alkoxide solution have been reviewed and discussed on the basis of Raman study. Various factors such as type of catalyst, alkoxide, solvent, drying control chemical additive and water content affect the conversion mechanism in sol-gel process.

**요약** 실리콘 알콕사이드 용액의 졸-겔 전이에 있어서 반응조건에 중요한 영향을 미치는 인자에 대하여 Raman 분광분석을 기초로 해서 고찰해 보았다. 촉매의 종류, 용매, 건조제어용 화학첨가제 및 물의 양과 같은 여러가지 인자가 졸-겔 과정에 있어 전이메카니즘에 영향을 주었다.

### 1. Introduction

Gelation of silicon metal alkoxide solutions take place as a result of the hydrolysis of the silicon metal alkoxides  $\text{Si}(\text{OR})_4$  and subsequent dehydration-polycondensation

leading to the formation of polymers and particles consisting of siloxane bonds. The reactions can be expressed by the following process,





These represent an extreme case, where the condensation reaction starts only after the completion of the hydrolysis reaction. Actually, however, it is possible that the condensation reaction starts at different stages of the hydrolysis of the silicon alkoxide, depending on the condition of the reaction. This means that the reaction conditions affect the nature of the resultant siloxane polymers or particles as well as their aggregation state and, accordingly, govern the characteristics of the sol and gel produced. In the present work, the effects of the reaction conditions on the properties of the silicon alkoxide sols and gels shall be reviewed and discussed as following; catalyst and pH value of the solution, water content, silicon alkoxide content, type of solvent and alkoxide, and addition of DCCA.

## 2. Experimental

Silicon metal alkoxides  $\text{Si(OR)}_4$  ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$  and  $\text{C}_4\text{H}_9$ ) were used as a starting materials. In order to study the sol-gel conversion mechanism, various catalyst, solvent and additives were introduced. The obtained sol and gel were characterized by SEM and Raman spectroscopy.

## 3. Results and discussion

### 3.1. Effects of catalyst and pH of the solution

Acid and base have been used as catalysts for the reaction of the silicon alkoxides in the sol-gel process on the basis of the idea that  $\text{H}^+$  and  $\text{OH}^-$  ions catalyze the hydrolysis reaction. It is known that the reaction patterns of hydrolysis and subsequent polycondensation are different according to whether the catalyst is acidic or basic. Yamanne et al. [1] showed that in tetramethoxysilane (TMOS) solution all the TMOS molecules rapidly disappear as a result of rapid hydrolysis under acidic conditions, whereas TMOS molecules remain until gelation because of a low rate of hydrolysis under basic conditions. We showed this by measuring the Raman spectra of the TMOS solution. The Raman spectra of the HCl-catalyzed solution in Fig. 1 show no peak assigned to TMOS immediately after the start of reaction, indicating that all the TMOS molecules are hydrolyzed very rapidly; however, in the spectra of the  $\text{NH}_3$ -catalyzed solution in Fig. 2, the peak assigned to TMOS is clearly found when the solution is gelled. This was confirmed by Brinker et al. [2] for tetraethoxysilane (TEOS).

In order to explain these phenomena, it is assumed [3-5] that in the presence of acid the hydrolysis of the silicon alkoxide is caused by the electrophilic attack of  $\text{H}_3\text{O}^+$  ion, and so the reactivity decreases as the number of OR radicals on the Si decreases with the progression of hydrolysis. This means (1) that the probability of formation of  $\text{Si(OH)}_4$ , which is produced by the hydrolysis of all four OR groups of an

