

Effects of alcohol solvents on formation of the hydrated silica gel

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Usually, when silica sol is prepared by adding inorganic acid to a diluted sodium silicate solution, a basic substance is added to adjust the pH of the silica sol in order to occur the gelation reaction of the silica sol. However, in this study, it was confirmed that the gelation of the silica sol could occur even when an alcohol is added instead of the basic substance. In order to examine the mechanism of gelation that occurred when alcohol was added to the silica sol, different solvents (protic and aprotic) were added to the silica sol and the gelation time was measured. The results revealed that the gelation occurred due to the tendency of the hydroxyl oxygen in the alcohol to bond to the hydroxyl hydrogen of the water molecules that had already formed a hydration shell around the silica particles. Therefore, it is presumed that the hydration shell was broken by the addition of the alcohol. This, in turn, led to the instantaneous polycondensation between the silica particles, which caused the gelation.

Key words: Sol-gel process, Water glass, Water, Polar protic solvent, Polar aprotic solvent, Gelation.

Introduction

Precipitated silica (SiO₂) is industrially produced by mixing silicate solution with an acid in a semi-batch process [1]. Subsequent polycondensation of monomeric silica leads to the formation of particles which aggregate and eventually form a particulate gel. Usually, silica gel is prepared by reacting a sodium silicate solution (water glass) with an inorganic acid to form silica sol. The silanol groups (Si-OH) are then transformed into siloxane bonds (Si-O-Si) through a polycondensation reaction initiated by the addition of a basic substance (e. g., NH₃), to produce hydrated silica gel (silica hydrogel) [2-5]. Next, the prepared silica hydrogel is continuously condensed into a white jelly-like precipitate, which is subsequently washed to remove the sodium salt (e. g., NaCl), dried, and activated to produce silica gel [1]. Silica alcogel is produced by reacting silicon alkoxide (Si-alkoxide) such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) via a sol-gel process. The siloxane (Si-O-Si) bond is eventually formed through hydrolysis and polycondensation [6, 7].

In this study, a new method for the preparation of hydrated silica gel was introduced, which included the formation of siloxane (Si-O-Si) bonds by adding

alcohol, a non-basic substance, to the sodium silicate solution. We investigated the effects of the alcohol on the gelation process in the formation of silica gel via alcohol addition to the silica sol. The gelation time was measured and analyzed by adding protic and aprotic solvents to the silica sol, and the mechanism of the gelation process was subsequently investigated

Experiment

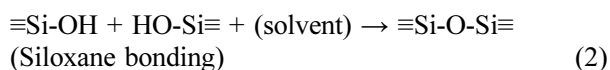
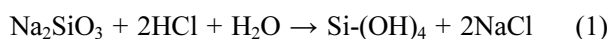
Experimental material

Water glass, i.e. sodium silicate (29 wt% SiO₂, Young I1 Chemical Co.), was used as a starting material for the silica sol synthesis. HCl (1 N, Samchun Chemical Co.) was used as the catalyst. Protic and aprotic solvents were used to investigate the mechanism of gelation. The hydrated silica gel was formed by adding an alcohol solvents to the prepared silica sol. The protic solvents used were methanol (MeOH, 99.5%, Samchun Chemical Co.), ethanol (EtOH, 95%, Samchun Chemical Co.), 2-propanol (*i*-PrOH, 99.5%, Samchun Chemical Co.), 1-butanol (*n*-BuOH, 99%, Samchun Chemical Co.), *tert*-butanol (*t*-BuOH, 99%, Samchun Chemical Co.), and 1-hexanol (*n*-hexanol, 100%, Junsei Chemical Co.). The aprotic solvents used were acetonitrile (MeCN, 99.9%, Samchun Chemical Co.), tetrahydrofuran (THF, 99.5%, Samchun Chemical Co.), and dimethyl sulfoxide (DMSO, 99%, Samchun Chemical Co.).

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Experimental method

Sodium silicate solution was used as a starting material in the investigation of the gelation mechanism in the process of hydrated silica gel formation in the silica sol. The sodium silicate used in the experiments was an alkaline solution (pH = 11.5) containing 29 wt% SiO₂, 9 wt% Na₂O, and a small amount of Fe₂O₃, with a viscosity of cPs > 100. Distilled water was added to the sodium silicate solution used for the experiment in order to adjust the sodium silicate solution to a suitable constant concentration. HCl was added to the diluted sodium silicate solution to form silica sol, i.e. silanol (Si-OH), as shown in equation (1). Protic and aprotic solvents were added to the resulting mixture to form hydrated silica gel, i.e. siloxane (Si-O-Si) through a polymerization reaction as shown in equation (2) [4].