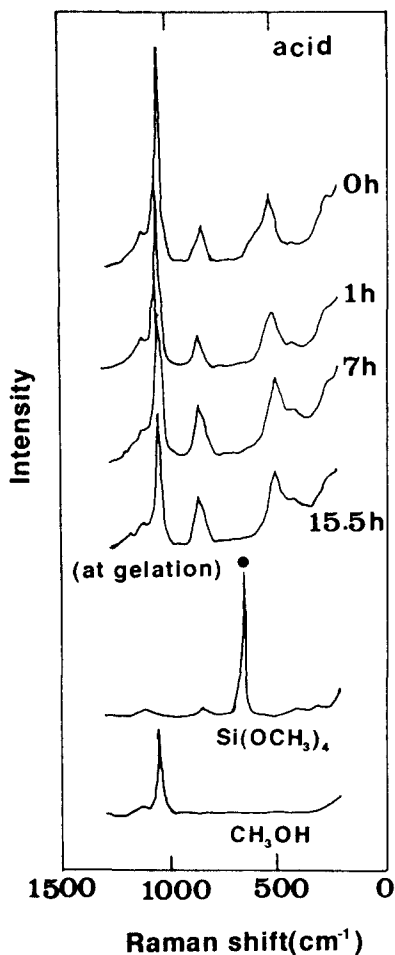


Fig. 1. Raman spectra of  $\text{Si}(\text{OCH}_3)_4$  solution kept at  $40^\circ\text{C}$ : Acid-catalyzed solution with molar ratio  $\text{Si}(\text{OCH}_3)_4 : \text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{HCl} = 1:1.5:2:0.01$  (●) peak due to  $\text{Si}(\text{OCH}_3)_4$  vibration.

alkoxide molecule, is small and (2) that the condensation reaction starts before the complete hydrolyzing of  $\text{Si}(\text{OR})_4$  to  $\text{Si}(\text{OH})_4$ .

On the other hand, the hydrolysis under basic conditions takes place by the nucleophilic substitution by  $\text{OH}^-$  ions and the reactivity increases as the number of OR

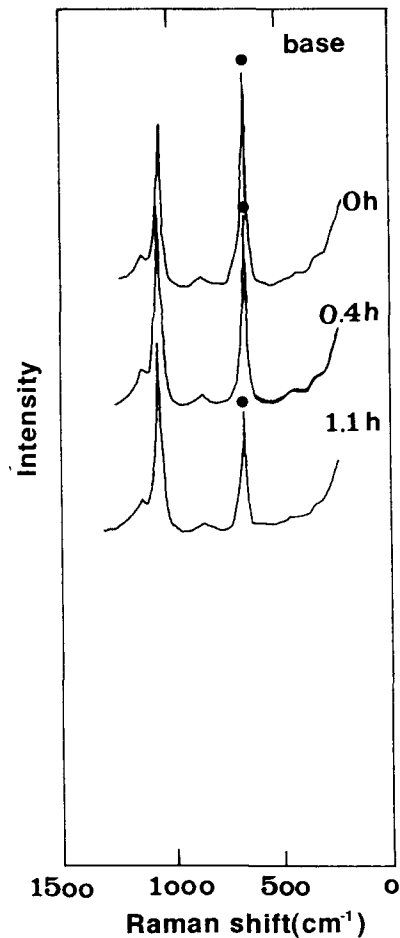


Fig. 2. Raman spectra of  $\text{Si}(\text{OCH}_3)_4$  solution kept at  $40^\circ\text{C}$ : Base-catalyzed solution with molar ratio  $\text{Si}(\text{OCH}_3)_4 : \text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 = 1:2:7:0.001$  (●) peak due to  $\text{Si}(\text{OCH}_3)_4$  vibration.

groups on a Si decreases as hydrolysis progresses. Consequently,  $\text{Si}(\text{OH})_4$  is easily formed by the preferential hydrolysis of the rest of the OR groups belonging to a partially hydrolyzed  $\text{Si}(\text{OR})_4$  molecule, and some silicon alkoxide molecules tend to remain nonhydrolyzed.

These differences in the reaction pattern would be revealed in the structure of reaction products. In the acid-catalyzed solutions, silicon alkoxide molecules with non-hydrolyzed alkoxy groups polymerize with each other, producing polymers in which the degree of cross-linking is low; however, in the base catalyzed solutions,  $\text{Si}(\text{OH})_4$  molecules participate in the polycondensation reaction, producing highly cross-linked polymers [3]. Sakka and Kamiya [6] showed,

by viscosity measurements, that one-dimensionally developed particles which give spinnability to the sol are formed in the acid-catalyzed solutions. The above structural characteristics of polymers were confirmed by the small-angle X-ray scattering measurements [2,7] and by  $^1\text{H}$ -NMR and  $^{29}\text{Si}$ -NMR measurements [8].

The very large concentration of acid catalyst, however, may produce round shaped particles in the solution. Orgaz-Orgaz and

Table 1

Effect of the HCl content on gelation properties of  $\text{TMOS} \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH} \cdot \text{HCl}$  solutions kept at  $40^\circ\text{C}$  in the open system<sup>1</sup>

Composition (mol)		Apparance at gelation	Gelling time (hr)	Spinnability
$\text{H}_2\text{O}/\text{TMOS}$	$\text{HCl}/\text{TMOS}$			
2.00	0.01	Transparent	12.6	Yes
2.00	0.40	Transparent	0.6	No
1.70	0.01	Transparent	13.4	Yes
1.70	0.40	Opalescent	1.0	No
1.44	0.01	Transparent	17.2	Yes
1.44	0.40	Opalescent (Sedimentation)	(1.4) <sup>*2</sup>	Yes <sup>*3</sup>
1.53	0.01	Transparent	14.5	Yes
1.53	0.15	Opalescent	3.6	No
1.53	0.20	Opalescent	2.9	No
1.53	0.25	Opaque	2.5	No
1.53	0.30	Opaque	1.9	No
1.53	0.35	Opaque (Sedimentation)	(1.6) <sup>*2</sup>	No
1.53	0.40	Opaque (Sedimentation)	(1.3) <sup>*2</sup>	No

<sup>1</sup>  $\text{CH}_3\text{OH}/\text{TMOS}$  was kept constant at 2.

<sup>2</sup> No clear determination was made, since gelation took place during sedimentation.

<sup>3</sup> Bottom phase.

Rawson [9] showed this with the TMOS solutions. Our study of the effect of HCl concentration on the behavior of sol and the structure of gel from the starting TMOS solutions with  $[\text{HCl}]/[\text{TMOS}] = 0.01 - 0.40$  showed that, at high HCl concentrations, round particles are produced and the sol becomes less spinnable when the amount of addition of HCl becomes high, as shown in Table 1. The scanning electron micrographs of the fracture surfaces of dried gels shown in Fig. 3 indicate that the sol with a low the content of 0.01 in  $[\text{HCl}]/[\text{TMOS}]$  produces a trans-

parent gel, in which no particulate microstructure is observed, whereas the sol with  $[\text{HCl}]/[\text{TMOS}] > 0.15$  becomes opaque before gelation and produces a dried gel, consisting of connected round particles. The Raman spectra of a TMOS solution with a high HCl content of 0.4 in  $[\text{HCl}]/[\text{TMOS}]$  show that all TMOS molecules present in the solution are subjected to hydrolysis in this

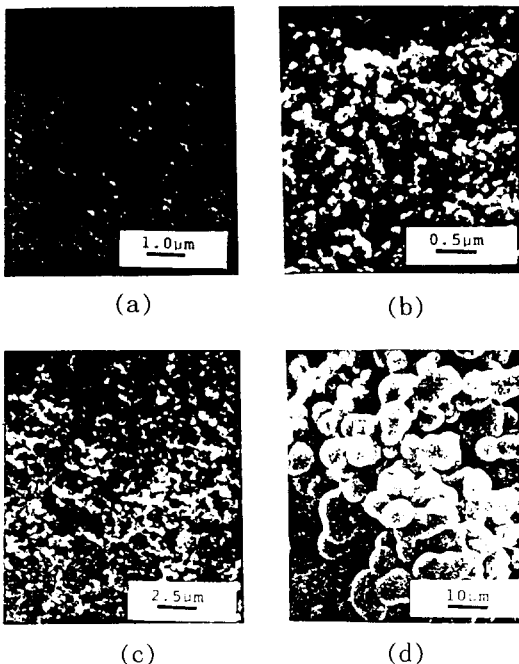


Fig. 3. Scanning electron micrographs of dried gels prepared from the starting solutions having the composition  $\text{Si}(\text{OCH}_3)_4 : \text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{HCl} = 1 : 1.53 : 2 : x$  in mol, where  $x = [\text{HCl}]/[\text{Si}(\text{OCH}_3)_4] = 0.01$ (a), 0.15(b), 0.25(c) and 0.40(d).