The amount of solvent added to the mixture was varied in order to investigate the solvent effects on the gelation in the process of hydrated silica gel formation through alcohol addition to the silica sol. In order to keep the distance of the silica particles in the silica sol constant, a fixed amount of sodium silicate (10 ml) was added. Distilled water (130 ~ 40 ml) was added to the sodium silicate, and subsequently 1M HCl (25 ml) was added in order to initiate the silica sol formation. The total volume of the mixed solution was adjusted to 185 ml. Accordingly, the amount of solvent added was varied (20~110 ml). Then, the gelation time and pH of the resulting solution were measured and analyzed.

Results and Discussion

Effects of the gelation time on the adding mount of alcohol solvent species

Table 1. The measured pH value in each process stage to form the hydrated silica gel.

Formation process of hydrated silica gel	pH
4.35 wt% Na ₂ SiO ₃	11.47
1 mol/L HCl	0.33
4.35wt% Na ₂ SiO ₃ + 1 mol/L HCl	10.47
4.35 wt% Na ₂ SiO ₃ + 1mol/L HCl + IPA (99.5%)	10.53

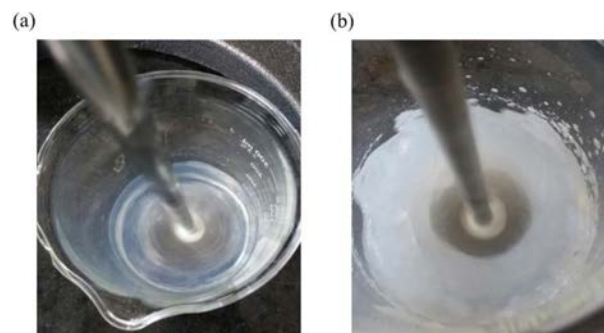


Fig. 1. A picture forming the silica sol by adding HCl to the diluted sodium silicate solution (a) and a picture forming siloxane during gelation process by adding IPA to the silica sol (b).

Usually, the gelation of silica gel is induced by increasing the pH of the silica sol to 2 ~ 3 and then increasing to the pH 4 ~ 6 by adding a basic catalyst such as ammonium hydroxide [4, 6, 8-11]. In this study, the mechanism of the gelation process occurring when alcohol solvents is added was examined by measuring the pH of the silica sol, prepared by adding 1 M HCl to a diluted sodium silicate solution, and the pH of the silica gel, prepared by adding IPA to prepared silica sol. Table 1 represented the measured pH value in each process stage to form hydrated silica gel. The results showed little change in pH after the addition of 1M HCl and subsequently IPA to the diluted sodium silicate solution. The fact that no change in the pH was observed after the addition of both HCl and IPA indicated that the pH of the silica sol does not dependent on the gelation factor. A picture

Table 2. The gelation time with respect to the amounts of distilled water, protic and aprotic solvents added to the sodium silicate.

	29wt% Water-glass (ml)	Hydrochloric acid (ml)	D.I water (ml)	Solvents (ml)	Isopropanol		Ethanol	
					Gelation time (s)	pH	Gelation time (s)	pH
Polar protic solvents	10	25	130	20	37	11.35	∞	11.21
			110	40	22	11.23	38	11.21
			40	110	4	10.99	7	11.12
	29wt% Water-glass(ml)	Hydrochloric acid(ml)	D.I water (ml)	Solvents (ml)	Dimethyl sulfoxide		Acetonitrile	
					Gelation time (s)	pH	Gelation time (s)	pH
Polar aprotic solvents	10	25	130	20	∞	11.14	∞	10.72
			110	40	40	11.41	34	11.37
			40	110	6	11.99	5	11.20

forming the silica sol by adding HCl to the diluted sodium silicate solution is presented in Fig. 1(a). Also a picture forming siloxane (Si-O-Si) during gelation process by adding IPA to the silica sol is shown in Fig. 1(b). These results showed that the gelation phenomena occurred by adding IPA to silica sol does not dependent on the pH change.