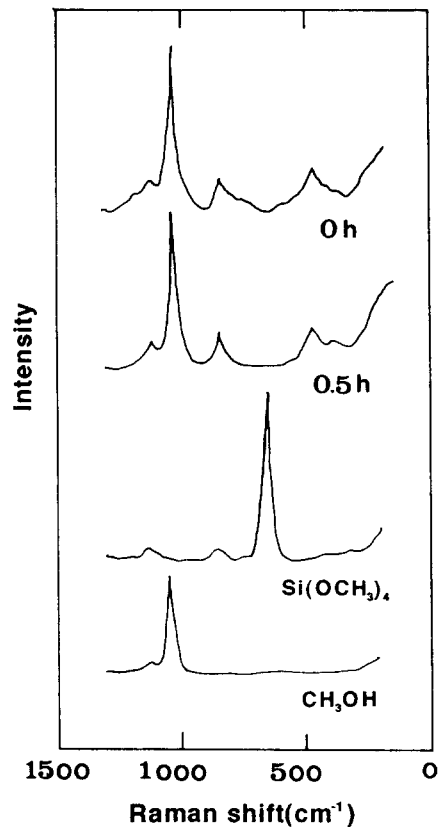


Fig. 4. Raman spectra of an  $\text{Si}(\text{OCH}_3)_4$  solution having the composition  $\text{Si}(\text{OCH}_3)_4 : \text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{HCl} = 1 : 1.53 : 2 : 0.4$  in mol. The spectra shown are those for transparent solutions. This solution became opaque at 1.1 hr, just before gelation.

case as in the solutions of low acid content (Fig. 4). This indicates that the mechanism of formation of round particles in the solution of very high acid content may be different from that in the base-catalyzed solution, although absence of spinnability and opaque appearance in the former are also seen in the latter. It has been shown that the kind of acid used as catalyst affects the gelation behavior. Pope and Mackenzie [10] and Mackenzie [11] suggested that the variation of the gelling time and the porosity of dried gel with the kind of acid cannot be explained by the pH of the starting solution alone, but has to be explained by the differences on the role of anions such as  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{CH}_3\text{COO}^-$ .

We investigated the change in gelation behavior with kind of acid with the TMOS solutions of high acid content. As shown in Table 2, the gel produced is opaque with HCl, less opaque (opalescent) with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , and transparent with  $\text{CH}_3\text{COOH}$ , and the gelling time increases in the order  $\text{HCl} < \text{HNO}_3 < \text{H}_2\text{SO}_4 < \text{CH}_3\text{COOH}$ . These variations of the gelation behavior can be related to the pH value of the starting solu-

tion, considering that the pH value decreases in the order  $\text{CH}_3\text{COOH} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$ , the same order as in the  $\text{pK}_a$  of the acid.

The change in the gelling time and viscous behavior of the sol has been investigated for the low-acid-content TEOS solutions having the composition  $\text{TEOS} : \text{H}_2\text{O} : \text{C}_2\text{H}_5\text{OH} : \text{acid} = 1 : 2 : 5 : 0.01$ . The solutions were reacted at  $60^\circ\text{C}$  in a tightly air-sealed flask. Table 3 shows that the gelling time is short in the starting solutions of high pH values containing acetic or formic acid. Figure 5 shows that the viscosity change with time for the solution containing acetic acid is characterized by steady increase throughout the reaction time, in contrast with the abrupt increase at the final stage just before gelling for solutions containing other acids. This would indicate that the reaction in the solution may differ according to kind of acid involved. The flow characteristics of the solution changes from Newtonian flow to structural viscosity and to thixotropic flow. It was found that the change gives information on the effects of the kind of acid.

Table 2

Catalytic effects of acids on gelation of TMOS solution having the composition  $\text{TMOS} : \text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{acid} = 1 : 1.53 : 2 : 0.4$  in mol, kept at  $40^\circ\text{C}$  in closed system

Catalyst	Apparent initial pH	$\text{pK}_a$ of catalyst	Gelling time (hr)	Appearance at gelation
HCl	- 1.1	- 7	1.3	Opaque
$(\text{H}_2\text{SO}_4)_{0.5}$	- 0.4	- 3.2	3.8	Opalescent
$\text{HNO}_3$	- 0.3	1.3	18	Opalescent
$\text{CH}_3\text{COOH}$	2.7	4.7	480	Transparent

Table 3  
Gelling time and initial pH of TEOS solutions containing various acids as catalyst

Acid	Initial pH	Gelling time (days)
HCl	0.02	35
(H <sub>2</sub> SO <sub>4</sub> ) <sub>0.5</sub>	0.35	37
HNO <sub>3</sub>	0.47	34
HCOOH	3.65	16
CH <sub>3</sub> COOH	4.76	8

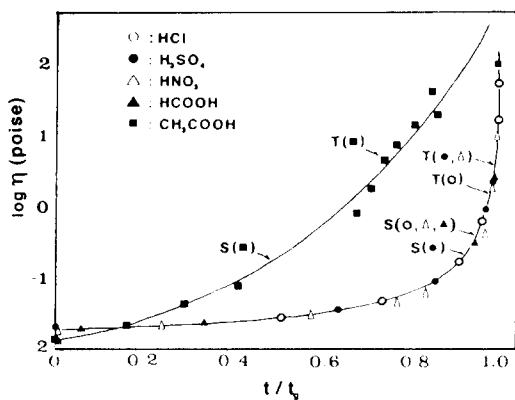


Fig. 5. Variation of viscosity with reduced time ( $t/t_g$ ). Compositions of the starting solutions are shown in Table 3. S and T shown in the figure denote the points of onset of structural viscosity and thixotropic flow, respectively.

### 3.2. Effects of H<sub>2</sub>O content

The water content of the silicon alkoxide solution markedly affects the structure and properties of the siloxane particles produced in the sol. Naturally, an increase in the water content increases the number of sites

to be hydrolyzed. Also, the number of OH groups per Si should increase with increasing water content, because water, a product of condensation of hydrolyzed alkoxides, retards the condensation reaction. This would be favorable for the formation of highly crosslinked products. Conversely, a reduction of water content increases the chance of polymerization of only partially hydrolyzed alkoxide molecules, producing less cross-linked polymers. These effects of the water content were confirmed by Keefer [3] based on small-angle X-ray scattering of the TEOS solutions. Sakka and Kamiya showed that, in an acid-catalyzed TEOS solution, chainlike particles causing spinnability are produced at low water content, whereas round or highly cross-linked particles are produced at high water contents.

We investigated the effect of water by measuring the Raman spectra during the hydrolysis-condensation reaction for TMOS solutions having water contents 1.5 and 4.0 in  $[H_2O]/[TMOS]$ . It was found that alkoxy groups rapidly disappear at higher water contents, whereas they remain until gelation at lower water contents. It was also shown that the solution of higher water content is characterized by a higher intensity, of  $420\text{ cm}^{-1}$  band. Which is assigned to Si-O-Si vibration in a three-dimensionally developed silica structure.

Generally, gelation is promoted and the gelling time is reduced with increasing water content [12], but too much water prolongs gelling time as a result of dilution of the solution. For hydrolysis, Schmidt et al.

[14] found that the rate of hydrolysis decreases with increasing water content in HCl-catalyzed solutions, whereas the rate increases in  $\text{NH}_3$ -catalyzed solutions. In order to explain this, it was assumed that the increase in water content decreases the activity of protons in the HCl solution and promotes the dissociation of  $\text{NH}_4\text{OH}$  in the ammonia solution.

### 3.3. Effects of silicon alkoxide content

Alcohols are often used as a solvent for both metal alkoxide and water in the sol-gel method. An increase in the alcohol content reduces the concentration of metal alkoxide, resulting in the reduction of the polymerization rate and prolonged gelling time. Yoldas [15] confirmed from  $^{29}\text{Si}$ -NMR measurements that an increase in alcohol content reduces the probability of mutual collisions of hydrolyzed alkoxide molecules, resulting in a decrease in the rate of polymerization reaction. Since alcohols are hydrolysis products from silicon alkoxide, an increase in the alcohol content may promote esterification, the reverse reaction, decreasing the apparent rate of hydrolysis [16].

A similar effect of the solvent content can be seen when we start from the solutions of the same composition and compare the viscous behavior of the solutions subjected to reaction in an open and closed system. As Table 4 shows, in the open system the concentration of the solution increases with time as a result of the vaporization of ethanol, and the volume of the solution at gelling is about 30 % of the volume of the starting solution; also, the solution shows a good spinnability just before gelation. In the closed system, no volume change of the sol is observed and no spinnability appears. The comparison of the changes of the viscosity with shear rate for the open and closed systems at a similar viscosity indicates that the solution remains Newtonian in the open system and is structural-viscous in the closed system. The difference may be explained on the basis of the concentration of the solution.