In order to investigate the solvent effects on the formation of the hydrated silica gel, the gelation time was measured with respect to the amount of solvent added to the silica sol. Table 2 represented the gelation time with respect to the amounts of distilled water, protic solvents and aprotic solvents adding to the sodium silicate. The amount of distilled water added to the sodium silicate (10 ml) was varied (130, 110, and 40 ml). Additionally, different amount of protic and aprotic solvents were added (20, 40, and 110 ml). These results indicated that the gelation time was rapidly reduced when the amount of both protic and aprotic solvents added to the silica sol was increased.

Effects of the alcohol solvent species on the gelation time

Next, the effects of the solvent species on formation of the hydrated silica gel were investigated. The silica sol was prepared according to the aforementioned procedure and the time at which gelation occurred was measured. The protic and aprotic solvents added to form the siloxane (Si-O-Si) had the same molar concentration (1M) with respect to the molecular weight, density, and purity of each solvent. The measured results are showed in Table 3, where π^*

represent the polarity-polarization of the solvent, α is the strength with which the hydroxyl hydrogen of the solvent attracts the molecular hydroxyl oxygen, and β is the strength with which the hydroxyl oxygen of the solvent attracts the molecular hydroxyl hydrogen [12-14].

From the results, it can be observed that the polycondensation reaction depends on the value of the β factor, rather than the α factor. The large β value led to the fast breaking of the hydration shell and promote the polycondensation reaction which formed bonds between of the silica. In contrast, the change of the α value did not show definite tendency on effects of the physicochemical bonding considering the relation between α value and the gelation time. It could be concluded that the gelation time was affected by the β value of the solvents that were capable of hydrogen bonding.

Based on the results shown in the Table 3, the relationship between the values of π^* , α , and β of protic and aprotic solvents, and the gelation time was potted in Fig. 2. In the case of protic solvents, the gelation time decreased with the increasing value of β and increased with the increasing value of α . In contrast, the aprotic solvent did not show clear tendency. In the case of aprotic solvents ($\alpha \approx 0$), it was easier to accelerate the formation of the physicochemical bonds, that is, the polycondensation reaction between silica particles [11, 15, 19-21]. This is because the aprotic solvents entirely depend on the value of β , which corresponds to the attraction of the molecular hydroxyl hydrogen from the solvent hydroxyl oxygen [21].

Table 3. Effect of the gelation time in various solvent species. Solvents had fixed concentrations of 1M calculated with respect to their molecular weight, density, and purity.

No.	solvent	Formula	π^*	β	α	Gelation time(s)	pH	Water-glass (ml)	Hydrochloric acid (ml)	D.I water (ml)	Solvent (ml)	Density (g/mL)	Molecular weight(g)
1	Hexanol (100%)	C ₆ H ₁₃ OH	0.41	0.84	0.80	∞	8.09			25	125	0.81	102
2	Butanol (99%) (BuOH)	C ₄ H ₉ OH	0.47	0.88	0.79	23	11.42			58	92	0.81	74.12
3	Methanol (99.5%) (MeOH)	CH ₃ OH	0.60	0.62	0.93	140	11.26			109	41	0.79	32.04
4	Ethanol (95%) (EtOH)	C ₂ H ₅ OH	0.54	0.77	0.83	25	11.13	10	25	88	62	0.79	46.07
5	Propanol (99%) (PrOH)	C ₃ H ₇ OH	0.52	0.83	0.78	18	11.27			74	76	0.80	60.10
6	Tert-butanol (99%) (t-BuOH)	C(CH ₃) ₃ OH	0.41	1.01	0.68	8	11.22			54	96	0.78	74.12
7	Isopropanol (99.5%) (i-PrOH)	(CH ₃) ₂ CHOH	0.48	0.95	0.76	12	11.32			73	77	0.79	60.10
8	Dimethyl sulfoxide (99%) (DMSO)	(CH ₃) ₂ SO	1.00	0.76	0.00	15	11.67			78	72	1.10	78.13
9	Acetonitrile(99.9%) (MeCN)	CH ₃ CN	0.75	0.31	0.19	33	10.98	10	25	98	52	0.79	41.05
10	Tetrahydrofuran (99.5%) (THF)	(CH ₂) ₂ O	0.58	0.55	0.00	11	11.45			68	82	0.89	72.11