### 3.4. Effects of type of solvent

With gels made from TEOS solutions containing different solvents, Mackenzie [11] showed that the specific surface area of gel

Table 4

Gelation of TEOS solutions having the composition  $\text{TEOS}:\text{C}_3\text{H}_5\text{OH}:\text{H}_2\text{O}:\text{HCl}=1:1:2:0.01$  in mol in the open and closed system

System	Gelling time (days)	Volume shrinkage at gelation (%)	Spinnability
Open	1.0	60	Yes
Closed	8.5	0	No



Table 5

Gelling time of silicon alkoxide solutions having the composition  $\text{Si}(\text{OR})_4 : \text{ROH} : \text{H}_2\text{O} : \text{HCl} = 1 : 7 : 2 : 0.01$  in mol kept at  $40^\circ\text{C}$  in the closed system

System	Gelling time (days)
$\text{Si}(\text{OCH}_3)_4 - \text{CH}_3\text{OH} - \text{H}_2\text{O} - \text{HCl}$	5
$\text{Si}(\text{OC}_2\text{H}_5)_4 - \text{C}_2\text{H}_5\text{OH} - \text{H}_2\text{O} - \text{HCl}$	>100
$\text{Si}(i\text{-OC}_3\text{H}_7)_4 - i\text{-OC}_3\text{H}_7\text{OH} - \text{H}_2\text{O} - \text{HCl}$	>100
$\text{Si}(n\text{-OC}_4\text{H}_9)_4 - n\text{-OC}_4\text{H}_9\text{OH} - \text{H}_2\text{O} - \text{HCl}$	>100

is small when the vapor pressure of the solvent is high. This indicates that the selection of the solvent is important in order to obtain a gel that has desirable pore and surface properties. It should be noted that the ligand OR or a silicon alkoxide may be exchanged with OR' of an alcohol; also, there are changes in the reactivity of the alkoxide used as starting material.

### 3.5. Effect of type of silicon alkoxide

The reactivity of the metal alkoxide differs depending on its type. Aelion et al. [4] showed that the rate of hydrolysis decreases with increasing size of alkoxy groups belonging to the alkoxide. Chen et al. [17] showed that the gelling time of the alkoxide solution increases with increasing size of the alkoxy group and explained this effect on the basis of the rate of hydrolysis and the concentration of the solution. The present authors attempted to gel the solutions of various silicon alkoxides,  $\text{Si}(\text{OR})_4$ , having  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$  or  $\text{C}_4\text{H}_9$  as R in the closed system (see Table 5). Only TMOS solution

gelled in 5 days and other solutions did not gel before more than 100 days. In the open system using the starting solutions having the composition  $\text{Si}(\text{OR})_4 : \text{H}_2\text{O} ; \text{ROH} : \text{HCl} = 1 : 2 : 7 : 0.01$  (or 0.40) mol, the rate of decrease in the volume of the solution (i. e., the rate of vaporization of the constituents) became smaller and gelling time increased with increasing size of the alkoxy group, as shown in Fig. 6.

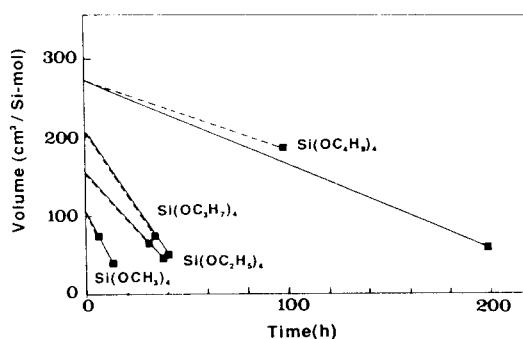


Fig. 6. Change of the volume of solutions with time. (■) Volume at gelation; (—)  $[\text{HCl}] / [\text{Si}(\text{OR})_4] = 0.01$ ; (···)  $[\text{HCl}] / [\text{Si}(\text{OR})_4] = 0.40$ . Compositions are shown in Table 5. Volume of the solutions shown is normalized to the volume ( $\text{cm}^3$ ) per mol Si.

### 3.6. Effects of addition of DCCA

Wallance and Hench [19] proposed the use of drying control chemical additive (e. g., formamide) in order to produce large gel monoliths without cracks. Adachi and Sakka found that N, N-dimethylformamide is very useful for this purpose. It was found that the addition of N, N-dimethylformamide makes the average pore size larger and the surface tension of the liquid in the pores of the gel smaller, contributing to the formation of large gel monoliths without cracks.

### 4. Summary

The effects of reaction conditions in sol-gel transition of silicon alkoxide solution on the properties of sols and gels have been reviewed and discussed. The following factors were considered : type of catalyst and pH values of the solution, water content in solution, type of solvent, type of alkoxide and addition of DCCA. These factors affect the reaction mechanism in sol-gel transition, the gelling time of solution, the nature of polymerized species formed in sol, the flow characteristics of sol, the bulk nature of gel, and so on. To understand the relationship between these reaction conditions and properties of resultant sols and gels, reaction mechanisms under various conditions were also discussed.

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