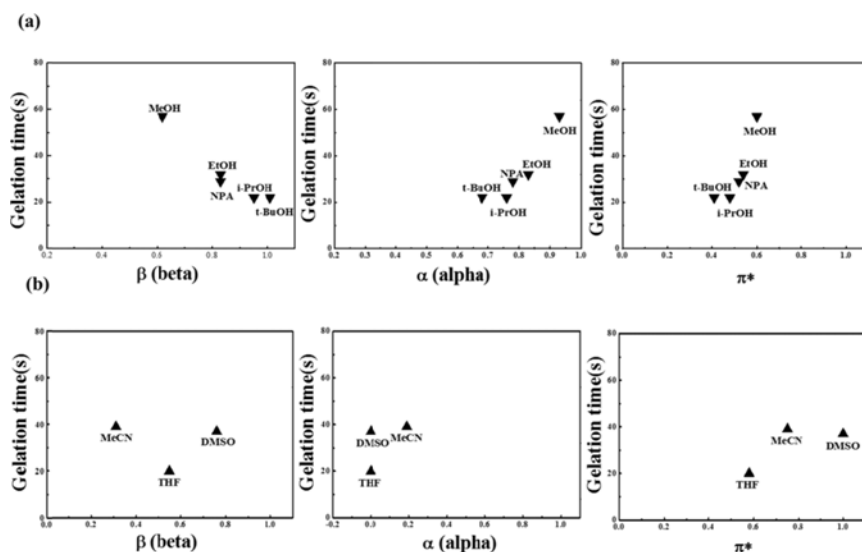


Fig. 2. Relationship between the hydrogen bonding factors and the gelation time for (a) protic and (b) aprotic solvents.

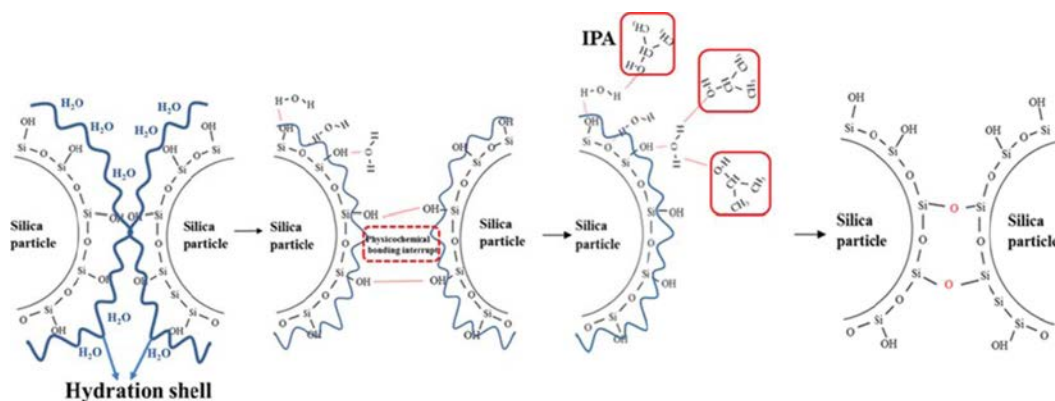


Fig. 3. Schematic diagram of gelation mechanism when isopropyl alcohol (IPA) is added to 1M HCl/diluted water glass.

Particularly, in the case of the highly polar MeOH with water-like properties, it was difficult to break the hydration shell formed by the water molecules around the silica surface because of the strong effect to form a hydrogen bond. Rather, the MeOH involved in the formation of the hydration shell around the silica surface, thus slowing down the polycondensation rate and increasing the gelation time [22, 23]. In the case of *n*-hexanol, it was confirmed that gelation did not occur due to the below reason. This is because the structure of *n*-hexanol contains a long chain of six carbon atoms which has hydrophobic properties. These hydrophobic chains must be mixed uniformly in order to break the hydration shell formed by the water molecules. However, due to the hydrophobic effects, the *n*-hexanol chains tend to accumulate together and form micelles [24, 25]. Therefore, presumably the hydration shell around the silica surface was not broken and the silica particles did not polycondensate, which inhibited the gelation process.

Fig. 3 represented a schematic diagram that explains

the gelation mechanism. It was found that the gelation occurred due to the siloxane (Si-O-Si) formation from the polycondensation reaction of silica particles. However, the water molecules around the surface of the silica particles formed a hydration shell, which interfered with the physicochemical bonding (polycondensation reaction) [15-18]. When IPA solvent was added, the hydroxyl oxygen of the IPA solvent interacted with the hydroxyl hydrogen of the water molecules around the surface of the silica particles through hydrogen bonding. This led to the breaking of the hydration shell and presumably an initiation of the gelation process due to an instant polycondensation reaction which formed bonds between the silica particles [11, 15, 19-21]. The results showed that gelation occurred in both protic and aprotic solvents. Therefore, these solvents did not directly participate in the chemical reaction but merely interacted through hydrogen bonding, thereby accelerating the polycondensation of the silica particles.

Fig. 4 and Fig. 5 represented the gelation time with respect to the added amount of protic and aprotic

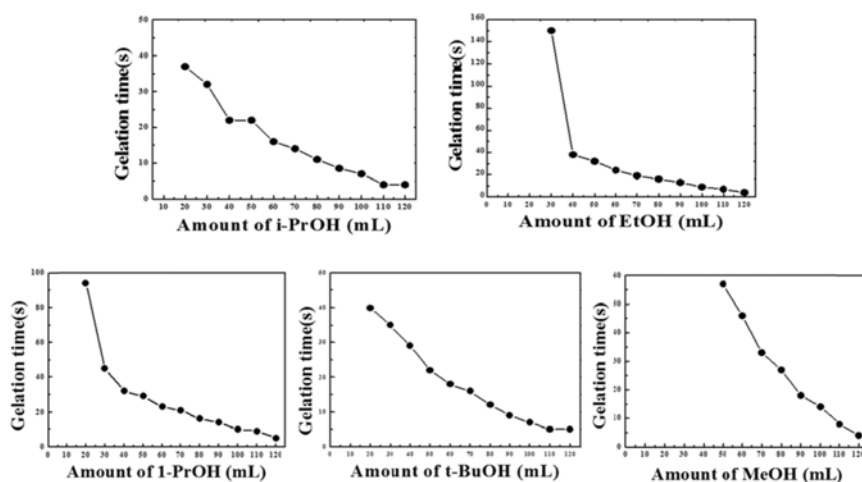


Fig. 4. Gelation time with respect to the amount of protic solvent.

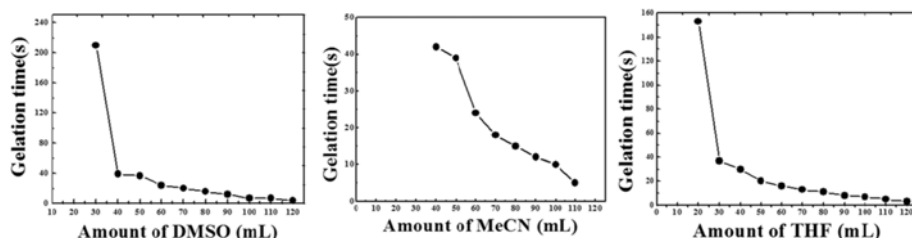


Fig. 5. Gelation time with respect to the amount of aprotic solvent.

solvent. The results showed that the gelation time decreased gradually as the amount of solvent increased (both protic and aprotic), and the gelation completely ceased below certain amount of solvent. Therefore, it is presumed that the solvent addition accelerated the siloxane (Si-O-Si) formation by breaking the hydration shell that the water molecules formed around the silica surface, which in turn enhanced the gel formation. Also, considering the fact that gelation did not occur when the amount of solvent added to the silica sol was 19 ml or less, it is important that more than constant amount of solvent is added. Moreover, the change in gelation time for the different species of solvent indicated that the gelation rate depended on the solvent species.

Conclusions

This study suggested that the hydroxyl oxygen of the protic or aprotic-solvents added to the silica sol attracted the hydrogens of the water molecules around the silica particles. That caused the breaking of the hydration shells around the silica particles. Therefore, it is presumed that the gelation occurred due to the momentary polycondensation between the silica particles as the hydration shells around the silica particles were being broken. In the case of the protic solvents, the gelation time decreased with decreasing in the strength (α) of the solvent hydroxyl hydrogen to bond to the

molecular hydroxyl oxygen. However, the gelation time decreased when the strength (β) of the solvent hydroxyl oxygen to bond to the molecular hydroxyl hydrogen increased. In contrast, the use of aprotic solvents showed no clear dependence. The increasing of the amount of both protic and aprotic solvents caused a gradual decrease in gelation time. Moreover, the gelation process did not occur below a certain amount of solvent. A investigation of the gelation mechanism in this study showed that solvents did not involved in the direct chemical reaction but rather promote the gelation through hydrogen bonding. Hitherto, no literature has been found that presents a gelation method that utilizes alcohol, and there have been no studies that have elucidated the gelation mechanism.

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